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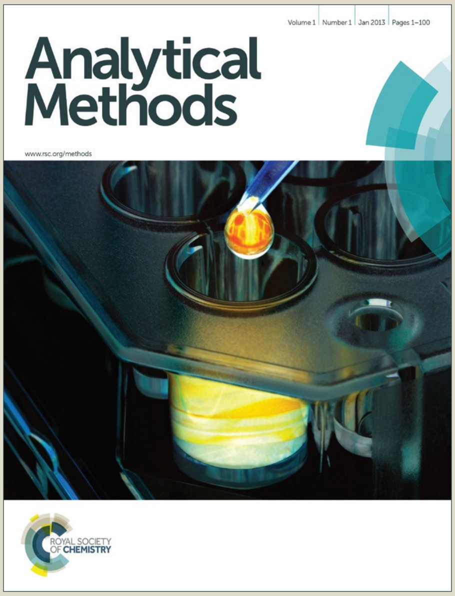

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Determination of cadmium, cobalt, copper, lead, nickel and zinc content in saline produced water from the petroleum industry by ICP OES after cloud point extraction

Francisco L. F. Silva, Wladiana O. Matos, Gisele S. Lopes*

Laboratório de Estudos em Química Aplicada, Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, Fortaleza, Ceará, BRAZIL.

*Corresponding author: gslopes@ufc.br

Abstract

The aim of this study was to develop a cloud point extraction (CPE) method to determine simultaneously cadmium, cobalt, copper, nickel, lead and zinc content in produced water by inductively coupled plasma optical emission spectrometry (ICP OES). A full factorial design with a central point was applied for optimization of experimental conditions. 8-hydroxyquinoline was used as the chelating agent and Triton X-114 as the surfactant for the trace element extraction. The ICP OES with axial view configuration was used in the trace element determination. According to desirability function, the chelating agent showed a negative influence on the extraction of the studied elements, which means increasing the amount of non-ionic molecules chelating agent may cause the opposite effect, since these molecules may be captured by the micelles decreasing the efficiency of extraction. In contrast, the extraction was positively influenced by the surfactant. Therefore, the following parameters were chosen: pH = 6.5; 0.500 mmol L^{-1} 8-hydroxyquinoline; and 0.1% v v^{-1} Triton X-114. The influence of salinity on the CPE was investigated. The slopes of the analytical calibration curves in saline media were studied. It was observed that increasing the NaCl concentration from 5 to 50‰ (w v^{-1}) led to a decrease in the angular coefficient of the calibration curves, which implies a decrease in the sensitivity of the method. Sc (2 mg L^{-1}) was added to standards and samples as internal standard to correct non-spectral interferences. The accuracy of the developed method was confirmed by spike recovery tests. The results present good recoveries, exceeding 86%, showing the successful application of the method for the simultaneous determination of the Cd, Co, Cu, Ni, Pb and Zn content in produced water samples. Limits of quantification (LOQ) were determined to be 2.0, 2.2, 3.2, 0.23, 2.2 and 1.9 µg L^{-1} for Cd, Co, Cu, Ni, Pb and Zn, respectively.

1. Introduction

The global expansion of the oil industry has resulted in an increased production of the water by-product called produced water (PW). This produced water is trapped in underground formations and brought to the surface along with oil and gas during petroleum production activities. Produced water accounts for a substantial volume of the liquid effluent in this type of extraction process. It is estimated that 260 million barrels of PW are produced each day worldwide [5,6].

The quality of the PW is closely linked to the composition of the oil, which depends on the region of the wells of oil extraction. The main constituents of the PW are dissolved minerals from the rock formations at the extraction site, residual chemicals from the production process, oil, microorganisms and dissolved gases [7].

Disposal of produced water into surface water is a major problem for the oil industry because this waste needs to be characterized and treated before being discharged into the environment to prevent environmental problems. These produced waters may also contain hydrocarbons and toxic elements such as lead, cadmium, chromium and arsenic [8]. However, the determination of metal content in produced waters is not a trivial task due to the high amount of dissolved solids and the high salinity of samples. In addition, analysis is often performed by limiting dilution steps because of the sensitivity of the techniques employed. This results in interference and unreliable results.

Previous studies reported in the literature recommend the use of a pre-concentration step such as cloud point extraction (CPE) for the determination of metals in saline PW samples, thereby extracting the analytes and minimizing interferences caused by the matrix [8-10]. However, complexation reactions in alkaline media (pH = 9)

[8,10] tend to hamper the experimental procedure, especially enhancing the risk of loss of cations by precipitation prior to their complexation. Furthermore, the use of methanol to dilute the oil-rich phase [9,10] must also be avoided because of the toxicity of this reagent. Alternatives to these procedures, such as use of complexing agents that would enable work to be undertaken at neutral pH was studied herein to determine six trace elements by ICP OES in samples of PW.

CPE is based on the separation between two isotropic phases generated in a micellar system. This process is a simple, cheap, efficient and less toxic method when compared with traditional liquid-liquid extraction procedures. CPE falls within what is conventionally called "Green Chemistry" because it uses small amounts of samples, besides the use of surfactants, which are non–flammable and have low volatility, minimizing risks within the extraction process [11-13].

Many spectrometric techniques have been used to determine the metals present in water after an extraction step. Such techniques include flame atomic absorption spectrometry (FAAS) [10, 12, 14-15], inductively coupled plasma optical emission spectrometry (ICP OES) [8, 17-19] and coupled mass spectrometry (ICP-MS) [20-21], and graphite furnace atomic absorption spectrometry (GF-AAS) [22-24].

The chemometric tools can be valuable to optimize methods involving many variables, such as CPE, considering all the factors involved can be varied simultaneously. Furthermore, the use of multielement techniques such as ICP OES may generate large amounts of data that can be better evaluated with the application of specific algorithms. The desirability function is an established function for the optimization of concurrent responses, modified by Derringer and Suich, 1980 [25], that specify the relationship between answers and dependent variables with the desirability of answers. This function find the better condition to all variable responses converting a response *Y* in a desirability individual function *d* which can range from 0 (representing a completely undesirable value) to 1 (representing an ideal response value).

In this work, CPE was used to extract Cd, Co, Cu, Ni, Pb and Zn in samples of PW and simultaneously to determine the trace elements by ICP OES. 8-hydroxyquinoline was successfully employed as chelating agent. The effects of different variables were studied using chemometric tools.

2. Experimental

2.1. Samples and reagents

Samples of saline produced water (PW) were acquired in the petroleum industry of Brazil and mixed together before the use in order to ensure high volume available to proceed all experiments. Samples were then stored at 15 °C in special vials provided by the company.

All solutions were prepared using ultrapure water (resistivity of 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). All glassware and polypropylene flasks were immersed in 10% v v^{-1} nitric acid (Merck, Darmstadt, Germany) for 24 h and rinsed with ultrapure water prior to use.

For the extraction procedure, a solution of 99% w w^{-1} 8-hydroxyquinoline (8-HQ, C_9H_7NO) (Sigma-Aldrich, Germany) was dissolved in a hydrochloric acid solution and octylphenoxypolyethoxyethanol surfactant Triton X-114 (Vetec, Sao Paulo, SP, Brazil). A Britton-Robison buffer solution was prepared using a mixture 0,1 mol L^{-1} of 65% w w^{-1} CH_3COOH (Vetec, Sao Paulo, SP, Brazil), 98% w w^{-1} H_3PO_4 (Sigma-

Aldrich, Germany), and 35% w w^{-1} H_3BO_4 (Vetec, Sao Paulo, SP, Brazil). The pH values were adjusted using NAOH 0.1 mol L^{-1} or HCl 0.1 mol L^{-1}. Nitric acid, 68% w w^{-1} (Vetec, Sao Paulo, SP, Brazil), was used for preparation of 50% v v^{-1} solutions to decrease the viscosity of the rich phase prior to analysis.

The calibration curves were prepared by dilution of the reference standard solution containing 1000 mg L^{-1} (Acros Organics, New Jersey, USA) of the trace elements in the study. The analytes concentrations were 0.5; 1.0; 2.5; 5.0 and 10.0 mg L^{-1}. As internal standard, Sc was added to all solutions, including the samples, to a 2 mg L^{-1} final concentration.

2.2. Instrumentation

A dual-view Optima 4300 DV (Perkin Elmer) ICP OES was used for Cd, Co, Cu, Ni, Pb and Zn analysis. The sample was introduced into the ICP using a Cross-Flow nebulizer with a double-pass spray chamber. The ICP OES operational parameters and the spectral lines are summarized in Table 1. A 2.4 mm tube internal-diameter alumina injector tube was used. The measurements were accomplished in the axial view of the instrument.

Table 1 - Instrumental parameters and spectral lines of the ICP OES

ICP OES conditions	
Spray Chamber	Double-pass
Nebulizer	*Cross-flow*
Alumina Injector (mm I.D)	2.4

Generator Frenquency (MHz)	40
Radio-frequency power (W)	1100
Plasma Ar flow rate (L min^{-1})	15
Nebulizer Ar flow rate (L min^{-1})	0.8
Auxiliary Ar flow rate (L min^{-1})	0.5
Sample flow rate (L min^{-1})	1.4
Spectral lines [a]	
Cd (nm)	226.502 (II)
Co (nm)	228.616 (II)
Cu (nm)	324.752 (I)
Ni (nm)	231.604 (II)
Pb (nm)	220.353 (II)
Sc (nm)	327.362 (I)
Zn (nm)	213.857 (I)

[a] spectral lines (I) and (II) for atomic and ionic lines, respectively.

2.3. Procedure for cloud point extraction

The procedure for cloud point extraction was implemented using 25 mL of a produced water sample and 0.500 mmol L^{-1} 8-hydroxyquinoline and 0.1% (v v^{-1}) Triton X-114 in a Britton-Robison buffer (0.1 mol L^{-1}, pH 6.5) medium. The cloud point was reached under heating in a controlled temperature bath at 55 °C for 25 min. After this, the samples were centrifuged at 3000 rpm for 15 min. The mixture was cooled down in an ice bath (5 min) in an effort to increase the viscosity of the surfactant-rich phase.

Then, the surfactant-rich phase was diluted to 2.5 mL by adding a volume of 250 µL of 50% v v^{-1} HNO_3 prior to the trace element determination by ICP OES using Sc as the internal standard.

The influence of salinity on the formation of cloud point was carried out preparing analytical calibration curves at different concentrations of NaCl (5‰, 20‰ and 50 ‰ w v^{-1}) and following the same cloud point extraction procedure. The slopes of the analytical calibration curves were compared.

2.4. Experimental design

A factorial experimental design was used to optimize the parameters of the procedure for cloud point extraction. The variables chosen for the optimization study were the chelating agent concentration, surfactant concentration, and the pH of the solution. An exploratory study of the interactions among the cloud point extraction variables using a full factorial design in two levels with a central point was performed (Table 2). The multiple responses were the concentrations of the trace elements measured by ICP OES in this study.

Table 2 - Levels of factors established for the experimental design

Variables	Minimum (-)	Maximum (+)	Center Point (0)
Chelating agent Concentration (mmol L^{-1})	0.1	0.7	0.4

Surfactant Concentration (% v/v)	0.04	0.10	0.07
Hydrogen Ionic Potential (pH)	5.0	7.0	6.0

3. Results and discussion

3.1. Evaluation of the experimental parameters of the proposed method

The cloud point extraction procedure was optimized using a full factorial design (FFD) in two levels considering three variables. In this type of experimental design, the influence of each variable in the extraction process can be observed, the interaction between them as well.

The chelating agent concentration is one of the most important factors to optimize to reach an efficient percentage of extraction. Normally, must use a chelating reagent in excess for dislocation of the equilibrium and to form the complex with the analyte. Previous studies using this chelating agent reported a concentration within the range of 0.1 to 0.7 mmol L^{-1} [19], and for this reason, the same concentration range was investigated in present study.

Triton X-114 is a surfactant that presents a low cloud point temperature of 23 to 26 ºC [19, 26] under high density, which facilitates the separation of the phases [27]. However, the addition of a heating step in the experiments performed in the present work showed that it is not possible to observe the cloud point formation without this step. This result is likely due to the high ionic strength of the produced water samples.

Surfactant-rich phases were diluted by adding nitric acid prior to the analysis by ICP OES to minimize possible interference of transport of the sample to the ICP. Despite the addition of nitric acid, the analysis was carried out using Sc as internal standard (Sc) in order to correct non-spectral interferences.

The chosen pH range was selected taking into consideration the chelating agent used within this study. The 8-HQ molecule C_9H_6OHN in acidic solution presents both hydroxyl (pKa=9.89) and nitrogen (pKa=5.13) in the protonated form, or ionic as $C_9H_6OHN^+$. The complexation of cations in solution by this chelating agent must be successful in alkaline or neutral media. The versatility in the selection of the pH value is valuable considering trace element analysis. As mentioned, 8-hydroxyquinoline is a weak acid, and it is necessary to deprotonate it to obtain the maximum chelation capacity of the trace elements present in the produced water sample. As such, it is necessary to work under alkaline conditions. However, under alkaline conditions, we might experience poor stability of the trace elements in solution as a consequence of their precipitation as hydroxides. Therefore, slightly acidic and neutral conditions were studied in this work.

According to the models of the obtained response surfaces for the trace elements studied in the experimental design, the coefficient β values for each variable of the equations that describes the models were determined and are presented in Table 3.

Most of values of the coefficients in equations relating to pH ($ß_3$) of the surface response methodology under study are negative values. The negative value means how this variable is changing the response. Higher values of pH may provoke precipitation depending on the concentration of the elements in the sample solutions. Zhao (2012) [19] also have observed decreasing of the concentration of the same elements when increased pH values in the solutions.

The Deringer's desirability function was used to find the experimental conditions (factor levels) that ensure compliance with criteria of all involved responses and, simultaneously, to provide the optimal value for all the evaluated variables [29]. Figure 1 shows the desirability function plot obtained for the selected experimental domain studied in this work. The global value of the desirability function obtained was 0.7. Figure 1 shows an increase of desirability in higher pH values. However, as mentioned before, under alkaline conditions poor stability of the trace elements in solution were observed compromising the repeatability of the measurements.

The results (Figure 1) reveal that the chelating agent concentration used in this study negatively influences the percentage of extraction of the trace elements. An excess of chelating agent is necessary to shift the equilibrium in relation to the complex molecules, but a large increase of the amount of non-ionic molecules of 8-HQ may cause the opposite effect, since these molecules are not captured by the micelles and the chelated elements may decrease the efficiency of extraction. In contrast, the extraction is positively influenced by the surfactant concentration. Therefore, the following parameters were chosen in the experiments of cloud point extraction: pH = 6.5; 0.500 mmol L^{-1} 8-hydroxyquinoline; and 0.1% v v^{-1} Triton X-114.

Table 3 – Coefficient β values of the equations for the response surface models

ELEMENTS	β1	β2	β3
Cd	-3.33×10^{-3}	2.50×10^{-2}	-6.25×10^{-4}

Co	-8.13×10^{-3}	2.08×10^{-3}	-6.25×10^{-5}
Cu	-1.02×10^{-2}	6.37×10^{-2}	-1.09×10^{-3}
Ni	0.429	13.058	-5.94×10^{-2}
Pb	-7.042×10^{-2}	-0.563	1.60×10^{-2}
Zn	-1.60×10^{-2}	5.21×10^{-2}	-6.69×10^{-3}

β1 = 8-Hydroxyquinoline Concentration; β2 = Triton X-114 Concentration; β3 = pH

3.2. Analytical figures of merit

The analytical characteristics of the proposed method can be seen in Table 4. We observe that the enrichment factors, defined as the ratio between the slope of the analytical curves before and after the pre-concentration procedure, range from 11 - 9.7. The enrichment factors are good considering the complexity of the matrix and the high salinity of the PW samples. Moreover, increasing the initial volume of sample for the CPE experiments may allow better enrichment factors. The Brazilian law[2] to dispose saline effluent allows high amounts of the elements studied, however, due to high salinity and the tolerance of the optical techniques, successive stages of dilution was needed. Thus, the sensibility of the employed techniques may not be adequate for the trace element determination. The separation of the saline matrix step is relevant to decrease the needed of dilutions prior the analysis.

The analysis of trace elements in water samples with high salinities is not a trivial task. Interference arising from the Na emission remains the major problem when using ICP techniques such as ICP OES. Thus, methodologies that enable the separation of the matrix in addition to pre-concentration of the trace elements are always very useful. The proposed method showed clear advantages in the separation of the saline matrix.

The limits of quantification were calculated taking into account the recommendations outlined by IUPAC (International Union of Pure and Applied Chemistry) using LOQ = 10 ∂/s, where ∂ is the standard deviation of the expression of the blank sample not containing the element (ultrapure water) from 10 independent measurements, and s is the slope of the analytical curve. These results are given in Table 5.

The LOQ found in the developed method present are in accordance to previous work in the literature [8], thus the implemented approach is suitable for trace element determinations in saline effluent as well as is reliable to check if they are in accordance to the Brazilian legislation [2] to be disposed.

Table 5 – Limits of quantification of the trace elements after the CPE procedure

Elements	LOQ (µg L^{-1})
Cd	2.0
Co	2.2
Cu	3.2
Ni	0.23
Pb	2.2
Zn	1. 9

The equilibrium formation constants of the complexes are negatively influenced by the ionic strength of the solution. The dependence on ionic strength in the CPE is shown in Table 6 and may be compared by the slope of the analytical calibration curves in saline media, 5‰, 20‰ and 50 ‰ NaCl concentration. The decreasing of slope values obtained for the calibration curves are more pronounced from 5‰ to 20‰ NaCl than from 20‰ to 50‰ NaCl. The slope values decreased around 80% for Cd, Co and Cu, and around 40% for Ni, Pb and Zn.

3.3. Application of the method to analyze produced water from the petroleum industry

The produced water sample was decanted and filtered to eliminate any oil traces that may be present in the sample before being subjected to the procedure. Tests of standard additions were performed by adding 0.02, 0.2 and 0.5 mg L^{-1} of the trace elements under study to verify the accuracy of the method (Table 7). The percentage of salinity of 30‰ of the produced water sample was determined by the Mohr method.

The relative standard deviations (RSD) found in this study vary from 0.22 to 2.93%. Handling the micellar phase is a critical feature for every CPE procedure, especially in terms in terms of reproducibility. Other authors reported higher RSD values varying from 4.2 to 5.6 working with samples of natural waters [19], and also comparable RSD values varying from 1.2 to 2.6 working with saline water samples [8].

The results show good recoveries, exceeding 86%. These results indicate the successful application of the present method for the simultaneous determination of Cd, Co, Cu, Ni, Pb and Zn by ICP OES in saline produced water samples.

4. Conclusion

The proposed method is effective for the extraction and pre-concentration of Cd, Co, Cu, Ni, Pb and Zn in saline produced water samples with acceptable limits of quantification and standard deviations. Moreover, the application of an easy to handle chemometric tools of factorial design and desirability function allows the optimization of the procedure for the extraction of the six elements simultaneously. The choice of the chelating agent combined with chemometric tools was important to allow working in lower pH values with accuracy.

Additionally, the method is simple and highly efficient for the determination of trace elements in complex matrices with high salinity.

The possibility of automation of the method to decrease the manipulation of the samples is currently under investigation in our group.

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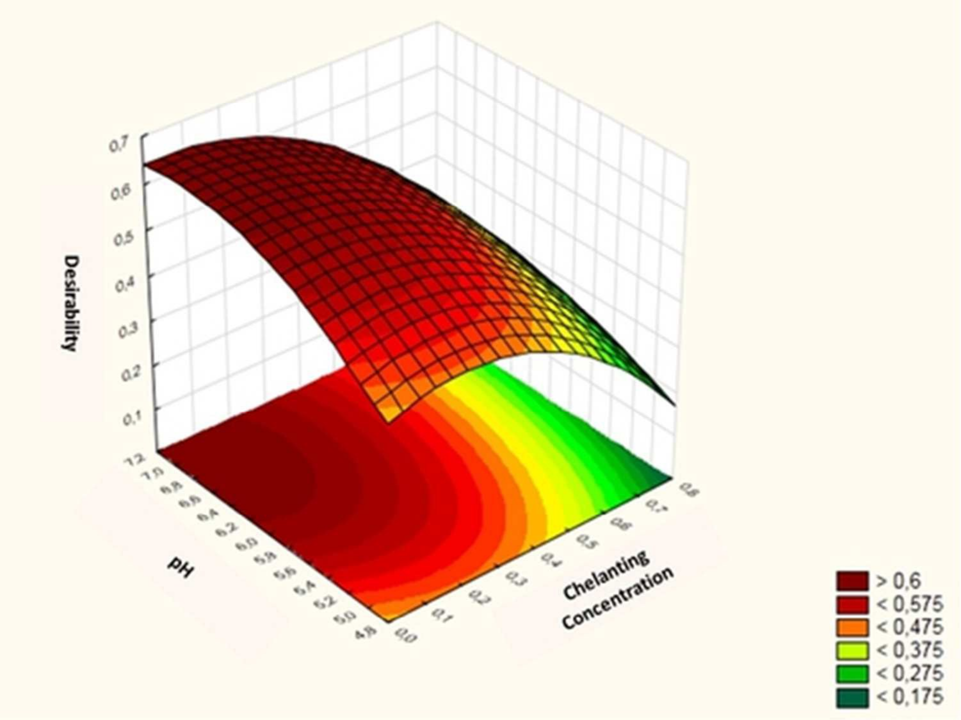


Desirability function plot
20x15mm (600 x 600 DPI)

Table 4 –

Analytical characteristics of the proposed method for the determination of trace elements present in PW samples by ICP OES

Elements	With CPE	R^2	Without CPE	R^2	EF
Cd	3332.63x – 20	0.9999	343.57x - 648.90	0.9999	9.7
Co	1853.05x + 3.1	0.9997	183.47x – 68.25	0.9998	10
Cu	3574.34x – 1059.1	0.9997	324.94x – 21749.4	0.9992	11
Ni	2269.72x + 3.5	0.9999	231.604x – 566.7	0.9997	9.5
Pb	265.92x – 6.9	0.9998	28.86x - 68.25	0.9995	9.9
Zn	3056.90x + 5.3	0.9998	304.68x – 843.86	0.9997	10

Table 6 –

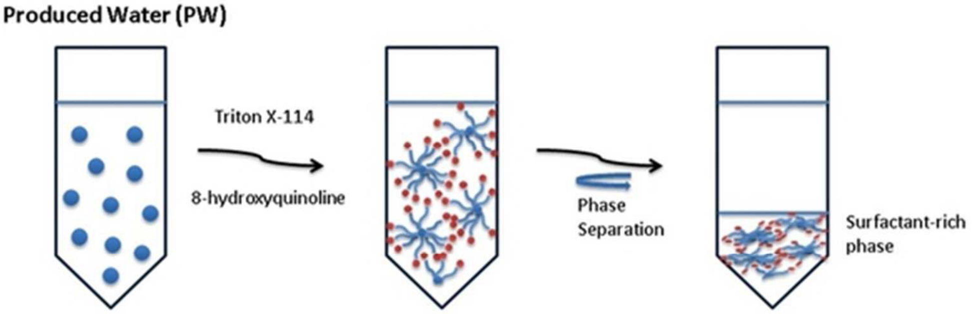
Effect of residual salinity on the analytical calibration curves parameters (n = 6)

Elements	**5 ‰ NaCl**	**R^2**	**20‰ NaCl**	**R^2**	**50 ‰ NaCl**	**R^2**
Cd	342.9x – 291,2	0.9379	78.43x – 109,71	0.9647	55.60x – 13.87	0.9700
Co	258.4x – 81,3	0.9261	37.39x – 82,73	0.9518	24.75x + 181.67	0.9618
Cu	2744.1x – 2533.7	0.9467	620.98x + 4000	0.9808	927.42x + 2032.09	0.9969
Ni	92.08x + 574,2	0.9927	68.99x + 138.33	0.9808	90.15x + 135.80	0.9998
Pb	16.06x + 8,03	0.9934	6.48x + 2,27	0.9782	5.42x – 3.66	0.9807
Zn	233.08x – 23,94	0.9435	107.56x – 344,86	0.9448	67.24x + 56.28	0.9902

Table 7 –

Results obtained for the analysis of produced water samples using CPE and the spike recovery test (n = 3)

		Spiked					
Elements	**Sample**	**0.02 mg L^{-1}**	**Recovery (%)**	**0.2 mg L^{-1}**	**Recovery (%)**	**0.5 mg L^{-1}**	**Recovery (%)**
Cd	0.206 ± 0.001	0.223 ± 0.001	99	0.422 ± 0. 003	108	0.714 ± 0.015	101
Co	0.216 ± 0.001	0.235 ± 0.003	100	0.483 ± 0.005	99	0.757 ± 0.010	108
Cu	0.240 ± 0.002	0.258 ± 0.001	99	0.427 ± 0.001	93	0.658 ± 0.002	84
Ni	0.245 ± 0.001	0.250 ± 0.001	94	0.423 ± 0.003	89	0.748 ± 0.010	101
Pb	0.274± 0.011	0.289 ± 0.004	98	0.446 ± 0.022	86	0.729 ± 0.015	91
Zn	0.278 ± 0.001	0.298 ± 0.003	100	0.479 ± 0.005	110	0.740 ± 0.012	92



Cloud Point Extraction for trace element analysis in samples of produced water
25x19mm (600 x 600 DPI)