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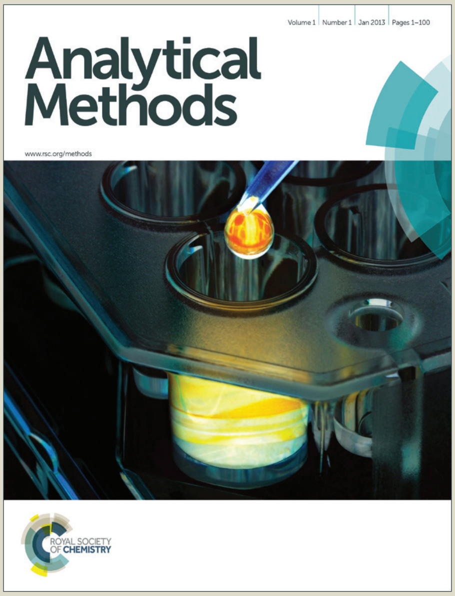

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Ionic liquid-based microextraction method for the determination of Cu and Ni in high-salinity produced waters from offshore petroleum exploration by GF AAS

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Abstract

This work reports the development of a novel method for the ionic-liquid microextraction and determination of Cu and Ni in high-salinity produced waters by Graphite Furnace Atomic Absorption Spectrometry (GF AAS). Studies were performed to set a suitable temperature program and to optimize the extraction conditions. Due to the presence of the ionic liquid in the extracts, a drying temperature of 300 °C was chosen for the temperature program. The pyrolysis and atomization curves indicated that the pyrolysis temperature for Cu and Ni should be set at 900 °C, and that the best atomization temperatures were 2100 and 2500 °C for Cu and Ni, respectively. The ionic-liquid microextraction was carried out by mixing 10 mL of sample with 1 mL of a 1% m/v ammonium pyrrolidine dithiocarbamate (APDC) solution and 1 mL of a Britton-Robinson buffer solution (total concentration 0.1 mol L^{-1}) with pH = 4.0. Then, 100 µL of the ionic liquid (1-hexyl-2-methylimmidazolium-hexafluorophosphate, C_6MImPF_6) were added and the mixture was shaken manually for 2 min. The obtained suspension was centrifuged for 15 min at 4500 rpm in order to promote the sedimentation of the ionic liquid. The ionic-liquid was separated from the upper aqueous phase using a micropipette and then, absolute ethanol enough to complete 1 mL was added. This final solution was introduced into the graphite tube for the determination of Cu and Ni. The method presented limits of quantification of 0.37 and 0.61 µg L^{-1} for Cu and Ni, respectively. The calibration of the method was possible using a matrix-matching approach using synthetic saline samples. Recovery tests were performed with the addition of aqueous standard solutions of the metal cations and resulted in the recovery percentages in the range of 76 - 126%.

Keywords: produced water, ionic liquid microextraction, GF AAS, trace elements

1. Introduction

Nowadays, the exploration/exploitation of petroleum is one of the most important industrial activities worldwide. Several countries, including Brazil, has spent many efforts to find new reservoirs in order to ensure an adequate supply of crude oil for fuel production, industrial uses, heating, electric energy generation and others. In Brazil, recent discoveries of large reservoirs of petroleum in the pre-salt layer is increasing the investments in this area and demanding the development of new technologies.[1,2]

Under the environmental point of view, the petroleum exploitation can cause many problems. Certainly, one of them is the production of large amounts of water along with petroleum. In some cases, the amount of water produced by a reservoir is five times the amount of oil. In the beginning of the operation of a well, the inner pressure is high, which allow the extraction of the crude oil without using any fluid to enhance the oil recovery. With time, the inner pressure decreases and water must be injected into the well to maintain the inner pressure and enhance the secondary recovery of crude oil. The water injected into the well is called of "injection water". The injection water is mixed with the water already present inside the reservoir (called formation water) and the mixture is taken out along with the crude oil. This water is called "produced water" and can contain a number of toxic organic substances such as benzene, toluene, xylenes, polycyclic aromatic hydrocarbons (PAH), phenols, alkylated phenols and organic acids. Additionally, inorganic contaminants such as radionuclides (NORM, from *normally occurring radioactive materials*) and toxic elements (As, Cd, Cr, Cu, Ni, Pb, V, among others) can be found in produced waters. The main characteristic of the produced water extracted from offshore platforms is the high salinity, which can reach values as high as 270‰.[3,4]

The extracted produced water has, in general, two destinations. It can be re-injected into the well or discarded in the ocean.[5] For discharging in the ocean, the production water must be treated to eliminate possible toxic contaminants and achieve the (good) quality imposed by the legislation. One of the most important parts of the treatment process is the determination of the toxic substances present in the produced water. This task is especially difficult due to the complex nature of this kind of sample, which includes its very high salinity. In the specific case of metals, some papers report their presence in produced waters from different origins.[6-9]

Despite the fact that the development of methods for the determination of metals in saline samples by atomic spectrometric techniques is frequently reported in the literature,[10-15] including the use of ionic liquids for separation/preconcentration purposes,[16-18] the development of analytical strategies for the determination of metals in produced waters is a subject relatively new. In this field, two different strategies have been followed: (i) direct determination of the analytes, which implies in the direct injection of the samples into the instruments[19-22] and; (ii) determination of the analytes after their separation/preconcentration from the samples.[23-24]

Oliveira et al.[19-20] proposed the use of combined chemical modifiers for the direct determination of Pb and Cr by ET AAS in produced waters from offshore petroleum exploration. In the first work, the use of HF combined with Ir-W permanent modifier provided efficient matrix elimination and suitable stabilization of Pb, allowing its quantification in samples with salinities up to 82‰.[19] Similar approach was employed in the determination of Cr in produced waters, but using HF combined with Pd modifier.[20]

Cassella et al.[21] employed $NH_4H_2PO_4$ as chemical modifier for the direct determination of vanadium in produced waters by ET AAS. The use of this modifier allowed the use of a pyrolysis temperature of 1500 ^{o}C, which was sufficient to set the background signals close to zero without significant loss of the analyte. Also, Cassella et al.[22] tested the Ir-W permanent modifier for the direct determination of Mn in produced waters using the same analytical technique. Samples with salinities that varied between 74 and 84‰ were analyzed. Nevertheless, the standard addition calibration had to be employed to overcome non-spectral interferences derived from the complex composition of the waters.

The separation of the analytes from the matrix is another option for the determination of metals in produced waters. In this approach, the analytes are transferred to another phase, which is simpler than the original sample. This process helps one to control possible interferences on the measurements and, in some cases, allows the preconcentration of the analytes, improving the limits of detection and quantification.

Oliveira et al.[23] determined ten elements (Cd, Pb, Ni, Zn, U, Mo, Fe, Co, V e Mn) in produced waters by ICP-MS after their separation from the saline matrix using the chelating resin Toyopear AF-Chelate-650M. The Chelex-100 resin was also successfully employed for this purpose. In this work, the authors separated five trace metals (Co, Cu, Mn, Ni and Pb) from the samples and quantified the analytes in the extracts by high resolution continuum source graphite furnace atomic absorption spectrometry.[24]

The goal of this work was to introduce, for the first time, the use of a hydrophobic ionic liquid (1-hexyl-3-methylimidazolium hexafluorophosphate, C_6MImPF_6) to promote the microextraction of Cu(II) and Ni(II) ions from high-salinity produced waters extracted along with petroleum in offshore operations. The quantification of the analytes in the extracts was performed by GF AAS. Also, a detailed study on the thermal behavior of the analytes in the presence of the ionic liquid was performed in order to set the best temperature program for the determination of the analytes by GF AAS.

2. Experimental

2.1. Apparatus

The absorbance measurements were performed with a Varian (Mulgrave, Australia), model AA240Z, atomic absorption spectrometer with a Varian GTA 120 graphite furnace atomizer unit and a Varian PSD 120 autosampler. The instrument was equipped with a Zeeman effect background corrector system (constant magnetic field of 0.8 T), which was utilized in all measurements. Graphite tubes with integrated L'vov platform were employed for the atomization of the analytes. They were also supplied by Varian. Argon (99.99% purity), supplied by Linde Gases (Macaé, Brazil), was employed as protective gas. Copper was measured at 324.8 nm with a slit width of 0.5 nm and using an individual hollow cathode lamp operated at 4.0 mA. Nickel was measured at 232.0 nm with a 0.2 nm slit width and using a hollow cathode lamp also operated at 4.0 mA.

The thermogravimetric analysis of the liquid ionic was performed with a SDT Q600 analyzer from TA Instruments (New Castle, DE, USA). Approximately 10 mg of the liquid ionic was directly inserted into the instrument and the temperature was varied from laboratory ambient temperature to 1000 ^{o}C under N_2 atmosphere. A heating rate of 20 ^{o}C min^{-1} was employed in the analysis.

An Eppendorff centrifuge (Hamburg, Germany), model 5804, was utilized to promote the separation of the phases. It was equipped with a variable angle rotor and an adaptor for polyethylene capped tubes of 15 mL capacity.

A Digimed (São Paulo, Brazil) pHmeter, model DM-22, was employed to determine the pH of the solutions. The pHmeter was equipped with a combined glass electrode, also furnished by Digimed. The salinity of the samples was measured with a hand-held refractometer, model RTS-101ATC, from Instrutherm (São Paulo, Brazil).

2.2. Reagents and solutions

Deionized water was obtained with a Direct Q-3 system, supplied by Millipore (Milford, USA). The deionized water employed throughout the experimental work always had resistivity of 18.2 MΩ cm, at least.

Standard solutions of Cu and Ni were prepared from the dilution of the stock standard solutions of 1000 mg L^{-1}, purchased from Tedia (Fairfield, OH, USA). The dilution was always carried out with a solution compatible with the solutions utilized in the extractions.

Ammonium pyrrolydine dithiocrabamate (APDC) was employed as ligand. A 1% m/v APDC solution was prepared by dissolving 0.1 g of the reagent, supplied by Sigma-Aldrich (St. Louis, MO, USA), in approximately 5 mL of deionized water. Afterwards, the obtained solution was diluted to 100 mL with deionized water.

The ionic liquid employed in the present work, 1-Hexyl-3-Methylimidazolium Hexafluorophosphate (C_6MImPF_6), was supplied by Sigma-Aldrich (St. Louis, MO, USA). Absolute ethanol employed in the dilution of the extracts was furnished by Tedia (Fairfield, OH, USA).

The Britton-Robinson buffer solution was prepared by dissolving convenient masses of sodium acetate (Sigma-Aldrich, Rio de Janeiro, Brazil), disodium hydrogen phosphate (Sigma-Aldrich, Rio de Janeiro, Brazil) and boric acid (Sigma-Aldrich, Rio de Janeiro, Brazil) in water sufficient to complete a final concentration of 0.1 mol L^{-1} of each component.

The samples of produced waters evaluated in this work were supplied by Petrobras. They were acidified to pH 1.8 with trace metal grade nitric acid (Seastar Chemicals, Sidney, Canada) and maintained in the refrigerator (4^{o} C) until their analysis. No additional treatment was dispensed to the water samples.

2.3. Extraction procedure

In a 15 mL polyethylene tube, 10 mL of sample (or diluted sample), 1 mL of buffer solution (Britton Robinson 0.1 mol L^{-1}, pH = 4.0) and 1 mL of a 1% m/v APDC solution were added and a clear solution was obtained. Then, 100 µL of the ionic liquid were introduced and the system was manually agitated for 2 min in order to ensure uniform dispersion of the ionic liquid in the medium. At this point, the formation of a turbid solution was observed due to the dispersion of the hydrophobic ionic liquid throughout the aqueous solution. Afterwards, the polyethylene tube was centrifuged for 15 min at 4500 rpm to promote the separation of the phases. After centrifugation, the ionic liquid phase containing the extracted metals was deposited in the bottom of the polyethylene tube. Then, the aqueous upper phase was taken out with the aid of a micropipette and absolute ethanol sufficient to complete 1 mL was added to the ionic liquid. This final extract was employed to determine Cu and Ni by GF AAS.

The optimization of the temperature program was performed with a 25 µg L^{-1} Cu and Ni ethanol solution containing 20% v/v (200 µL in each 1 mL of solution) of ionic liquid.

2.4. GF AAS measurements

A volume of 20 µL of extract was introduced into the graphite tube for the determination of Cu and Ni in the extracts. In the case of Cu, 10 µL of a 500 µg mL^{-1} Pd modifier solution was introduced immediately after the extract. Then, the temperature program was run and the measurements were carried out in integrated atomic absorbance mode. The temperature programs used for Cu and Ni determination in the extracts are listed in Table 2 and were obtained after a proper optimization, which will be described in the section 3.1.

3. Results and discussion

3.1. Optimization of the temperature program

The first part of this work was to set a convenient temperature program for the determination of the analytes by GF AAS in the ethanolic medium containing the ionic liquid. It is important to remember that the ionic liquids present very low vapor pressure and tend to volatilize at high temperatures. In this sense, initially, the drying step of the temperature program was optimized.

Before starting the experiments with the GF AAS, a thermogravimetric analysis of the ionic liquid was performed to identify its thermal characteristics and orientate us in the optimization of the drying step of the temperature program. As displayed in Fig. 1, the loss of mass of the ionic liquid started at approximately 275 ^{o}C, which indicated that a regular temperature used for drying aqueous samples (120 ^{o}C) could not be adequate to promote a convenient drying of the extracts inside the graphite tube. Therefore, the first parameter optimized in the drying step was the final temperature of this step.

The drying step was composed of different stages. In the first stage, the temperature was elevated up to 95 ^{o}C and then to 120 ^{o}C, in order to eliminate all ethanol present in the extracts and any residue of water. Then, the temperature was increased to a final temperature, which was evaluated in this study. Additionally, the influence of the heating ramp and the holding time of this stage on the signals of Cu and Ni was evaluated.

Firstly, the final temperature of the drying step was varied from 150 to 600 °C. The absorbance signals for both Cu and Ni did not vary significantly, being only observed a little decrease of them at temperatures higher than 550 °C. It is important to remark that, at the lowest temperatures employed in the study, typically between 150 and 250 °C, an incomplete drying of the extracts was observed. So, we decided to set the final temperature of the drying step at 300 °C, which was compatible with the data obtained in the thermogravimetric analysis.

After optimizing the final temperature of the drying step, the ramp (18 - 180 s) and holding (3 - 7 s) times were evaluated. Both parameters did not influence the absorbance signals of Cu and Ni. In order to avoid that the temperature program was excessively long, the ramp and holding times were then set at the lowest values, i.e., 18 s and 3 s, respectively. A ramp of 18 s represented a heating rate of 10 $^{o}C\ s^{-1}$.

Optimum pyrolysis and atomization temperatures were determined according to the classical procedure, which was based on the construction of the pyrolysis and atomization curves. In this experiment, the curves were constructed using two solutions: (i) a 25 µg L^{-1} of Cu and Ni in water and (ii) a 25 µg L^{-1} of Cu and Ni in ethanol containing the ionic liquid (see section 2.4). The obtained results are shown in Fig. 2A and 2B.

As it can be seen in Fig. 2, the difference observed between the curves obtained with the solutions prepared in water and in the ethanol/ionic liquid medium was small, evidencing that the adopted drying step was efficient for the elimination of the solvents (and ionic liquid) without volatizing the analytes. Even though, the pyrolysis and atomization temperatures were chosen taking into account the values obtained with the solution prepared in the medium containing ethanol and ionic liquid, since it tends to be very similar to the composition of the extracts. Under these conditions, the pyrolysis temperature set for Cu and Ni was the same, 900 ^{o}C; and the atomization temperatures were 2100 and 2500 ^{o}C, for Cu and Ni, respectively.

3.2. Optimization of the extraction conditions

Once established the operational conditions for the determination of Cu and Ni in the extracts by GF AAS, the next step of the work was the optimization of the experimental conditions for the microextraction of the analytes using the ionic liquid.

3.2.1. Effect of the pH on the extraction

The first parameter evaluated, related to the microextraction process, was the pH. It was expected that pH presented a remarkable effect on the complexing capacity of APDC, which behaves as an weak acid in solution. Also, pH affects the formation of hydroxy complexes of Ni(II) and Cu(II), which could impair the formation of the respective metal-APDC complexes.

The experiment was carried out using the same conditions expressed in the section 2.3, but using 200 µL of ionic liquid. The pH of the solution was varied by changing the pH of the Britton-Robinson buffer in the range of 4 - 10. The results obtained are shown in Fig. 3. This variable had no noticeable influence on the extraction in the range of pH studied, being observed a practically constant signal along the whole range. This result indicated that the complexing capacity of APDC was not affected by the pH in this range, which was already expected, since the pKa of the APDC is 3.29.[25] Studies with pH lower than 4 were not performed due to the difficult to maintain the pH without increasing the buffer concentration and to avoid the degradation of the reagent, a typical phenomenon observed for dithiocarbamate-containing reagents. In front of these results, the pH 4.0 was employed in all further experiments.

3.2.2. Effect of the APDC concentration

Other parameter that could influence the microextraction of the metal cations from solution was the reagent concentration. The study of this parameter is important because the amount of reagent must be enough to chelate the metal cations and provide their quantitative extraction to the hydrophobic ionic liquid phase

The concentration of APDC was tested in the range of 0.25 - 1.5% m/v. All other conditions were those described in section 2.3, except the volume of ionic liquid, which was 200 μL. The signals of both Cu and Ni presented the same behavior with the variation of the APDC concentration (Fig. 4). A soft increase of the signals was observed when the APDC concentration was increased from 0.25% m/v to 1.0% m/v. Beyond this point, the signals remained practically constant, indicating that no more ions could be chelated by the reagent. Therefore, in order to use a lower amount of reagent as possible, an APDC concentration of 1.0% m/v was set for the method.

3.2.3. Influence of the volume of ionic liquid

Liquid-liquid microextraction is characterized by the large difference between the volumes of extractant solution and sample employed in the process. The use of a very small volume of extractant phase (in relation to the sample volume), in general, results in the observation of a large preconcentration factor. However, the use of an excessively small volume of extractant phase can result in incomplete or inefficient extractions. In the case of the use of ionic liquids as extractant, their high-cost must also be considered.

In order to achieve the best condition, in terms of volume of ionic liquid, an experiment was performed to evaluate the influence of this variable on the method. In the experiments, the volume of sample was kept constant (10 mL) and the volume of ionic liquid employed in the extraction was varied between 25 and 200 µL. The other conditions were those already optimized.

The increase of the volume of ionic liquid caused a remarkable increase of the analytical signals for both Cu and Ni, to volumes up to 100 µL (Fig. 5). Beyond this volume, for Cu, the signals remained practically constant, indicating that maximum extraction of this analyte could be achieved even with 100 µL of ionic liquid were used. In the case of Ni, only a little increase in the signals was observed when 200 µL of ionic liquid was used. Therefore, we decided to set a volume of 100 µL of ionic liquid for the method in order to save this high-cost reagent without losing extraction efficiency.

3.2.4. Influence of salinity

The method presented in this work was conceived to be employed in the separation and determination of the analytes in highly saline waters obtained from offshore petroleum exploration. In order to evaluate the performance of the extraction procedure under these conditions, an experiment was performed to investigate the influence of salinity on the extraction process. Also, the results obtained in this experiment could indicate the efficiency observed in the separation of the analytes from the rest of the sample.

The influence of salinity was studied by carrying out the extraction of Cu and Ni from solutions containing NaCl concentrations in the range of 0 (no addition of salt) - 2 mol L^{-1}. Blank experiments were always run by applying the same procedure in the analysis of NaCl solutions without adding the analytes. Figure 6 shows the results obtained in this experiment. It is important to highlight that such results show the net integrated absorbances, i.e., the integrated absorbance obtained in the experiment with addition of the analytes less the integrated absorbance obtained in the experiment without adding them.

The increase of NaCl concentration in the solutions caused a decrease of the analytical signals for both Cu and Ni. This decrease was more pronounced for Ni than for Cu, being observed analytical signals approximately 60 and 40%, respectively, smaller than those observed when no NaCl was present in the samples. These results can be credit to the influence of NaCl on the extraction process, since no significant disturbance of the peak profiles and the increase of background absorbance were verified in the determination of the metals by GF AAS.

3.3. Evaluation of the calibration strategy

The results obtained in the evaluation of the effect of the salinity indicated that this parameter could cause significant influence on the accuracy of the method, being responsible for important interference on the quantification strategy. In order to find a suitable a calibration approach, taking into account the salinity of the samples, two curves were prepared for each metal in the range of 1 - 10 µg L^{-1}. The first curve was constructed using standard solutions of the metal cations prepared in deionized water, whereas the second one was constructed by spiking the sample A (160‰ salinity) with Cu(II) and Ni(II). The sample was 10-fold diluted for application of the procedure. The results are shown in Table 3.

Remarkable differences were noted when the calibration was performed with the saline sample, for both Cu and Ni. The curves prepared in saline medium presented smaller slopes than the curves prepared in water, which indicated the occurrence of a matrix interference on the extraction due to the ionic strength (salinity). These differences evidenced that the calibration could not be performed with aqueous standard solutions of the analytes and that a matrix-matching approach should be tested. Therefore, in order to evaluate this hypothesis, a new calibration curve was prepared with standard solutions prepared in a synthetic saline sample with 150‰ salinity (also 10-fold diluted). The composition of the synthetic saline sample is shown in Table 4.

As expected, the slopes were not significantly different of those observed when the calibration curves were constructed with the sample A, which had similar salinity. This result reinforced the idea that the salinity was the parameter responsible for the matrix interference on the extraction process and that a matrix matching approach must be used as calibration strategy in the quantitative analysis of the samples.

Once the experimental conditions were established for the application of the proposed method, the analytical features were estimated. The limits of detection and quantification were estimated using a calibration curve prepared in water. The estimated limits of detection (3σ criterion) for Cu and Ni were 0.1 and 0.2 µg L^{-1}, respectively, whereas the limits of quantification (10σ criterion) were 0.4 and 0.6 µg L^{-1}, respectively. These limits were derived for guidance purposes only, since they can be affected by the salinity of the medium employed for calibration. Linear calibration curves were always constructed in the range of 2.5 - 10 µg L^{-1} for both analytes. The typical equations were: $A = 0.0346$ [Cu (µg L^{-1})] - 0.0086 ($r^2 = 0.999$) and $A =$ 0.0353 [Ni (µg L^{-1})] + 0.0059 ($r^2 = 0.999$). Relative standard deviations of 4.0 and 7.5% were verified for Cu and Ni, respectively, in five independent measurements of an extract obtained from the extraction of a solution containing 1.0 µg L^{-1} of each analyte. The intermediary precision was evaluated by the analysis of the sample D in three different days and it was 11 and 13% for Cu and Ni, respectively.

3.4. Application of the proposed methodology

The developed method was applied in the determination of Cu and Ni in six samples of produced water, using two synthetic saline samples (55 and 150‰) for the preparation of calibration curves. The synthetic samples (Table 4) were diluted to provide a medium with a salinity as close as possible of the samples, which were 10-fold diluted.

Recovery tests were also performed to evaluate the accuracy of the method. For this purpose, the samples were spiked with 2.5, 5.0 and 10 µg L^{-1} of each analyte and analyzed employing the optimized conditions. The results obtained in the recovery tests are presented in Table 5 and the results obtained in the analysis of the samples are displayed in Table 6.

As it can be seen, the proposed extraction method showed to be suitable for the separation of both Cu and Ni from the saline matrices in order to allow their determination by GF AAS. The proposed method presented suitable analytical capacity for the quantification of the analytes in all samples, which were present in concentrations always higher than the limit of quantification derived for the methods.

Recovery percentages in the range of 76 - 126% were observed, indicating that the method has suitable accuracy for the determination of low concentrations of Cu and Ni in this kind of sample.

4. Conclusions

The separation method developed in this work was efficient for the isolation of the targeted analytes from the very saline samples, since no influence of the matrix was observed in the determination of both Cu and Ni in the extracts by GF AAS. The results obtained also indicated that the microextraction using ionic liquids can be considered an excellent option for the separation of metal cations from high-salinity produced waters originated from petroleum exploration in offshore conditions. Maybe, the use of other analytical techniques such as ICP-

MS for the determination of the metals in the extracts can increase the sensitivity of the method.

The results obtained in the study of the thermal behavior of the analytes in the medium of the ionic liquid showed that elevated drying temperatures should be used in the temperature program to eliminate adequately the ionic liquid, which was in agreement with data obtained in the thermogravimetric analysis of the ionic liquid. Also, it is important to remark that the choice of the calibration strategy was of fundamental importance for ensuring the accuracy of the proposed method. The saline matrix caused significant non-spectral interferences, which could be conveniently corrected by using the matrix-matching approach.

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Table 1. Operational conditions employed in the determination of Cu and Ni by GF AAS.

Parameter	**Cu**	**Ni**
Wavelength (nm)	324.8	232.0
Lamp current (mA)	4.0	4.0
Slit width (nm)	0.5	0.2
Measurement mode	Integrated absorbance	Integrated absorbance

Table 2. Temperature program employed in the determination of Cu and Ni in the ionic liquid-rich extracts by GF AAS.

Step	Temperature (^{o}C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Drying I	95	5	-	300
Drying II	120	10	-	300
Drying III	300	18	3	300
Pyrolysis	900	1	5	300
Atomization	2100 (Cu) 2500 (Ni)	1	4	0
Cleaning	2200 (Cu) 2600 (Ni)	2	-	300

Table 3. Slopes of the calibration curves prepared in different media, expressed as slope value ± standard error.

Medium	Cu	Ni
Water	0.035 ± 0.002 L µg^{-1} s^{-1}	0.035 ± 0.003 L µg^{-1} s^{-1}
Sample A (160‰)*	0.018 ± 0.004 L µg^{-1} s^{-1}	0.023 ± 0.003 L µg^{-1} s^{-1}
Synthetic saline sample (150‰)*	0.020 ± 0.003 L µg^{-1} s^{-1}	0.026 ± 0.003 L µg^{-1} s^{-1}

* Both samples were 10-fold diluted before application of the extraction procedure.

Table 4. Composition of the synthetic saline samples utilized in this work.

Substance	**Concentration (g L^{-1})**	
	Synthetic sample (150‰)	**Synthetic sample (55‰)**
KCl	0.50	0.10
$MgCl_2.6H_2O$	0.66	0.32
$CaCl_2.2H_2O$	5.60	0.84
$BaCl_2.2H_2O$	0.19	0.070
$SrCl_2.6H_2O$	0.40	0.20
$FeCl_3.6H_2O$	0.030	-
$NaHCO_3$	-	0.44
Na_2SO_4	0.070	-
NaCl	91	30
NaBr	0.15	0.080
Sodium acetate	0.029	-

Table 5. Results obtained in the recovery test applied to the analysis of the produced waters by the proposed procedure. Results are expressed as mean ± standard deviation (n = 3). The salinities of the samples are indicated between parenthesis.

Sample	Concentration added (μg L^{-1})^{a}	Cu recovery (%)	Ni recovery (%)
A (160‰)	2.5	88 ± 2	80 ± 12
	5.0	98 ± 1	76 ± 15
	10	89 ± 8	78 ± 9
B (62‰)	2.5	88 ± 5	80 ± 3
	5.0	97 ± 2	95 ± 9
	10	100 ± 6	98 ± 9
C (33‰)	2.5	88 ± 14	76 ± 4
	5.0	84 ± 7	89 ± 12
	10	76 ± 4	88 ± 2
D (234‰)	2.5	84 ± 13	120 ± 5
	5.0	85 ± 2	110 ± 11
	10	81 ± 13	118 ± 3
E (182‰)	2.5	88 ± 7	80 ± 7
	5.0	88 ± 9	95 ± 5
	10	97 ± 8	98 ± 5
F (270‰)	2.5	92 ± 4	126 ± 6
	5.0	86 ± 8	125 ± 10
	10	89 ± 16	118 ± 10

[a] The analytes were added directly to the diluted sample employed in the procedure.

Table 6. Concentrations of Cu and Ni found in the samples of produced waters employing the matrix matching approach. Results expressed as mean ± standard deviation (n = 3).

Sample	**Cu (µg L^{-1})**	**Ni (µg L^{-1})**
A	29.9 ± 1.4	75.4 ± 13.4
B	< LOQ	< LOQ
C	17.9 ± 0.6	2.64 ± 0.13
D	20.1 ± 2.7	29.9 ± 3.3
E	13.1 ± 1.4	7.13 ± 1.42
F	22.1 ± 1.7	11.9 ± 1.3

Figure 1

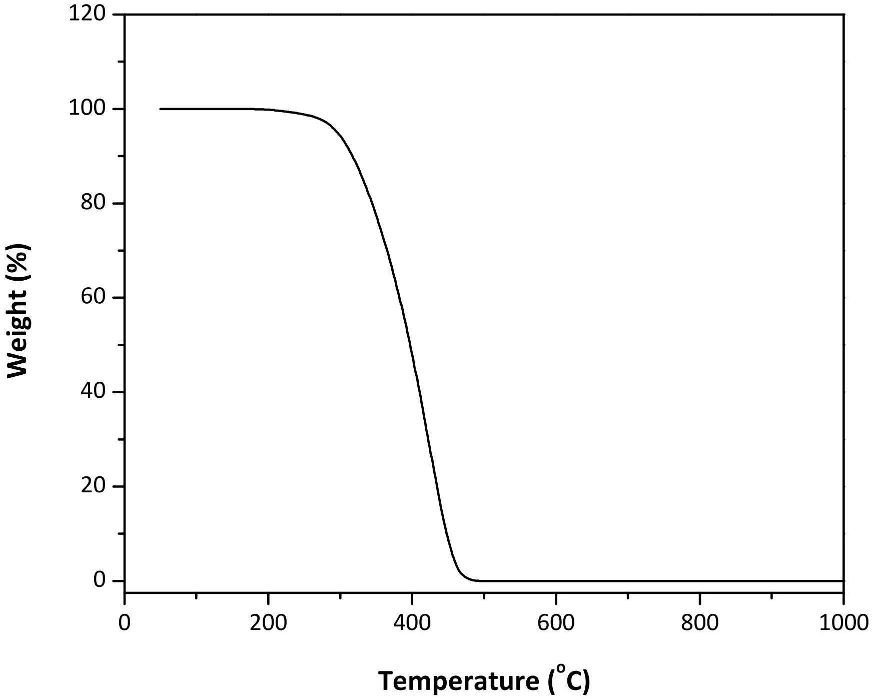

Figure 1. Thermogravimetric curve of the ionic liquid (C_6MImPF_6) employed in this study. The thermogram was obtained under nitrogen atmosphere and using a heating rate of 20 °C min^{-1}.

Figure 2

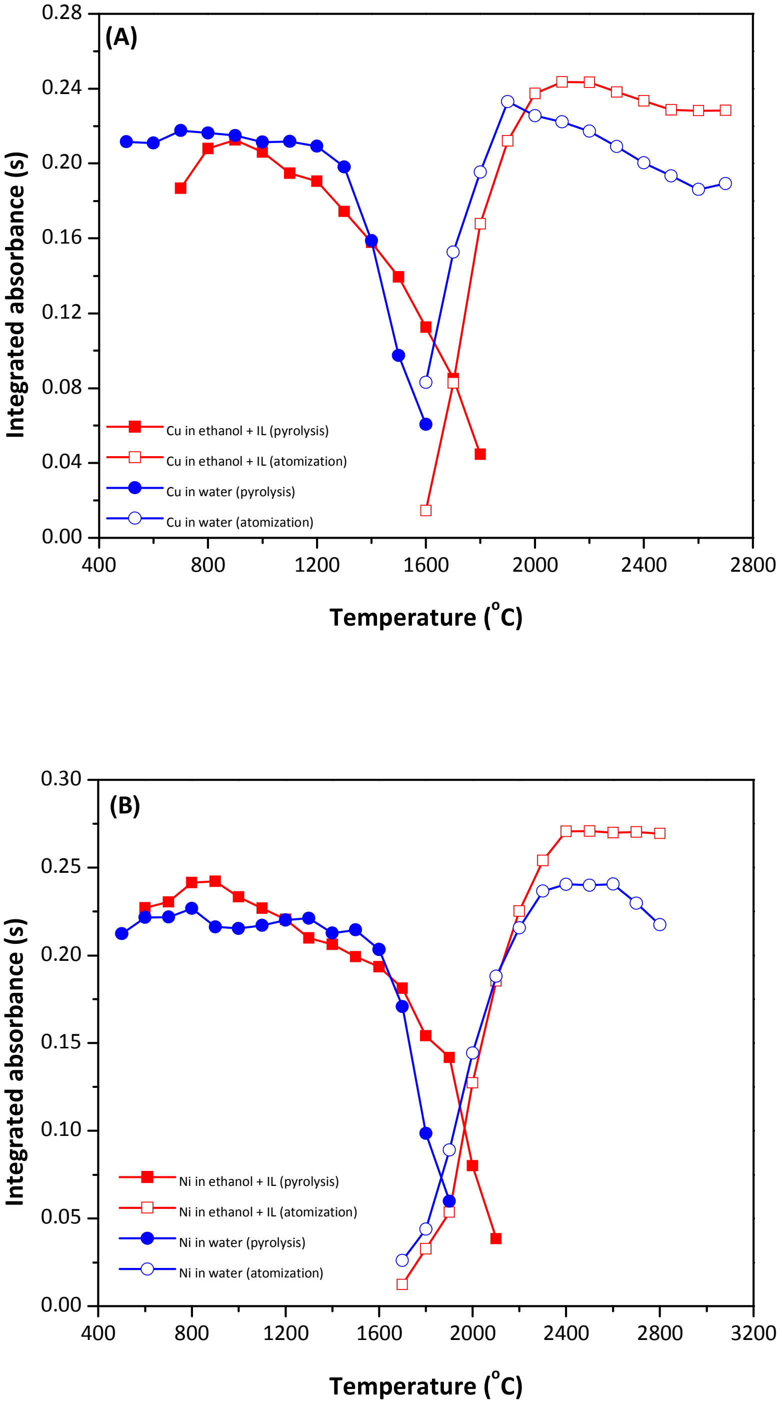

Figure 2. Pyrolysis and atomization curves for Cu (A) and Ni (B) in water and ionic liquid-rich extract media.

Figure 3

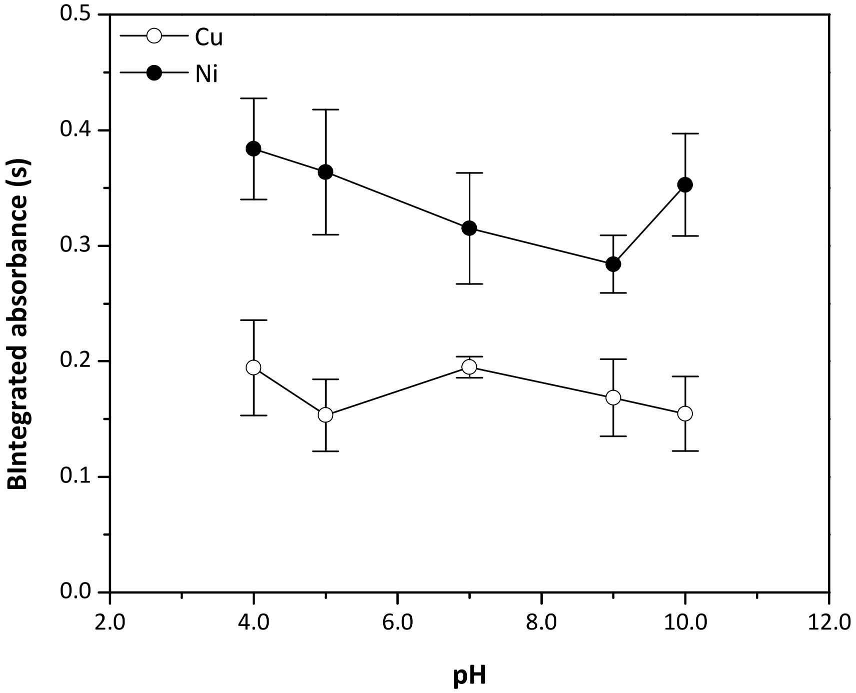

Figure 3. Influence of pH on the extraction of Cu(II) and Ni(II) using the ionic liquid-based microextraction. Volume of ionic liquid = 200 µL and APDC concentration = 1% m/v.

Figure 4

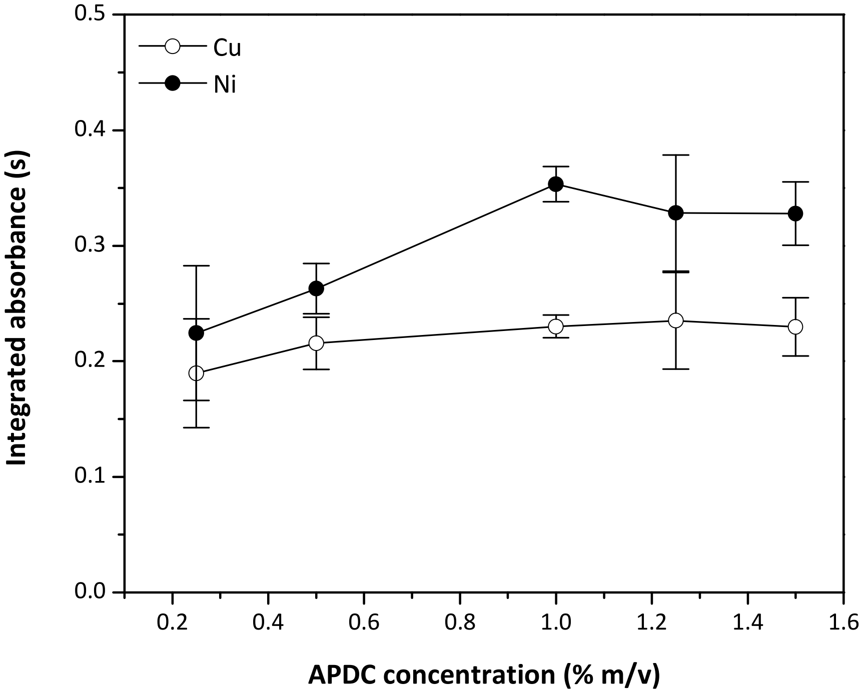

Figure 4. Influence of APDC concentration on the extraction of Cu and Ni using the ionic liquid-based microextraction. Volume of ionic liquid = 200 µL and pH = 4.0

Figure 5

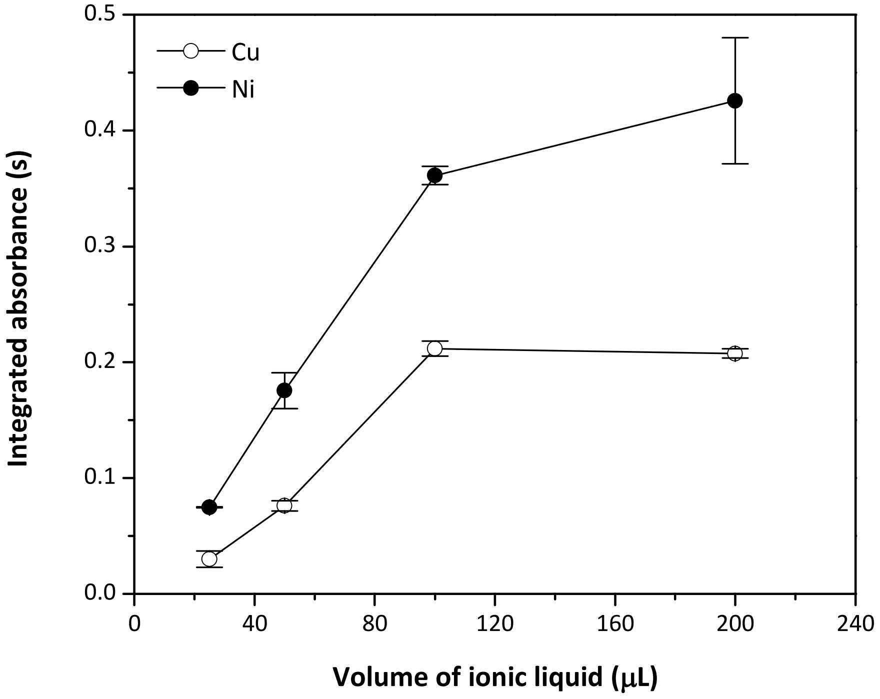

Figure 5. Influence of the volume of ionic liquid on the extraction of Cu and Ni using the ionic liquid-based microextraction. APDC concentration = 1% m/v and pH = 4.0.

Figure 6

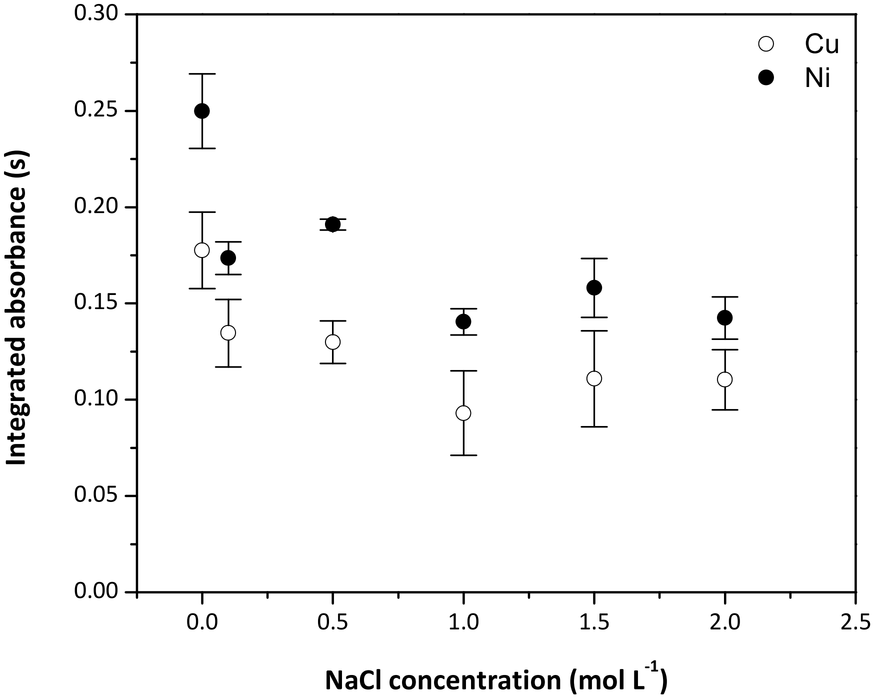

Figure 6. Effect of salinity on the ionic-liquid based microextraction of Cu and Ni by the proposed method.