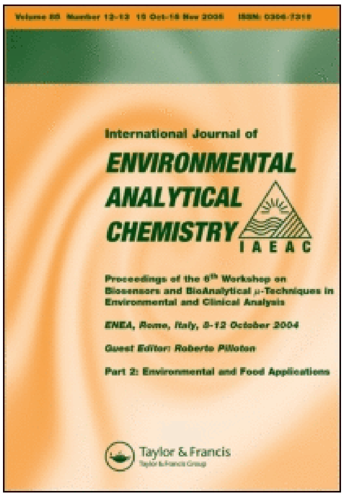

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Preconcentration procedure for determining trace amounts of Ni, Cd, Pb and Cu in high-salinity waters after cloud-point extraction

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A procedure for determination of Cd, Pb, Cu and Ni in high-salinity waters by inductively coupled plasma optical emission spectrometry has been developed. It is based on cloud-point extraction of these metals as complexes of diethyldithiocarbamate (NaDDTC) in micellar media of non ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114). Multivariate optimisation techniques have been applied to optimise the experimental variables. A full two-level factorial design was used to evaluate the influence of variables and Doehlert design was performed to find the optimum values. The effect of interference from residual salinity in surfactant-rich phase was also investigated. The developed procedure allows to achieve enhancement factors of 20.0, 20.4, 19.5 and 20.6, along with limits of detection ($3\sigma_B$) of 0.030, 2.1, 0.62 and $0.27\,\mu g\,L^{-1}$, and precision expressed as relative standard deviation ($\%RSD, n=10$) of 3.7 ($40.0\,\mu g\,L^{-1}$), 5.7 ($20.0\,\mu g\,L^{-1}$), 6.6 ($20.0\,\mu g\,L^{-1}$) and 3.1% ($10.0\,\mu g\,L^{-1}$) for Cd, Pb, Cu and Ni, respectively. The accuracy was evaluated by spike tests on the seawater (salinity of 35‰) and petroleum produced formation waters (salinity between 15‰ and 75‰). It was obtained by recoveries between 79% and 105%.

Keywords: produced formation water; seawater; ICP OES; cloud-point extraction; multivariate optimisation

1. Introduction

Petroleum produced formation water is the waste generated in largest volume during production of oil and gas from offshore platforms and this effluent is originated by the formation of water in the reservoir and the injected seawater into the well for increase in the oil recovery. Petroleum produced formation water contains a wide variety of chemicals, such as, inorganic salts, several metals and metalloids, and a wide variety of organic chemicals that have been dissolved or dispersed from the fossil fuels and the geologic reservoir containing the formation water [1,2].

This saline effluent has to be treated to remove dispersed oil, and sometimes salts, before re-injection or disposal. Thus, the determination of metals is of greatest

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environmental concern in this water destined for ocean disposal, because of their potential for bioaccumulation and toxicity to living species [3]. However, determination of trace metals in produced water is not a simple task because the high salinity of samples complicates its direct analysis by atomic techniques such as GF AAS, ICP OES and ICP-MS [4]. Then, separation and pre-concentration procedures must be implemented to ensure that analytes are extracted from its complex matrix and suitable analyte concentration is obtained for an accurate determination.

Cloud-point extraction (CPE) is a separation and pre-concentration procedure that has been extensively applied for trace metal determination in several different matrixes, such as, water [5–9], blood [10], urine [11], hair [12], geological materials [13], medicines [14], wine [15], saliva [16], parenteral solutions [17], plants [18,19], saline effluents [20] and petroleum produced saline waters [21]. CPE is based on the phenomena of phase separation that occurs when aqueous solutions of a non-ionic or zwitterionic surfactant, above its critical micellar concentration, are submitted to an alteration caused by changes of temperature and pressure or by the use of addictives [22].

The use of CPE, offers an efficient alternative to the conventional extraction procedures. Compared with conventional solvent extraction, CPE uses solutions of surfactant and avoids the use of large amounts of expensive, toxic and flammable organic solvents. In addition, CPE can lead to higher recovery efficiency and a large pre-concentration factor because in the end of the process it obtained a very small volume of micellar phase which entraps, efficiently, the analyte that was dispersed in the original matrix. Recent reviews have summarised the principles, advantages, limitations and relevant applications of this separation and pre-concentration technique [23–25]. Concerning to the final surfactant-rich phase obtained after a CPE from saline solutions, it is important to know the behaviour of analytical signal studied due to its composition such as the presence of methanol and salt residuals from original matrix.

This article presents the development of a procedure for the simultaneous pre-concentration of Pb, Cu, Ni and Cd from petroleum produced waters with salinities below 75‰ and its determination by inductively coupled plasma optical emission spectrometry (ICP OES) coupled with an ultrasonic nebulisator for increasing the sensitivity of the analytical technique. This procedure is based on CPE of these metals into micellar media of octylphenoxypolyethoxyethanol surfactant (Triton X-114) after complexing these metals with sodium diethyldithiocarbamate (NaDDTC).

2. Experimental

2.1 *Instrumentation and apparatus*

A Jobin Yvon (Longjumeau, France) Ultima 2 sequential ICP OES instrument with radial view equipped with the automatic sampler AS 421 and an ultrasonic nebuliser CETAC, model U-5000AT was used. Data acquisition was carried out by the software Analyst JY 5.1. The metal determinations were performed under the conditions indicated in Table 1.

A Celm Centrifuge, model LS-3 plus (São Paulo, Brazil) was used to accelerate the separation of the aqueous and micellar phases.

Salinity measurements were performed with a hand-held refractometer model S/Mill-E furnished by Atago (Saitama, Japan).

Table 1. Instrumental parameters used for metals determination by sequential ICP OES after CPE.

Parameter	Value
RF generator power (kW)	1.2
Nebuliser gas flow rate (L $\min^{-1}$)	0.45
Auxiliary gas flow rate (L $\min^{-1}$)	0.40
Plasma gas flow rate (L $\min^{-1}$)	12
View height small window (mm)	15
View height large window (mm)	51
Nebuliser type	Ultrasonic
Nebuliser pressure (bar)	2.48
Integration time (s)	1
Stabilisation time (s)	15
Purge gas	Ar
Analytical wavelengths (nm)	
Cd	228.802
Cu	324.754
Ni	221.647
Pb	220.353

2.2 *Reagents and solutions*

All reagents were prepared using ultra pure water (Elix and Synergy, Millipore, Badford, MA, USA) and analytical grade chemicals. Nitric acid and ethanol were of Suprapur quality (Merck, Germany). Laboratory glassware was kept overnight in 10% nitric acid solution. Before use, the glassware was rinsed with ultra pure water and dried in a dust-free environment.

Cadmium, Cu, Ni and Pb solutions were prepared by diluting 1000 $\mu g\,mL^{-1}$ standard solutions (CertiPrep SPEX, Metuchen, USA).

A 0.5% (w/v) solution of NaDDTC was prepared by dissolving 0.50 g of the compound (Carlo Erba, Italy) in 80 mL of ultra pure water, heated and shaked for 24 h. Later, the volume was transferred to a 100.0 mL volumetric flask and the volume was set.

A 10% (m/v) Triton X-114 (Acros Organics, New Jersey, USA) solution was prepared by diluting 10.0 g of compound in water, shaking for 24 h and the volume was finally set to 100.0 mL.

Borate buffer solution (0.5 $mol\,L^{-1}$, pH 8.0) was prepared by dissolving 15.5 g of H_3BO_3 (Carlo Erba, Italy) in 400 mL of ultra pure water and adjusted to pH 8.1 with 2.0 $mol\,L^{-1}$ aOH (Merck, Germany) solution. Then, the final volume is completed to 500 mL.

A methanol solution 50% (v/v) acidified with HNO_3 (1% v/v) was prepared by mixing 50 mL methanol with 1 mL concentrated HNO_3 and the volume was set with ultra pure water. This solution was used to decrease the micellar phase viscosity.

Synthetic seawater was prepared in such a way that its final composition (in $g\,L^{-1}$) was 27.9, 1.4, 2.8, 0.5 and 2.0 of NaCl, KCl, $MgCl_2$, NaBr and $MgSO_4$, respectively.

2.3 *Petroleum produced water and superficial seawater samples*

Petroleum produced waters from offshore platforms located on the coast of northeast Brazil and a seawater sample from the coast of Rio de Janeiro state were collected in polypropylene bottles that were previously cleaned by soaking in 10% v/v nitric acid. Samples were filtered through a 0.45 μm membrane filter acidified with 1 mL concentrated nitric acid and stored in frozen until analysis.

2.4 *Optimisation*

The optimisation process was carried out using multivariate methodologies. Two-level full factorial design [26] was applied for preliminary evaluation of the significance of the factors involved in the system. Dohelert design [27] was performed in order to determine the optimum conditions to perform the experiments. In relation to factorial design, the experimental error was evaluated from sum of square residuals to Doehlert designs, errors were evaluated from replicate of central point.

Four parameters (pH, concentration of NaDDTC, concentration of surfactant Triton X-114 and time of reaction) were regarded as factors. The experimental data were processed by using the STATISTICA software. All the experiments in this step were carried out in random order, using saline solutions ($0.7\,\mathrm{mol\,L^{-1}}$ NaCl or approximately 41‰ of salinity) of Pb, Cu, Ni and Cd, respectively, in the following concentrations 50, 25, 25 and $12.5\,\mu\mathrm{g\,L^{-1}}$.

The responses were obtained as analytical signal (counts per second) for each metal studied. To allow the optimisation of four responses simultaneously, they were combined in a unique response. Each individual response is transformed in an adimensional scale which can vary from 0 to 1 by their division by the major signal of the set for each metal. Later, these four individual responses must be summed generating a unique response which was evaluated in the optimisation process.

2.5 *General procedure for CPE*

A 40.0 mL sample, 0.5 mL buffer solution and 1.5 mL NaDDTC solution was added in a centrifuge tube. A 0.4 mL Triton X-114 solution was added after shaking and the volume was completed to 50 mL with ultra pure water and homogenised. This system was heated at 40°C in a water bath for 15 min. To separate the phases, the mixture was centrifuged for 10 min at 3000 rpm. Afterwards, this solution was cooled in an ice-bath for 15 min and the micellar phase was separated by inverting the tube to discard the aqueous phase. A volume of 1.0 mL of a solution composed by 1% HNO_3 and methanol 50% (v/v) was added to the micellar phase to decrease the viscosity of the extract. Finally, the volume was set to 2.0 mL and the determination of Pb, Cu, Ni and Cd was performed by ICP OES using ultrasonic nebuliser for sample introduction.

2.6 *Evaluation of matrix effect on the analytical signal*

To evaluate the influence of the residual salinity from original matrix in the nebulisation process and its consequence in the signal of metals, its standard solutions made in four different saline media were submitted to CPE. Thus, analytical solutions of Pb, Cu, Ni and Cd prepared in several NaCl concentrations (salinities of 10‰, 40‰, 60‰ and 80‰) were submitted to the CPE procedure and the analytical curves were obtained to evaluate the influence of the residual salinity in the micellar phase on the metal signals.

3. Results and discussion

3.1 *Factorial design*

A full two-level factorial design was used for the screening study. The results are summarised in Table 2 and its behaviour can be visualised from the Pareto chart (Figure 1). The Pareto chart shows the effects sorted by their absolute size and there is a vertical line to indicate the minimal magnitude of statically significant effect allowing to review a large number of factors simultaneously and to extract information about the system. The evaluation demonstrates that three studied factors are statistically significant (pH, concentration of surfactant and concentration of NaDDTC) and require a final optimisation. As it can be observed, pH is the factor that presents major influence in the extraction. According to positive estimated effect for pH, its increase allows improve the CPE, but this linear mathematical model does not establish a practical limit which will be determinate in the Doehlert design. Moreover, the factor *time of reaction* does not present a significant effect inside the studied experimental field and must have its value fixed (30 min) in the next step for optimisation. The Pareto graph also shows that interactions pH–NaDDTC and pH–surfactant present significant effect. These interactions are the evidence of synergic effect between these pairs of variables and they will be selected for further optimisation. The Doehlert design must be applied to become feasible to the localisation of optimum values of three variables that present significant effect.

Table 2. Panel A: Factors and levels used in the full two-level factorial design and Panel B: response obtained from application of experimental matrix.

Panel A

Variables	Low level (−1)	High level (+1)
pH	3.0	8.0
NaDDTC concentration (%)	0.001	0.050
TX-114 concentration (%)	0.05	0.20
Reaction time (min)	10	30

Panel B

Exp.	pH	NaDDTC	TX-114	Reaction time	Response
1	−1	−1	−1	−1	0.2999
2	+1	−1	−1	−1	2.9665
3	−1	+1	−1	−1	1.4466
4	+1	+1	−1	−1	2.4169
5	−1	−1	+1	−1	0.5625
6	+1	−1	+1	−1	3.020
7	−1	+1	+1	−1	1.2779
8	+1	+1	+1	−1	3.2477
9	−1	−1	−1	+1	0.9498
10	+1	−1	−1	+1	2.9927
11	−1	+1	−1	+1	1.2874
12	+1	+1	−1	+1	2.4091
13	−1	−1	+1	+1	0.4281
14	+1	−1	+1	+1	3.6197
15	−1	+1	+1	+1	1.2586
16	+1	+1	+1	+1	3.3717

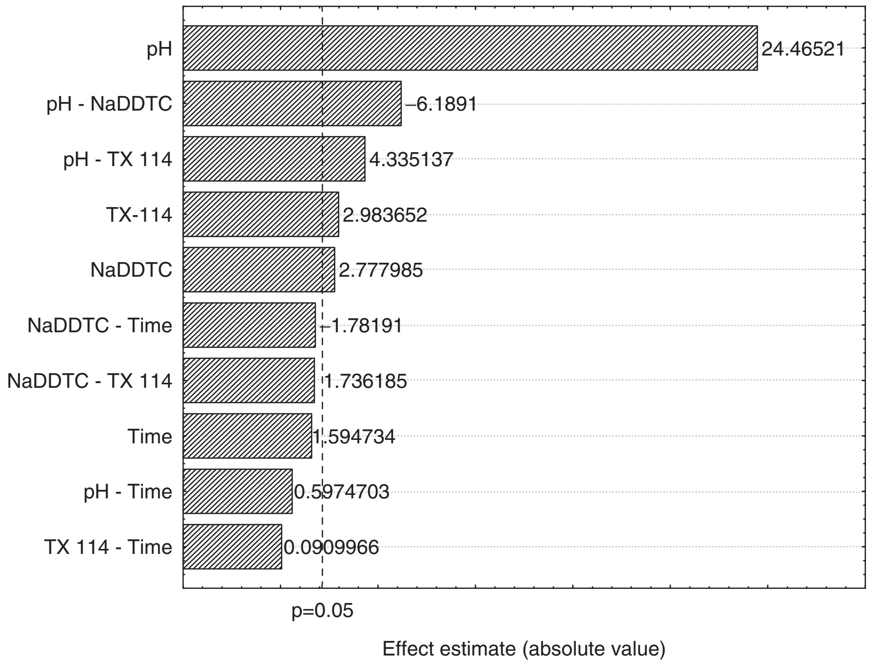

Figure 1. Pareto chart for the full factorial design. Dashed line represents the limit to significant values according to a confidence interval of 95%.

Table 3. Doehlert design with real and coded values for optimisation of following variables Panel A: Triton X-114 X pH and Panel B: NaDDTC X pH.

Panel A

Exp.	Triton X-114	pH	Response
1	0.25 (1)	7 (0)	1.045
2	0.20 (0.5)	10 (0.866)	1.933
3	0.05 (−1)	7 (0)	3.997
4	0.10 (−0.5)	4 (−0.866)	1.457
5	0.20 (0.5)	4 (−0.866)	0.104
6	0.10 (−0.5)	10 (0.866)	3.689
7A	0.15 (0)	7 (0)	3.659
7B	0.15 (0)	7 (0)	3.565
7C	0.15 (0)	7 (0)	3.153

Panel B

Exp.	NaDDTC	pH	Response
1	0.015 (0)	10 (1)	0.219
2	0.025 (0.866)	9 (0.5)	1.46
3	0.015 (0)	6 (−1)	2.086
4	0.005 (−0.866)	7 (−0.5)	0.595
5	0.005 (−0.866)	9 (0.5)	1.523
6	0.025 (0.866)	7 (−0.5)	1.204
7A	0.015 (0)	8 (0)	2.718
7B	0.015 (0)	8 (0)	2.973
7C	0.015 (0)	8 (0)	2.646

3.2 *Doehlert design 1 – optimisation of TX-114 concentration and pH*

A Doehlert matrix for two variables was applied to find the optimum conditions for TX-114 concentration and pH. In this procedure, NaDDTC final concentration was fixed at 0.011%. The experimental results obtained with the Doehlert design for these variables together with the coded and real values for the variables studied are shown in Panel A of Table 3. The equation below illustrates the relationship of these two variables and the response (*R*), where (*R*) is the combination of the four individual signals for Pb, Cu, Ni and Cd. The data were processed using coded values.

$$R = 3.45 - 1.50(\text{TX-114}) - 0.94(\text{TX-114})^2 + 1.17(\text{pH}) - 1.91(\text{pH})^2 - 0.23(\text{TX-114})(\text{pH})$$

The corresponding surface response is shown in Figure 2(a). Lagranje criteria [28] applied to this equation indicate that the critical point is characterised as a maximum.

The derivatisation of this general equation as (pH) and (TX-114) results in two new equations:

$$\frac{\partial R}{\partial(\text{TX} - 114)} = -1.50 - 1.88(\text{TX} - 114) - 0.23(\text{pH}) = 0$$

$$\frac{\partial R}{\partial(\text{pH})} = 1.17 - 3.82(\text{pH}) - 0.23(\text{TX} - 114) = 0$$

The critical values for the variables are found by solving these equations system. Thus, critical values were −0.85 (pH) and 0.36 (TX-114) which correspond to the real values 8.2 (pH) and 0.070% (TX-114 final concentration).

3.3 *Doehlert design 2 – optimisation of NaDDTC concentration and pH*

To perform this set of experiments related to second the Doehlert design, final concentration of TX-114 was fixed to 0.15%. The experimental results obtained with the Doehlert together with the coded and real values for these two variables studied are shown in Panel B of Table 3. The equation obtained for fitted second-order mathematic model to experimental data is presented below:

$$R = 2.78 + 0.16(\text{NaDDTC}) - 1.57(\text{NaDDTC})^2 - 0.43(\text{pH}) - 1.63(\text{pH})^2 - 0.39(\text{NaDDTC})(\text{pH})$$

The corresponding surface response is shown in Figure 2(b). Lagranje criteria also indicate that the critical point associated to this surface is characterised as a maximum.

The derivatisation of this general equation as (NaDDTC) and (pH) generate the equation system that allows calculating the optimal values:

$$\frac{\partial R}{\partial(\text{DDTCNa})} = 0.16 - 3.14(\text{DDTCNa}) - 0.39(\text{pH}) = 0$$

$$\frac{\partial R}{\partial(\text{pH})} = -0.43 - 3.26(\text{pH}) - 0.39(\text{TX-114}) = 0$$

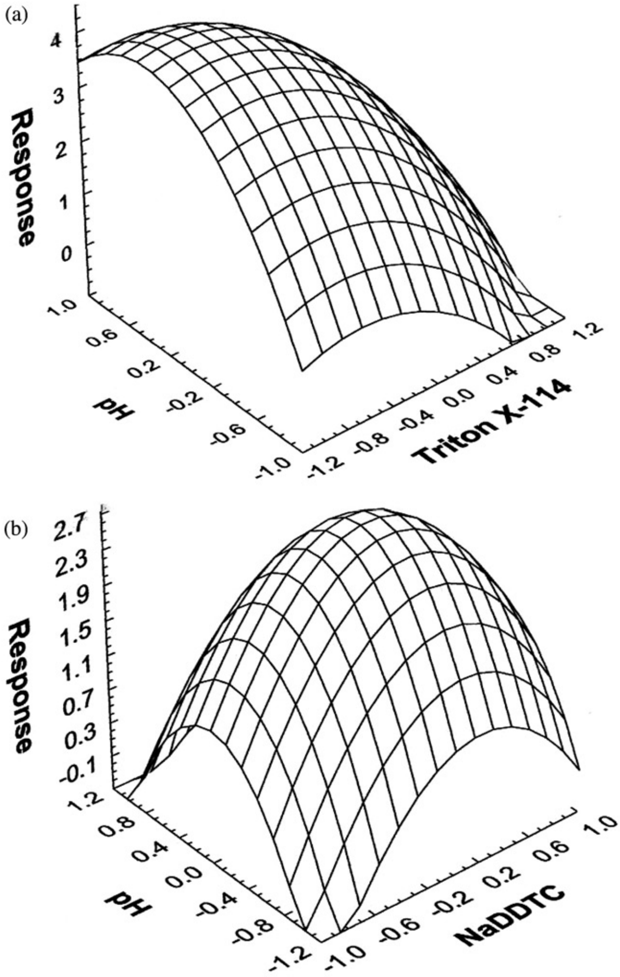

Figure 2. Response surfaces for (a) Triton X-114 versus pH and (b) NaDDTC versus pH.

Critical values were 0.067 (NaDDTC concentration) and −0.14 (pH) which correspond to the real values 0.015% (NaDDTC final concentration) and 7.8 (pH).

As observed, for both designs, values found for pH is near. Surface presented in Figure 2(b) shows that in this range, variations on analytical response are inside the experimental error. Thus, was chosen as optimal value for pH the media of value found in the two designs (8.0).

3.4 *Evaluation of matrix effect on analytical signal*

Seawater generally does not present a range of salinity variation as large as water produced from petroleum exploration. Petroleum produced water can present a large variation of salinity, ranging from zero to values as high as 150‰. Additionally, it is known that the micellar phase always presents some residual salinity from the matrix and

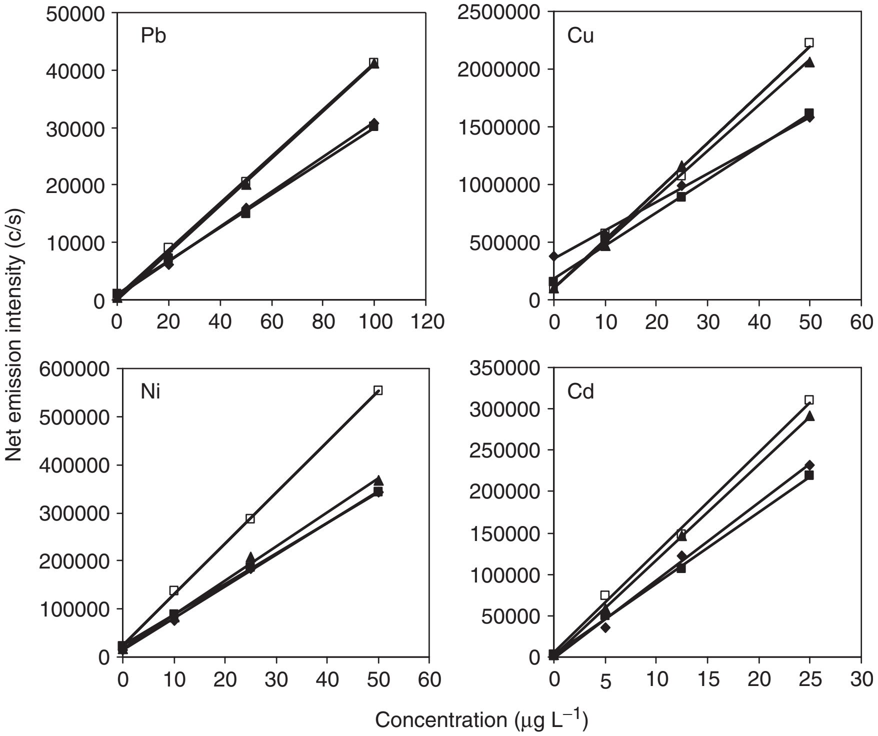

Figure 3. Evaluation of residual salinity interference in the signal of lead, copper, nickel and cadmium in the micellar phase obtained from solutions of NaCl after CPE. Legend: (□) 10‰, (▲) 40‰, (■) 60‰ and (◆) 80‰ salinity of NaCl in the initial solution.

this residual salinity in the surfactant-rich phase depends on the original concentration in the sample solution in which the extraction was made.

Variation of residual salinity in the micellar phase obtained after a CPE can generate a great problem of non-spectral interference in ICP OES mainly using ultrasonic nebulisation [29] because, depending on its final salt concentration, the ratio of solutions nebulisation become different. Thus, it is of concern to evaluate the influence of residual salinity in the nebulisation process and consequently in the analytical signal for each studied metal to assure that they can be determinated accurately.

This study was made through construction of analytical curves for Pb, Cu, Ni and Cd in four different salinities (10‰, 40‰, 60‰ and 80‰). Figure 3 shows that there is a general tendency for the slopes of the analytical curves to decrease when the salinity increases in the original solution. However, depending on determinate metal, some variation in the residual salinity can be tolerated without causing significance variation in the analytical signal.

Results of this study indicate that, it is necessary that the metallic standards used for calibration curves must present salinity compatible (in the same range of salinity) with the analysed samples for avoiding matrix matching differences in the transport of aerosol to the plasma. In the case of seawater samples that generally do not present large variation of salinity, it is feasible to use an external analytical curve constructed from CPE of standards in saline solution of 35‰. However, to water produced from petroleum industry, whose salinity can present a large variation, the best alternative is the use of the standard addition calibration method for analysis of these samples.

3.5 *Analytical features*

The proposed procedure using CPE for metal pre-concentration and determination by ICP OES have their analytical characteristics accessed. Table 4 presents some analytical characteristics of the developed procedure and allows a comparison with the procedure without the pre-concentration stage of the cloud-point. All analytical parameters were obtained using solutions that present salinities of 40‰. The calibration equations, obtained after pre-concentration by CPE of analytical solutions under the optimum conditions were given as function of the signal. The concentrations of the standards for construction of the analytical curves ($n = 5$) for the CPE ICP OES is also showed. The experimental enrichment factors were calculated as the ratio of the slopes of the calibration graphs with and without pre-concentration.

The limits of detection and quantification, defined as $\mathrm{LOD} = 3\sigma/S$ and $\mathrm{LOQ} = 10\sigma/S$, where S is the slope of the analytical curve, and σ is the standard deviation of 10 consecutive measurements of the blank were also estimated. The relative standard deviation ($n = 10$) achieved from synthetic seawater containing 40.0, 20.0, 20.0 and 10.0 $\mu g\,L^{-1}$ of Pb, Cu, Ni and Cd were respectively in this order: 3.7, 5.7, 6.6 and 3.1%. The LOD found were 0.030, 2.1, 0.62 and 0.27 $\mu g\,L^{-1}$ and LOQ were 0.10, 7.00, 2.07 and 0.90 $\mu g\,L^{-1}$ for Cd, Pb, Cu and Ni, respectively.

3.6 *Accuracy and application*

After defining optimum conditions for simultaneous extraction of, Pb, Cu, Ni and Cd from saline matrixes, the developed methodology was applied in two saline produced formation waters from offshore platforms and a seawater sample.

The accuracy of the developed procedure to the metal determination was verified by spike tests. Two produced water samples from PETROBRAS (Brazilian Oil Company), collected at offshore oil production platforms in northeast Brazil and a seawater sample were used to test accuracy and for the application of the method to real samples. The obtained results presented in Table 5 showed recoveries of 86% and 105%, which could be considered suitable for metal determinations at the micrograms per litre level in saline matrices. Table 5 also shows the results found in the analysis of the samples. Considering the large volumes of water recovery along with oil (it can be 10 times more than the oil volume), and that this water is discharged into the sea, the determination of trace metal concentrations are of environmental concern. Brazilian legislation (CONAMA resolution 357/2005) [29] establishes that the maximum concentrations allowed to be discharged in saline water class I (waters for more restrictive uses) are: 5 (Cd), 5 (Cu), 10 (Pb) and 25 (Ni) $\mu g\,L^{-1}$. From Table 5 we can observe that the trace metal levels in the produced waters analysed did not exceed the Brazilian guidelines.

4. Conclusions

Application of full factorial designs and a Doehlert matrix allowed the efficient optimisation of a procedure for simultaneous pre-concentration of Pb, Cu, Ni and Cd using CPE from saline samples and its posterior determination by ICP OES. Matrix effects

Table 4. Analytical curves equations ($n = 5$) for metal determination using CPE from solutions of salinity of 40‰ and without preconcentration step.

	Without preconcentration			Cloud-point extraction ($S = 40$‰)			
Metal	Curve	Intervals[a]	R^2	Curve	Intervals[a]	R^2	PF
Cd	$y = 3219$ [Cd, μg L^{-1}] $- 13870$	0–250	0.9980	$y = 64{,}487$ [Cd, μg L^{-1}] $- 21499$	0–12	0.9962	20.0
Pb	$y = 96$ [Pb, μg L^{-1}] $+ 11144$	0–1000	0.9941	$y = 1954$ [Pb, μg L^{-1}] $+ 5666$	0–50	0.9984	20.4
Cu	$y = 1362$ [Cu, μg L^{-1}] $+ 36931$	0–500	0.9970	$y = 26{,}502$ [Cu, μg L^{-1}] $+ 29202$	0–25	0.9981	19.5
Ni	$y = 257$ [Ni, μg L^{-1}] $+ 5748$	0–500	0.9973	$y = 5303$ [Ni, μg L^{-1}] $+ 1292$	0–25	0.9963	20.6

[a] Concentrations in μg L^{-1}; PF, Pre-concentration factor; S, salinity.

Table 5. Results for the analysis of petroleum produced water samples using CPE ICP OES and recovery test ($n = 3$).

Sample (salinity)	Metal	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Seawater (35‰)	Cd	0.0	< 0.03	–
		5.0	4.5 ± 0.4	90.0
		10.0	8.6 ± 0.1	86.0
		12.5	12.5 ± 0.4	100.0
	Pb	0.0	< 2.1	–
		20.0	17.3 ± 2.3	86.5
		40.0	36.0 ± 2.4	90.0
		50.0	50.6 ± 0.9	101.2
	Cu	0.0	3.8 ± 1.2	–
		10.0	13.4 ± 0.3	96.0
		20.0	22.3 ± 1.3	94.0
		25.0	31.4 ± 2.5	105.2
	Ni	0.0	0.9 ± 1.3	–
		10.0	8.8 ± 0.9	79.0
		20.0	18.7 ± 1.1	89.0
		25.0	23.2 ± 1.0	89.2
Petroleum formation produced water 1 (15‰)	Cd	0.0	< 0.03	–
		12.5	12.2 ± 0.6	97.6
	Pb	0.0	< 2.1	–
		50.0	46.1 ± 2.9	92.2
	Cu	0.0	< 0.62	–
		25.0	20.7 ± 0.5	82.8
	Ni	0.0	< 0.27	–
		25.0	24.9 ± 0.6	99.6
Petroleum formation produced water 2 (75‰)	Cd	0.0	< 0.03	–
		10.0	9.6 ± 0.3	96
	Pb	0.0	< 2.1	–
		20.0	8.9 ± 0.7	89
	Cu	0.0	3.7 ± 0.2	–
		10.0	13.9 ± 0.5	102
	Ni	0.0	1.5 ± 0.1	–
		10.0	11.8 ± 0.5	103

from residual salinity in the micellar phase were evaluated to assure accurate determination of metals from samples of different salinities.

The availability of simple and fast analytical methods to analyse produced water for trace metal determination is very important because CONAMA in its new Resolution (CONAMA 393/2007) imposed the Oil Companies in Brazil [30] to perform surveys for monitoring some metal concentrations (including Pb, Cu, Ni and Cd) in produced water prior to its disposal into the sea. The developed method is able to perform accurate measurements of Pb, Cu, Ni and Cd in saline samples such as produced formation water from offshore production, using ICP OES after metal separation and pre-concentration by CPE.

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References

[1] J.M. Neff, S. Johnsen, T.K. Frost, T.I.R. Utvik, and G.S. Durel, Mar. Environ. Res. **62**, 244 (2006).
[2] E.P. Oliveira, R.E. Santelli, and R.J. Cassella, Anal. Chim. Acta **545**, 85 (2005).
[3] M.C.T. Scholten, C.C. Karman, and S. Huwer, Toxicol. Lett. **112/113**, 283 (2000).
[4] R.J. Cassella, E.P. Oliveira, and O.I.B. Magalhães, Talanta **69**, 48 (2006).
[5] H.S. Ferreira, M.A. Bezerra, and S.L.C. Ferreira, Microchim. Acta **154**, 163 (2006).
[6] M.A. Bezerra, A.R.A. Nogueira, S.G. Lemos, and S.L.C. Ferreira, Intern. J. Environ. Anal. Chem. **88**, 131 (2008).
[7] A.M. Faria, R.P. Dardengo, C.F. Lima, A.A. Neves, and M.E.L.R. Queiroz, Intern. J. Environ. Anal. Chem. **87**, 249 (2007).
[8] A. Afkhami, T. Madrakian, and H. Siampour, Intern. J. Environ. Anal. Chem. **86**, 1165 (2006).
[9] F. Shemirani, R.R. Kozani, and M.R. Jamali, Intern. J. Environ. Anal. Chem. **86**, 1105 (2006).
[10] D.L.G. Borges, M.A.M.S. Veiga, V.A.L. Frescura, and B. Welz, J. Anal. At. Spectrom. **18**, 501 (2003).
[11] C. Ortega, S. Cerutti, and A.O. Roberto, J. Pharmaceut. Biomed. **36**, 721 (2004).
[12] J.L. Manzoori and A. Bavili-Tabrizi, Anal. Chim. Acta. **470**, 215 (2002).
[13] M.A.M. Silva, V.L.A. Frescura, and F.J.N. Aguilera, J. Anal. At. Spectrom. **13**, 1369 (1998).
[14] C.C. Nascentes and M.A.Z. Arruda, Talanta **61**, 759 (2003).
[15] E.K. Paleologos, D.L. Giokas, and S.M. Tzouara-Karayanni, Anal. Chim. Acta. **458**, 241 (2002).
[16] M.O. Luconi, R.A. Olsina, L.P. Fernandez, M.F. Silva, and J. Hazard, Mater. **128**, 240 (2006).
[17] G.M. Wuillound, J.C.A. Wuillound, R.G. Wuillound, M.F. Silva, R.A. Olsina, and L.D. Martinez, Talanta **58**, 619 (2002).
[18] A.C.S. Bellato, A.P.G. Gervasio, and M.F. Gine, J. Anal. Atom. Spectrom. **20**, 535 (2005).
[19] H. Filik, F. Dondurmacioglu, and R. Apak, Intern. J. Environ. Anal. Chem. **88**, 637 (2008).
[20] M.A. Bezerra, A.L.B. Conceição, and S.L.C. Ferreira, Microchim Acta **154**, 149 (2006).
[21] M.A. Bezerra, S.M.N. Maêda, E.P. Oliveira, M.F.B. Carvalho, and R.E. Santelli, Spectrochim. Acta **62B**, 985 (2007).
[22] M.A. Bezerra and S.L.C. Ferreira, *Extração Em Ponto Nuvem: Princípios E Aplicações Em Química Analítica* (Edições Uesb, Vitória da Conquista, 2006).
[23] M.A. Bezerra, M.A.Z. Arruda, and S.L.C. Ferreira, Appl. Spectrosc. Rev. **40**, 269 (2005).
[24] E.K. Paleologos, D.L. Giokas, and M.I. Karayannis, Trac-Trend Anal. Chem. **24**, 426 (2005).
[25] M.F. Silva, E.S. Cerutti, and L.D. Martinez, Microchim. Acta **155**, 349 (2006).
[26] R.M. Cespon-Romero and M.C. Yebra-Biurrun, Intern. J. Environ. Anal. Chem. **88**, 539 (2008).
[27] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, and L.A. Escaleira, Talanta **76**, 965 (2008).
[28] S.L.C. Ferreira, W.N.L. Santos, C.M. Quintella, B.B. Neto, and J.M. Bosque-Sendra, Talanta **63**, 1061 (2004).
[29] CONAMA, (2005) Resolução 357/2005, 17 de março de 2005 (Conselho Nacional do Meio Ambiente, Ministério do Meio Ambiente, Brasília, Brazil. <http://www.mma.gov.br> (accessed 1 July 2008).
[30] CONAMA, (2007) Resolução 393/2007, 08 de agosto de 2007 (Conselho Nacional do Meio Ambiente, Ministério do Meio Ambiente, Brasília, Brazil. <http://www.mma.gov.br> (accessed 1 July 2008).