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Article

Dispersive Liquid Phase Microextraction (DLPME) as a Strategy for Cd^{II} Separation and Determination in High-Salinity Produced Waters by Graphite Furnace Atomic Absorption Spectrometry

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In this study, we propose a microextraction method for the determination of Cd^{II} in produced waters. The process is based on the conversion of Cd^{II} ions into a hydrophobic diethyldithiocarbamate (DDTC) complex with its subsequent dispersive liquid phase microextraction (DLPME) from the aqueous medium with chloroform. The organic phase was then diluted with ethanol and Cd absorbance was measured by graphite furnace atomic absorption spectrometry (GF AAS). The experimental conditions related to the DLPME process were investigated, and the best microextraction conditions were achieved at pH = 6.0 (acetate buffer), 7.5×10^{-6} mol L^{-1} of DDTC, and when using 200 µL of chloroform as the extracting solvent. No dispersing solvent was needed, which allowed the recovery of approximately 140 µL of chloroform extract. Pyrolysis and atomization temperatures of the GF AAS program were determined through the construction of the respective curves. The estimated limits of detection (LOD) and quantification (LOQ) were 5 and 17 ng L^{-1}, respectively, whereas the enrichment factor for the method was 17. Six samples of seawater and five samples of produced waters with salinities between 30 and 270‰ were analyzed as well as two certified reference materials of saline waters.

Keywords: produced waters, cadmium, dispersive liquid phase microextraction, saline waters

Introduction

The determination of (sub)trace concentrations of metals in saline samples by spectrometric techniques remains a challenge in the field of environmental monitoring. The presence of high concentrations of dissolved salts in the samples can result in several problems during the analysis, affecting the transportation of the samples, causing poor performance of the instrumentation, and also leading to the occurrence of strong specific interferences in the measurement step. These problems can vary in intensity depending on the technique used in the analysis and the salinity of the samples. In this sense, it is almost impossible to analyze high-salinity samples by atomic spectrometric techniques without subjecting them to pretreatment before the analysis.

Certainly, produced waters from petroleum exploration are one of the most difficult types of saline samples to be analyzed. They occur due to the mixing of the formation water (already present in the reservoir) with the injection water,[1] which is the fluid introduced into the well to keep the pressure and allow more efficient extraction of the oil.[2] The most common fluid used in offshore platforms is seawater, which already presents an average salinity of approximately 35‰.[3] Due to the specific conditions found inside the oil wells, the salinity of produced waters is prone to be higher than seawater. Besides the very high concentration of dissolved salts, produced waters can contain several other components, such as various types of organic substances, NORM (normally occurring radioactivity materials), and metals.[2,4-7] Large amounts of produced water are generated during petroleum extraction; therefore, these waters are the most important waste of this kind of operation. They must be treated before discharging, and for this reason, analytical tools are required to monitor the concentration of possible pollutants such as metals.

The current literature reports the development of some analytical methods for the determination of metals in produced waters. Despite the initial developments made by our research group to propose some alternatives for the direct injection of samples for metals determination in produced

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waters by graphite furnace atomic absorption spectrometry (GF AAS), using specific chemical modifiers,[8-11] the best strategy seems to be to carry out the separation of metallic analytes and the matrix before the analysis. In this field, different approaches have been proposed.

Oliveira *et al.*[12] and Freire and Santelli[13] proposed the retention of metallic cations onto commercially available resins, such as Toyopearl AF-Chelate-650M and Chelex-100, respectively, to separate the analytes from the saline matrix before determining them by atomic spectrometric techniques. Santelli *et al.*[14] developed a resin for the solid-phase extraction of metals from produced waters and their determination by inductively coupled plasma mass spectrometry (ICP-MS). The competition between the large concentration of cations already present in the samples and analyte ions by the active sites of the resins seems to be a major drawback of this approach.

Some specific strategies have been developed for Hg quantification in produced waters. They have explored the possibility to convert Hg in gaseous species. In this context, Francisco *et al.*[15] proposed the online photochemical vapor generation of Hg induced by formic acid for its separation from the saline matrix before determination by inductively coupled plasma optical emission spectrometry (ICP OES). Miranda-Andrades *et al.*[16] promoted the speciation analysis of Hg through the distillation of Hg species followed by the analysis by gas chromatography coupled to atomic fluorescence spectrometry.

Cloud point extraction has been chosen by some research groups for the separation/preconcentration of metallic analytes from this kind of sample probably because the presence of high concentrations of dissolved salts favors the process. Escaleira *et al.*[17] and Silva *et al.*[18] explored this approach to determine several metals in produced waters by ICP OES, whereas Gondim *et al.*[19] optimized a cloud point extraction procedure for the determination of dissolved iron by flame atomic absorption spectrometry (F AAS). Bezerra *et al.*[20] also extracted metals from produced waters using cloud point extraction for their determination by ICP OES. However, they had to correct non-specific interferences due to the occurrence of residual salinity in the extracts through the application of an internal standardization calibration procedure with yttrium.

We have used some other approaches to perform metals determination in produced waters. In the work of Cruz and Cassella,[21] it was employed the ionic liquid 1-hexyl-2-methylimidazolium-hexafluorophosphate in the extraction of Ni^{II} and Cu^{II} from saline waters extracted with petroleum in offshore operations.[21] In this work, the analytes were complexed with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with the ionic liquid, which was diluted with ethanol before introduction into the GF AAS. Recently, we proposed the use of a semipermeable membrane filled with chloroform to extract Cd^{II} from produced waters.[1]

In this study, we propose a preconcentration method for the determination of Cd in produced waters by GF AAS, at ng L^{-1} concentration, after dispersive liquid phase microextraction (DLPME) of the hydrophobic Cd^{II}-diethyldithiocarbamate (DDTC) complex with chloroform.

Experimental

Apparatus

A Varian AA240Z graphite furnace atomic absorption spectrometer (Mulgrave, Australia) was employed in the measurement of Cd absorbance in the extracts. The spectrometer was equipped with a Varian GTA 120 atomizer unit (Mulgrave, Australia) and a Varian PSD 120 autosampler (Mulgrave, Australia). The atomization of Cd was carried out with graphite tubes containing L'Vov platforms made of electrolytic graphite coated with pyrolytic graphite, also provided by Varian. A hollow cathode lamp of Cd was used as the radiation source. The instrumental conditions used in the Cd determination by GF AAS are given in Table 1.

Table 1. Instrumental conditions employed in the Cd determination by graphite furnace atomic absorption spectrometry

Parameter	Value
Wavelength / nm	228.8
Slit width / nm	0.5
Lamp current / mA	4.0
Background correction	Zeeman-effect[a]
Protective gas	99.99% argon[b]

[a]Operated at 0.8 T magnetic field; [b]supplied by Linde Gases (Macaé, Brazil).

We measured the pH of the solutions with a pH meter from Digimed (São Paulo Brazil), model DM-22, which was connected to a glass electrode combined with an Ag/AgCl reference electrode. We also measured the salinity of the samples with a portable salinometer from Instrutherm (São Paulo, Brazil), model RTS 101ATC.

The separation of organic and aqueous phases was induced with an Eppendorf (Hamburg, Germany) centrifuge, model 5804. The ultrapure hydrochloric acid used in this work was obtained by distillation with a sub-boiling distillation apparatus (BSB-939-IR) from Berghof (Eningen, Germany). The analytical grade concentrated hydrochloric acid was supplied by Tedia (Fairfield, OH, USA)

Reagents and solutions

A Direct Q3 water purification system supplied by Millipore (Milford, MA, USA) was utilized to prepare the deionized water employed throughout the experimental work.

The standard solutions of Cd^{II} were prepared from adequate dilution, with deionized water, of a 1000 mg L^{-1} standard stock solution furnished by SPEX (Metuchen, NJ, USA).

Sodium diethyldithiocarbamate (DDTC) solutions were prepared by dissolving the solid reagent, purchased from Sigma-Aldrich (St. Louis, MO, USA), in deionized water. The mass of the reagent and the volume of water were calculated according to the desired concentration of the DDTC solution.

Britton-Robinson buffers were employed in the study of the influence of the pH on the extraction. They were prepared at 0.10 mol L^{-1} concentration with sodium acetate trihydrate (Vetec, Rio de Janeiro, Brazil), boric acid (Sigma-Aldrich, St. Louis, MO, USA), and sodium phosphate monobasic (Sigma-Aldrich, Steinheim, Germany). The pH of each buffer solution was adjusted with NaOH and HCl solutions. Once the optimum pH was identified, an acetate buffer solution of 0.10 mol L^{-1} and pH 6.0 was used. It was prepared by dissolving 1.37 g of sodium acetate trihydrate (Vetec, Rio de Janeiro, Brazil) in 80 mL of deionized water and subsequent adjustment of the pH to 6.0 with diluted solutions of NaOH and HCl. Then, the volume was completed to 100 mL in a volumetric flask.

All solvents used in this work (ethanol, chloroform, toluene, xylene, and octanol) were at least of analytical grade (Tedia, Fairfield, OH, USA). The solid NaOH and concentrated HCl employed in the experiments were supplied by Sigma-Aldrich (St. Louis, MO, USA) and Tedia (Fairfield, OH, USA), respectively.

General DLPME procedure

The samples were analyzed using the optimized procedure. For this purpose, 15 mL of sample (or standard solution) were pipetted to a 25-mL volumetric flask, 2.5 mL of a 0.010 mol L^{-1} acetate buffer solution (pH = 6.0) and 25 µL of a 7.5×10^{-3} mol L^{-1} DDTC solution were added, and the volume was completed to the mark. Afterward, 5 mL of this solution were transferred to a 15-mL capped polyethylene flask and 200 µL of chloroform was rapidly injected into the solution with the aid of a micropipette. The turbid solution that formed was gently shaken. Then, the flask was centrifuged for 5 min at 1800 rpm, which was enough time to induce total separation of the phases. Approximately 140 ± 10 µL of chloroform were separated from the aqueous solution. This volume of chloroform was collected with a syringe and diluted to 500 µL with ethanol. The final diluted extract was taken to the vial of the GF AAS for analysis.

GF AAS analysis of the extracts

The quantification of Cd in the organic extracts obtained by application of the DLPME method was carried out by GF AAS using the temperature steps listed in Table 2. It was optimized through the construction of pyrolysis and atomization curves, which allowed us to choose the optimum temperatures. The volume of solution (extract diluted in ethanol) employed in each determination was 20 µL. It was injected together with 20 µg of Pd as a chemical modifier.

Table 2. Temperature program employed in Cd determination in the organic extracts by GF AAS after DLPME

Step	Temperature / °C	Ramp / s	Hold / s	Ar flow rate / (mL min^{-1})
Drying	85	5		300
	95	40	0	300
	120	10	0	300
Pyrolysis	800	5	4	300
Atomization	1800	1	3	0
Cleaning	2200	2	0	300

Samples

Produced water samples were provided by Petrobras and stored in low-density polyethylene bottles. They were acidified to a pH of 2.0 to avoid Cd^{II} adsorption on the bottle walls and maintained in the refrigerator until the analysis.

Seawater samples were collected from the beaches of the city of Niterói (Rio de Janeiro, Brazil) and were subjected to the same treatment given to the produced waters.

Results and Discussion

To facilitate the understanding and discussion of the results, this section was divided into three sub-sections: (*i*) optimization of the sample preparation procedure based on Cd^{II} microextraction; (*ii*) adjustment of the temperature program of the GF AAS, which was completed through the determination of pyrolysis and atomization temperatures; and (*iii*) evaluation of the calibration strategy and application of the developed method in the analysis of real samples of saline waters (seawater and produced water). All results are expressed in terms of Cd normalized response, which was calculated as the ratio A_n/A_m, where A_n represents the integrated absorbance verified in each point of the experiment, and A_m represents the maximum integrated absorbance observed in the experiment.

Optimization of microextraction conditions

Influence of the pH on Cd^{II} microextraction

The pH of the sample is a very important variable in the method because it is dependent on the complexation of Cd^{II} by DDTC and the subsequent extraction of the non-polar complex from the aqueous medium to the organic phase. As DDTC acts as a weak acid in the water medium, its ability to efficiently complex Cd^{II} ions depends on the pH. As already reported in the literature,[22,23] Cd^{II} bonds with DDTC through the two sulfur atoms present in the molecule that act as electron donors, forming a metal-ligand complex in a 1:2 ratio. As the pK_a of DDTC is 3.95,[24] the influence of pH was evaluated in the interval between 2.0 and 10.0. The experiments were run with a 2 μg L^{-1} Cd^{II} solution, a DDTC concentration of 7.5×10^{-5} mol L^{-1}, 100 μL of $CHCl_3$ as the extracting solvent, and 400 μL of ethanol as the dispersing solvent. The turbid solution obtained after the addition of the extracting solvent was agitated on a roller mixer for 5 min to improve the extraction, and the pH was adjusted using Britton-Robinson buffers (0.010 mol L^{-1}) to keep the ionic strength constant.

The obtained results (Figure 1) demonstrated that at a pH lower than 6.0, the analytical response tends to decrease, reflecting the fact that the complexation is not effective at these conditions due to the protonation of sulfur atoms. In addition, in an acid medium, DDTC can decompose into carbon disulfide and hydrogen sulfide, decreasing the availability of the complexing agent in the solution.[23] On the other hand, at a pH above 6.0, the response achieved a maximum value and remained constant beyond this value. Therefore, we selected a pH of 6.0 for the method to work in a condition in which minimum formation of hydroxy complexes of Cd^{II} was expected.

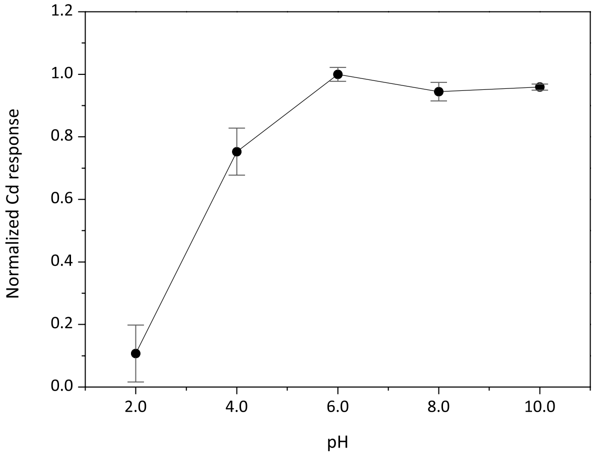

Figure 1. Influence of the pH on the microextraction of Cd^{II} with DDTC. Volume of $CHCl_3$ (extracting solvent) = 300 μL; volume of dispersing solvent = 400 μL of ethanol; DDTC concentration = 7.5×10^{-5} mol L^{-1}; and Cd^{II} concentration = 2 μg L^{-1}.

Influence of the volume and nature of the extracting solvent

The choice of the extracting solvent is one of the main parameters to be optimized in microextraction procedures. This solvent should present a suitable density and boiling point besides low solubility in water, low toxicity, selectivity, good extraction efficiency, and compatibility with the analytical technique used in the measurements.[25,26] In this study, four solvents were tested for extraction: chloroform, xylene, octanol, and toluene.

As can be seen in Figure 2, the four solvents presented a reasonable performance in extracting Cd^{II}-DDTC complexes from water. The performance of chloroform was slightly better, yielding higher analytical responses. Besides, in practical terms, the work with chloroform was facilitated because it is denser than water and deposits in the bottom of the extraction flask. On the other hand, toluene, octanol, and xylene floated on the water surface, which made it very difficult to collect the extracts. Therefore, chloroform was chosen as the extracting solvent.

Once the extracting solvent was chosen, we tested the influence of its volume on the Cd^{II} microextraction. This factor was evaluated by varying the volume of chloroform

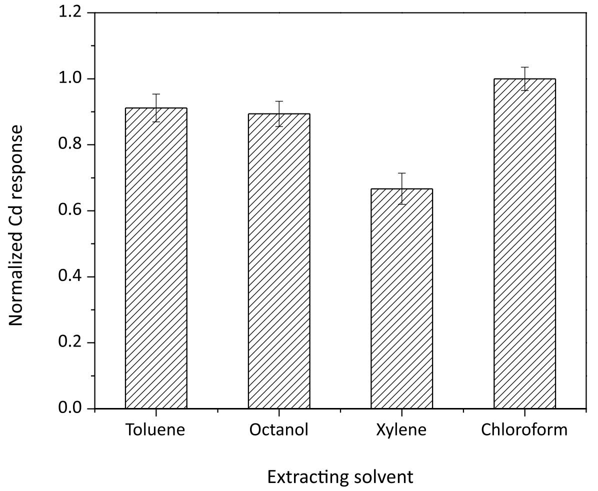

Figure 2. Influence of the type of extracting solvent employed in the microextraction of Cd^{II} from produced water. Volume of extracting solvent = 300 μL; volume of dispersing solvent = 400 μL of ethanol; DDTC concentration = 7.5×10^{-5} mol L^{-1}; pH = 6.0 (acetate buffer) and Cd^{II} concentration = 2 μg L^{-1}.

used in the extraction between 50 and 300 µL. It is important to highlight that after extraction, the collected solvent was always diluted to the same volume (500 µL) with ethanol.

Efficient extraction of Cd (as the Cd^{II}-DDTC complex) was achieved in the range of 200 and 300 µL of chloroform (Figure 3). The use of 50 µL of solvent was not enough to promote an efficient extraction of Cd and, besides, impaired the repeatability of the procedure because of the very low final volume separated deposited in the bottom of the flask, which made the collection difficult. In this scenario, we selected a volume of 200 µL of chloroform as the extracting solvent as a compromise between an efficient extraction and lower use of the solvent.

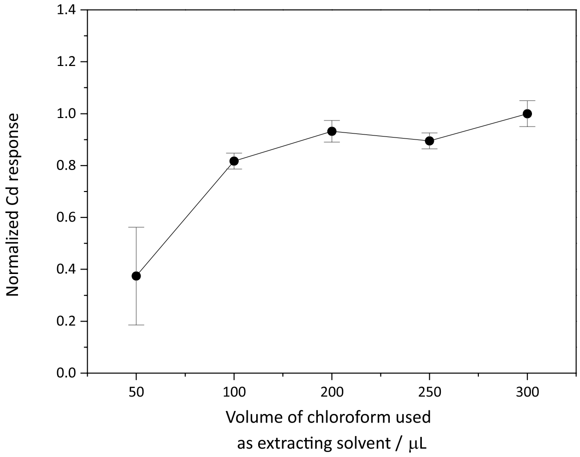

Figure 3. Influence of the volume of $CHCl_3$ used as the extracting solvent in the microextraction of Cd^{II} from produced water. Volume of dispersing solvent = 400 µL of ethanol; DDTC concentration = 7.5×10^{-5} mol L^{-1}; pH = 6.0 (acetate buffer) and Cd^{II} concentration = 2 µg L^{-1}.

Influence of the dispersing solvent

It is almost a consensus that the use of a dispersing solvent is needed to improve the dispersion of the extracting solvent in the aqueous medium in dispersive liquid-liquid microextraction. For this reason, we used 400 µL of ethanol as the dispersing solvent in all previous experiments. The presence of ethanol improved the dispersion of chloroform (and other solvents) in water but also caused a problem: it increased the solubility of the extracting solvent in the medium, making it possible to only recover a very small volume of this solvent at the end of the procedure. Therefore, we tested the actual necessity of using the dispersing solvent in the method. For this purpose, we varied the volume of the dispersing solvent (ethanol) from 0 (no use of the dispersing solvent) to 600 µL. Again, it is important to note that the amount of chloroform recovered in each experiment was diluted to 500 µL with ethanol before injection into the GF AAS.

The results obtained showed that there were no significant differences among the analytical responses with the variation in the volume of ethanol. Therefore, we decided to abdicate using any dispersing solvent, especially because, in this situation, the volume of chloroform recovered was higher (approximately equal to 140 µL). Beyond this point, the studied method could be defined as a DLPME procedure instead of a DLLME, according to the classification proposed by Šandrejová *et al.*[27]

Influence of the DDTC concentration

The strategy employed in the present work was based on the solvent microextraction of Cd^{II} ions as Cd^{II}-DDTC complex, which exhibits poor solubility in water[1] and high affinity with low-polarity solvents like chloroform. In this sense, the DDTC concentration is an important factor to be investigated because it significantly contributes to the formation of the Cd^{II}-DDTC complex, enhancing the extraction process. As mentioned previously, ML_2 complexes are formed between Cd^{II} and DDTC,[23] requiring that the concentration of DDTC be strictly controlled to ensure the formation of the extracted complexes. For this reason, the concentration of DDTC added to the medium was studied and the results are presented in Figure 4. This parameter was investigated, in detail, in the interval of 0 (absence of DDTC) to 2.0×10^{-5} mol L^{-1}. As expected, we could not observe Cd^{II} extraction in the absence of DDTC, evidencing that uncomplexed Cd^{II} ions are not significantly transferred to the organic phase. With the increase in the DDTC concentration, we observed a rapid increase in the extraction up to 7.5×10^{-6} mol L^{-1} DDTC, which was chosen as the optimum DDTC concentration for the method. Beyond this concentration, the response remained statistically constant, probably because maximum Cd^{II} extraction was achieved.

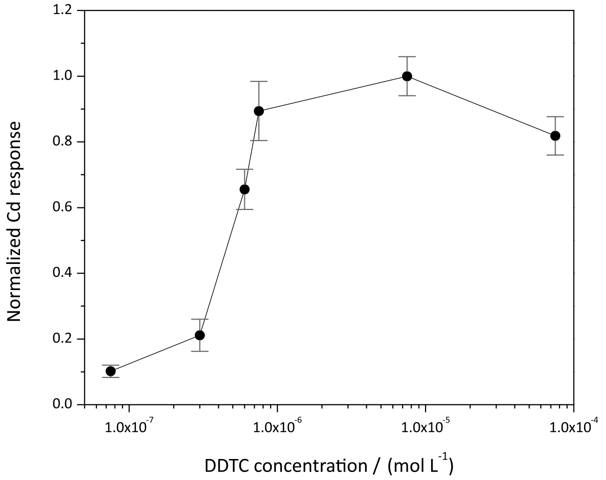

Figure 4. Influence of the DDTC concentration employed in the DLPME of Cd^{II} from produced water. Volume of $CHCl_3$ (extracting solvent) = 200 µL; pH = 6.0 (acetate buffer) and Cd^{II} concentration = 2 µg L^{-1}.

Determination of pyrolysis and atomization temperatures

The GF AAS temperature program utilized for the measurement of Cd in the chloroform final extracts was optimized from the standard program suggested by the instrument manufacturer, which can be usually applied in the analysis of aqueous solutions. The drying step remained unchanged even though the final temperature of the standard program is recommended when water is the main solvent. As chloroform and ethanol (extracting and diluting solvents, respectively) have boiling points lower than water, we observed the total elimination of the solvent using the regular temperatures recommended by the manufacturer. Therefore, the optimization of the temperature program was centered on the determination of suitable pyrolysis and atomization temperatures.

It is important to know that the measurement of the Cd signal was always carried out in the presence of 20 µg of palladium as a chemical modifier, which was used to thermally stabilize the analyte inside the graphite tube and allow the use of higher pyrolysis temperatures. The use of higher temperatures is advantageous because it allows more efficient elimination of other components of the sample, minimizing the occurrence of spectral interferences on the Cd measurement.

The pyrolysis curve was built up using an atomization temperature of 1800 ºC. In this experiment, the pyrolysis temperature was tested in the range of 200-1300 ºC. In turn, when we evaluated the atomization temperature, the pyrolysis temperature was set at 800 ºC, and the atomization temperature was varied in the interval of 1100-2000 ºC. The curves were constructed with a sample extract obtained from sample PW_1 and an aqueous standard solution of Cd^{II} with 1.5 µg L^{-1} of the analyte (direct injection of the aqueous solution). The profiles of the obtained curves are shown in Figure 5.

As can be seen in Figure 5, the shapes of both curves were very similar, presenting the same optimum pyrolysis and atomization temperatures. This result can indicate that no interferences should be present in the measurement of the organic extract originated in the DLPME procedure. Therefore, we selected a pyrolysis temperature of 800 ºC and an atomization temperature of 1800 ºC. In these conditions, the background absorption was always lower than 0.6 absorbance units, which could be easily corrected by the Zeeman-effect corrector device of the instrument.

Method evaluation and application

The first part of the method evaluation was to test possible calibration strategies because it was designed to be used in total Cd determination in high-salinity waters, such as the produced waters extracted along with petroleum during petroleum exploration. It is also important to note that the standard solutions were subjected to the same extraction procedure applied to the samples because we did not expect an exhaustive extraction of Cd^{II}. In this experiment, we compared two calibration curves: one prepared with aqueous solutions of Cd^{II} and another prepared using a sample of the produced water (standard addition approach) with a salinity of 160‰ (PW_1).

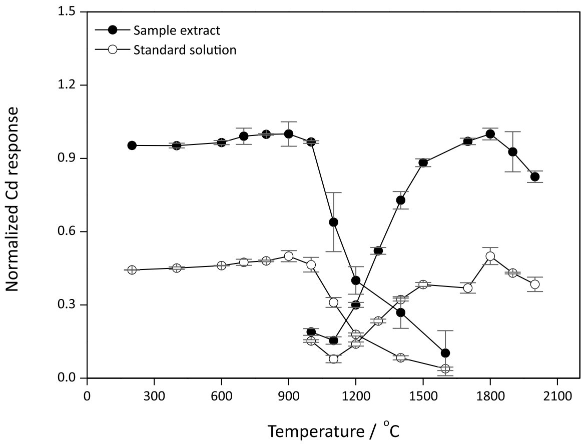

Figure 5. Pyrolysis and atomization curves for Cd constructed with a Cd^{II} standard solution (1.5 µg L^{-1}) and an extract obtained from sample PW_1, under optimized conditions.

The calibration curve prepared with standard solutions of Cd^{II} yielded a curve with an equation of $A = 1.29 (\pm 0.07) [Cd^{II}] + 0.0023$ ($r^2 = 0.992$), whereas the standard addition curve presented an equation of $A = 1.33 (\pm 0.07) [Cd^{II}] + 0.0717$ (coefficient of determination, $r^2 = 0.992$). The concentration of Cd^{II} in the solutions used in the calibration experiments was in the range of 0.025 to 0.20 µg L^{-1}. There was no significant difference between the two slopes (at 95% confidence level), indicating that no matrix interferences due to the salinity affected the extraction procedure. Therefore, we assumed that the method could be calibrated using standard solutions of Cd^{II}, but they should be subjected to the same microextraction procedure applied to the samples.

Once the calibration strategy was established, we determined the figures of merit of the method through the determination of the limits of detection and quantification which were calculated according to the recommendation of Miller and Miller,[28] using the 3σ and 10σ criteria, respectively. In this case, σ corresponds to the evaluation of the instrument noise, estimated as the standard deviation of 10 measurements of the blank. The precision and the enrichment factor were calculated as the ratio between the slopes of the calibration curves with and without the application of the DLPME.[29] The analytical features of the method are presented in Table 3.

Table 3. Analytical characteristics of the proposed method for Cd determination in produced waters after DLPME

Parameter	Value
Typical calibration curve	A = 1.29 [Cd^{II}] + 0.0023 (r^2 = 0.992)
Limit of detection / (ng L^{-1})	5
Limit of quantification / (ng L^{-1})	17
Intermediary precision^a / %	15
Repeatabilility^b / %	5.8
Enrichment factor	17

^{a}Calculated as the coefficient of variation of five determinations of sample PW$_5$ in different days; ^{b}calculated as the coefficient of variation of three determinations of sample PW$_2$ in the same day. r^2: coefficient of determination.

Table 4 presents a comparison of the proposed method with others developed for the determination of Cd in produced waters. As one can see, the limits of detection and quantification of the proposed method are, in general, better than those observed for other methods already developed for Cd determination in produced waters, except in the cases in which ICP-MS was employed as the analytical technique. The sample preparation procedure developed in this work is simple and does not require the use of any special material (such as membranes or resins) in the separation process. Besides, differently of other liquid-liquid extraction systems, we did not use any solvent for the dispersion of the extractant phase.

We evaluated the accuracy of the method by analyzing two certified reference materials from National Research Council of Canada. One of estuarine water (SLEW-3) and one of nearshore seawater (CASS-3). The results are presented in Table 5.

There was excellent agreement between the Cd concentration found by applying the developed method and the certified value. The Student's *t*-test was utilized to compare the two values (found and certified). The values of *t* were 2.59 and 2.31 for the CASS-5 and SLEW-3, respectively, being lower than the critical value of t at 95% confidence level (analysis in triplicate, degrees of freedom = 2), which is 4.30. Therefore, no significant differences were verified, confirming that no systematic errors were present in the determination of Cd by the developed method.

As the salinity of the great majority of produced waters is much higher than that of seawaters and there are no certified reference materials of produced waters, we spiked the five samples of produced waters with known concentrations of Cd^{II} and analyzed them by the proposed method to test its performance for the analysis of high-salinity samples. In addition, we analyzed six seawater samples using the proposed method and also performed a

Table 4. Comparison of different methods for Cd determination in produced waters

Sample preparation approach	Analytical technique	LOD	LOQ	Reference
Separation of Cd^{II} using a semi permeable membrane device filled with chloroform	GF AAS	0.08 µg L^{-1}	0.24 µg L^{-1}	1
Analyte separation from saline matrix using a Toyopearl AF-Chelate-650M resin	ICP MS	0.7 ng L^{-1}		12
Matrix separation using a styrene divinyl-benzene polymeric resin modified with 4-(5'-bromo-2'-tiazolilazo) orcinol	ICP MS	4.2 ng L^{-1}	14 ng L^{-1}	14
Cloud-point extraction of Cd^{II} using DDTC and Triton X-114	ICP OES	0.03 µg L^{-1}	0.10 µg L^{-1}	17
Cloud-point extraction of Cd^{II} using 8-hydroxiquinoline and Triton X-114	ICP OES		2.0 µg L^{-1}	18
Cloud point extraction of Cd^{II} using dithizone and Triton X-114	ICP OES		93 ng L^{-1}	20
Vortex-assisted dispersive microextraction with CCl_4 as extracting solvent and methanol for dispersion	ICP OES	0.006 µg L^{-1}	0.02 µg L^{-1}	30
Dispersive liquid phase extraction (DPLME) of Cd^{II} using chloroform (extracting solvent) and DDTC; no use of dispersing agent was needed	GF AAS	5 ng L^{-1}	17 ng L^{-1}	this work

LOD: limit of detection; LOQ: limit of quantification; GF AAS: graphite furnace atomic absorption spectrometry; ICP MS: inductively coupled plasma mass spectrometry; ICP OES: inductively coupled plasma optical emission spectrometry; DDTC: diethyldithiocarbamate.

Table 5. Results obtained in the determination of Cd in the certified reference materials employing the proposed method. Results are expressed as mean ± standard deviation (n = 3)

Certified material	Cd concentration found / (µg L^{-1})	Cd certified concentration / (µg L^{-1})
CASS-5 (nearshore seawater)	0.023 ± 0.001 (6.9%)^a	0.0215 ± 0.0018
SLEW-3 (estuarine water)	0.052 ± 0.003 (8.3%)^a	0.0480 ± 0.004

^{a}Difference between found and certified values is between parentheses.

Table 6. Results obtained in the analysis of real samples of saline waters and the recovery test. They are expressed as mean ± standard deviation (n = 3)

Type of sample	Sample	Salinity / ‰	Concentration found / (µg L^{-1})	Concentration added / (µg L^{-1})	Recovery / %
Seawater	SW_1	31	< LOQ	0.10	105 ± 5
	SW_2	33	< LOQ	0.05	105 ± 5
	SW_3	35	0.058 ± 0.003	0.20	94 ± 3
	SW_4	30	< LOQ	0.10	101 ± 3
	SW_5	35	0.044 ± 0.001	0.025	93 ± 8
	SW_6	36	0.034 ± 0.008	0.10	91 ± 8
Produced water	PW_1	160	0.26 ± 0.03	0.5	90 ± 5
	PW_2	62	0.48 ± 0.03	1.0	101 ± 16
	PW_3	33	0.37 ± 0.04	0.5	98 ± 11
	PW_4	234	3.05 ± 0.11	1.0	106 ± 9
	PW_5	270	2.68 ± 0.31	2.0	95 ± 4

LOQ: limit of quantification.

recovery test with these samples. The addition of Cd^{II} varied between 0.025 and 2.0 µg L^{-1}, which covers almost the entire range of concentration of Cd^{II} found in the samples. All results are shown in Table 6. The recovery percentages ranged between 90 and 106%, indicating that the method does not suffer from non-specific interferences. Besides, taking into account the elevated selectivity of the technique used, we confirmed that the method is accurate even for the analysis of produced waters with very high salinity.

Conclusions

The analytical method proposed in this work was simple, fast, and promoted an efficient separation of the Cd^{II} from the high salinity matrix, thus avoiding possible interferences in the measurement step due to the presence of dissolved salts. It proved to be very sensitive for the determination of cadmium in produced waters at the ng L^{-1} level.

The use of a dispersing solvent typically used in DLLME methods was avoided, which simplified the experimental operations and also permitted the recovery of a higher volume of the extractant solvent. The calibration was simple and could be performed with aqueous standard solutions of Cd^{II}, although it was necessary to subject the standard solutions to the entire microextraction procedure.

Accurate results were obtained in the analysis of two certified reference materials of seawater with the developed method. Recovery tests were performed with real samples of produced waters (and seawaters) and provided recovery percentages between 90 and 106%, confirming that the method can be employed in the determination of Cd in saline waters.

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