Surface active ionic liquid‑assisted cloud point extraction method for preconcentration of nickel in environmental samples before its FAAS determination

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ABSTRACT Green, rapid and modified surface-active ionic liquid assisted cloud point extraction method (SAIL-CPE) was developed to preconcentrate trace levels of nickel Ni(II) ions in environmental samples perior to its detection by FAAS. The proposed method based on utilizing a mixture of a nonionic surfactant (Triton X-114) and a surface-active ionic liquid, 1-hexadecyl-3-methylimidazolium chloride ($C_{16}MeImCl$), as an extracting phase for Ni(II) ions after the complexation with sunset yellow FCF at pH 6.5. The impact of different analytical parameters on improving the extraction efficiency was invistigated. In the range of 2.0-600 µg L^{-1}, the calibration graph was linear with correlation coefficient of 0.9998. Limit of detection and preconcentration factor were 0.6 and 100. The reliability and precision of the proposed SAIL-CPE system as the relative standard deviation (RSD %) in the presence and absence of SAIL were examined by applying ten replicate determinations of 300 µg L^{-1} of Ni(II), and RSD % of the recoveries were found to be 1.40 and 2.9%, respectively. The validation of the proposed procedure was verified by test of certified reference materials (TMDA-51.3 fortified water, TMDA-53.3 fortified water and SRM spinach leaves 1570A) applying the standard addition method. Finally, the proposed SAIL-CPE method was developed and applied to preconcentrate and determine of trace levels of Ni(II) ions in real water, food and tobacco samples with satisfactory results.

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INTRODUCTION

Nickel (Ni(II)) is considered to be one of the important hazardous heavy metals used in industry and it is toxic for living organisms at low concentration levels. Ni(II) was categrized as a carcinogen compund to humans and awide variety of chronic problems related to respiratory tract, lung cancer and skin dermatities were caused by high exposure to Ni(II) [1]. Therefore, the estimation of trace Ni(II) in different types of various samples is a very important objective for chemists using effective methods [2,3]. Trace quantities of Ni(II) in real samples are less than the of detection limit of some instruments like FAAS or GF-AAS and the co-existing ions interference are two limitations in estimations [4,5]. Methods of preconcentration and separation are substantial before the measurements to overcome these limitations by increasing the sensitivity and enhancing estimation accuracy. The development of different methods to separate and enrich of trace Ni(II) from different samples, such as cloud point extraction [5-11], solid-phase extraction [12-14], co-precipitation [15] liquid-liquid extraction [16-23], and has recently been documented in the literature.

In micelle-mediated extraction methods such as CPE, the extracting phase is homogeneously dispersed (as microdroplets) in aqueous phase, on the other hand for separation of micelles from the aqueous phase at temperatures more than CPT, centrifuging and cooling in unavoidable. Usually, at the last step, adhesion of some parts of the settled extractant (commonly a nonionic surfactant) at the inner layer of the wall of test tube is a common problem, which would affect the accuracy and precision of the determination step. In fact, the analyst encounters a viscose and sticky mass of extractant in the test tube which should be prepared for the analysis step. To overcome this problem, usually a diluting solvent is used to complete the dissolution and then removal of extracting phase from the separator tube. This dilution has a direct influence on the enrichment factor and thus the detection limit and sensitivity of the method. In addition, incomplete separation of traces of aqueous phase from organic phase, and on the other hand, remaining of some traces of this phase in the test tube (as discussed above) at the end of the extraction process could affect the reproducibility of the final results [24].

Analytical chemists have tried to reduce or omit the hazardous toxic and volatile extraction solvents using liquid phase microextraction as a sample enrichment method and ionic liquids (IL) as an extraction phase [19]. The ionic liquids (ILs) were used as environment-friendly solvents because of their excellent physicochemical characteristics like frivolous vapor pressure, economical, green, selective solubility, thermal stabilities and good extractabilities for various organic compounds and metal ions [25,26]. Besides these features of ILs, some kinds of them show aggregation behavior in aqueous solutions. This property has introduced them as an alternative to conventional surfactants in various scientific and technological fields [27–29]. The behavior and properties of surface-active ionic liquids (SAILs) in aqueous and nonaqueous solvents have been extensively studied by researchers. For instance, the structural properties of SAILs in oil microemulsion were investigated and methods to adjust the structural parameters of microemulsions using different ionic liquids were reported [30,31].

Surface activity of imidazolium-based ionic liquids with long-chain hydrocarbon groups was considered by some researchers in recent years [32,33]. Like other surfactant molecules, micelle formation of a surface-active ionic liquid (SAIL) occurs at concentrations above a critical value. Measurement of critical micelle concentration (CMC) of imidazolium-based SAILs has been investigated in different ways [34–37]. On the other hand, according to some reports, this property (surface activity) of ILs has been considered as a drawback in IL-based extraction methods. Remaining of some amounts of the extracted analyte species in the aqueous phase by trapping in the aggregated ILs, and thus the incomplete recovery of the analyte, is considered as a major disadvantage of using these kinds of ILs in extraction

processes [32, 34]. So, the utilization of SAIL-CPE method combined with FAAS has some advantages such as simplicity, economic, lower limit of detection, higher preconcentration factor and environment-friendly.

The aim of the proposed study was to develop green, simple and modified SAIL-CPE method in combination with FAAS for preconcentration and accurate determination of trace levels of Ni(II) ions in real water, food and tobacco samples. In the proposed technique, the micelle formation of the IL phase provides a homogenously dispersed extracting phase; therefore, efficient extraction of the analyte would be possible without the need for dispersion techniques. On the other hand, separation of the extraction phase (ionic liquid micelles) from the aqueous phase is a challenging step in SAIL-based extraction methods. A mixed-micellar system consisting of C_{16}MeImCl and Triton-X114 (**Figure 1**) was used as extracting phase and sunset yellow FCF as complexing agent were selected. The new method has been developed to estimate concentrations of Ni(II) ions in real water, food and tobbacco samples with satisfactory results.
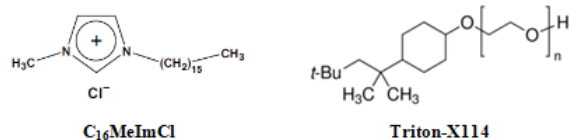

Figure 1. Chemical structure of C_{16}MeImCl and Triton-X114.

EXPERIMENTAL

Apparatus

Atomic absorption spectrophotometer (Agilent 55 AA; Agilent Technologies Inc., Santa Clara, USA), was utilized to determine the analyte metal. The instrumental conditions were set in accordance with the instructions of manufacturer. Micro injection method was utilized to introduce the sample to the nebulizer of the FAAS. An Adwa AD1000 pH-meter (Szeged, Hungary) was utilized to measure the pH-values of prepared buffer solutions. A centrifuge (Isolab, Germany) was utilized to accelerate the separation of analyte from sample

solution. A thermostated water bath with good temperature control was used for the CPE experiments. Milli-Q was utilized to obtain deionized/bidistilled water (Millipore, USA). Glass wares were kept in nitric acid (5.0% v/v) overnight, rinsed and cleaned many times with bidistilled water prior to the experiment.

Reagents and solutions

All reagents and chemicals used were of high purity and acquired from Merck (Darmstadt, Germany) and Sigma Aldrich (St. Louis, USA) companies. High-quality concentrated HNO_3 (65 % m/m), HCl (37 % v/v) and NH_3 (25% v/v) solutions were used. The stock solution of Ni(II) (1000 µg mL^{-1}) was intended from $Ni(NO_3)_2.6H_2O$ of high purity, (Fluka Chemie AG, Basel, Switzerland). Diluted Ni(II) working solution was obtanied through sequent dilution of the stock standard solution daily. The IL, C_{16}MeImCl was purchased from Acros Organics (Geel, Belgium) and the non-ionic surfactant polyethylene glycol tert-octylphenyl ether (Triton X-114) (Sigma–Aldrich, USA) were selected as the extraction solvent. without further purification. Aqueous solution of C_{16}MeImCl (0.1 mol L^{-1}) was prepared by dissolving the appropriate weight of C_{16}MeImCl in 100 mL of bidistilled water in 100 mL volumetric flask with stirring. Aqueous 1.0% (v/v) solution of Triton X-114 was prepared by dissolving 1.0 mL of Triton X-114 in 100 mL of bidistilled water in 100 mL volumetric flask with stirring. A 0.2% (w/v) solution of sunset yellow FCF was obtained by dissolving proper weight of sunset yellow FCF (Sigma-Aldrich, St. Louis, MO, USA) in ethanol Sigma Aldrich (St. Louis, USA). The pH values was adjusted using a series of buffer solutions [38]. The solutions of various cations and anions used for the interference study were obtained from the respective high purity inorganic salts (Sigma-Aldrich, USA) by proper dilution in bidistilled water. TMDA 51.3 fortified water and TMDA 53.3 fortified water (National Water Research Institute, Environment Canada, Burlington, Canada) and spinach leaves (SRM 1570a) (National Institute of Standard Technology

(Gaithersburg, MD, USA) were utilized as certified reference materials.

Preconcentration SAIL-CPE procedure

Aliquots of 40 mL of the sample solution containing 2.0-600 µg L^{-1} of Ni(II) were placed in a conical-bottom glass centrifuge tube (50 mL) and mixed with 3.0 mL of phosphate buffer solution (pH 6.5). Subsequently, sunset yellow 0.2% (w/v) (1.0 mL), 100 µL of C$_{16}$MeImCl solution (0.1 M), 200 µL of Triton-X114 (1.0% v/v), and 1.0 mL of NaCl (2.0%, w/v) were added, respectively. The solution was diluted to the mark (50 mL) with bidistilled water. After that, the tubes were transferred to a water bath for 5.0 min at 45° C. To speed up phase separation, the solution was centrifuged at 4000 rpm for 5.0 min. The tubes were taken away and obscure in an ice bath for 5.0 min and cloudy turbid solution was formed. The IL-phase was subsequently sedimented at the bottom of the tube. Using syringe, the upper aqueous phase was rejected. Finally, the remaining IL phase was diluted using acidic methanol to 0.5 mL and aspirated into the conventional nebulizer of FAAS using microinjection system.

Pretreatment of real samples and CRMs
Water Samples

The proposed procedure was successfully applied to water samples "tap, mineral, sea, and wastewater" acquired from Egypt and stored in polyethylene bottles. All water samples are filtered through a cellulose membrane filter of 0.45-µm pore size (Millipore Corporation, Bedford, MA, USA) to eliminate hanging materials before being acidified with diluted HNO$_3$ and stored at 4°C. To oxidize the organic content of water samples, H$_2$O$_2$ (1.0 % v/v) and HNO$_3$ (65 % m/m) were utilized. The same preconcentration SAIL-CPE technique has been used to the CRM (TMDA-51.3 and TMDA 53.3 fortified water). The Ni(II) concentrations were evaluated by FAAS.

Food and tobacco samples

The different vegetables (cabbage, spinach, tomato and potato) and tobacco samples were gained from local markets of Egypt. For 24 hours in an electric oven, the food samples are dried at 80 °C and homogenized by grinding in an agate mortar. For a wet acid digestion procedure, SRM 1570a spinach leaves, food and tobacco samples (0.2 g) were treated with 2.0 mL of a mixture of concentrated HNO$_3$–H$_2$O$_2$ (2:1, v/v) into beaker and kept at room temperature for 10 min, then heated on an electric hot plate until semi-dried mass was obtained. digested semi-mass samples were dissolved in 10 mL of deionized water and filtered through a cellulose membrane filter of 0.45-µm pore size. Then the developed SAIL-CPE procedure was satisfactorily applied to the samples.

RESULTS AND DISCUSSION

Influence of pH

The pH has a crucial impact on the extraction yield and the formation of metal-chelate complex [39-41]. Consequently, the influence of pH on the SAIL-CPE technique of Ni(II)-sunset yellow complex was studied at a pH range of 3.0-9.0. As illustrated in **Figure 2**, the extraction efficiency increased with increasing pH from 3.0-6.0 and maximum quantitative values are accomplished till the pH rang 6.0-7.0. On the other hand, a miniscule decrease at higher pH values is obvious. The decrease in extraction of Ni(II) at pHs lower than 6.0 might be attributed to the lower affinity of complex formation between Ni(II) ions and sunset yellow in this pH range, while the reduction in the absorbance at higher pH values could be attributed to the hydrolysis of Ni(II) ions. In subsequent studies, 3.0 mL of phosphate buffer solution (pH 6.5) was chosen.
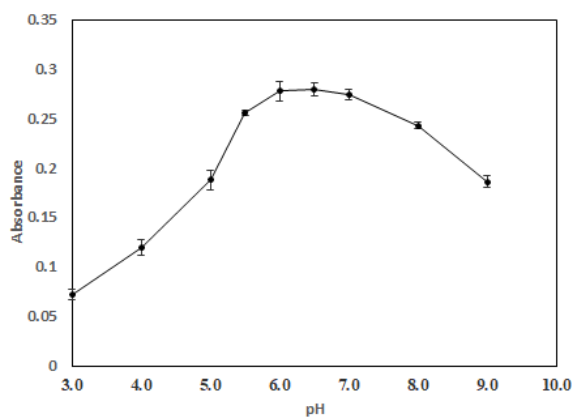
Figure 2. Effect of pH on the extraction efficiency of Ni(II) through SAIL-CPE method. Conditions: (Ni(II) concentration, 300 µg L^{-1}; concentration of sunset yellow, 0.2% (w/v); C$_{16}$MeImCl (0.1 M) volume, 100 µL; Triton X-114 (0.5% v/v), 200 µL; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

Influence of sunset yellow concentration

The sunset yellow concentration has important influence on the extraction efficiency of Ni(II)-sunset yellow complex to give quantitative results. Various concentrations of sunset yellow were examined within the range of 0.05-0.3 % (w/v) and results curvature is shown in **Figure 3**. The absorbance has been increased by increasing the sunset yellow concentration up to 0.2 % (w/v) and higher amounts of sunset yellow have no significant effect in the extraction recovery. Therefore, 1.0 mL of sunset yellow (0.2% w/v) was utilized as the optimum amount for total complexation and maximum extraction recovery in further studies.
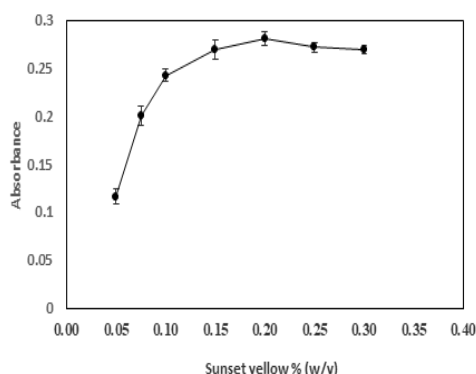

Figure 3. Effect of the sunset yellow concentration on the extraction efficiency of Ni(II) through SAIL-CPE method. Conditions: (Ni(II) concentration, 300 µg L^{-1}; pH 6.5; C$_{16}$MeImCl (0.1 M) volume, 100 µL; Triton X-114 (0.5% v/v), 200 µL; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

Influence of extracting phase composition

In the proposed study, choice of type and volume of surfactant was important which has a large influence on the Ni(II) extraction efficiency. In present work, different non-ionic surfactant (Triton X-114 Triton X-100 and Tween-80) were tested, and the experimental results show that the Triton X-114 was the best one for the extraction of Ni(II)–sunset yellow complex. The variation in extraction efficiency of Ni(II) within the Triton X-114 concentration range of 0.1–1.0% v/v was examined. The maximum absorbance was observed at 0.5% v/v Triton X-114 (**Figure 4**). Afterward, the effect of concentration of C$_{16}$MeImCl as SAIL on the extraction efficiency was examined by adding various amounts of C$_{16}$MeImCl from (0.02-0.2 M) to the extraction mixture. According to the obtained results (**Figure 5**), the maximum extraction efficiency was observed in the presence of 0.1 M C$_{16}$MeImCl. It should be mentioned that all experiments were conducted in the presence of (2.0% w/v) NaCl as salting-out agent.
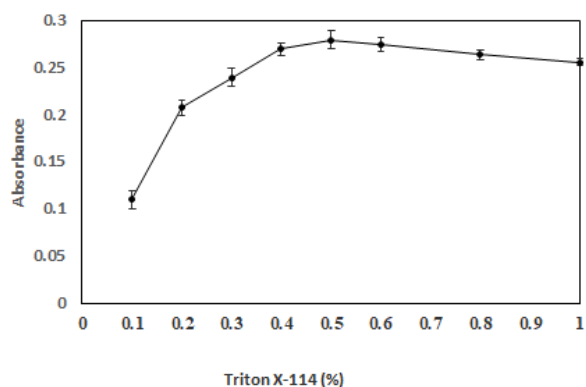

Figure 4. Effect of Triton X-114 concentration on the extraction efficiency of Ni(II) through SAIL-CPE method. Conditions: (Conditions: (Ni(II) concentration, 300 µg L^{-1}; pH 6.5; concentration of sunset yellow, 0.2% (w/v); C$_{16}$MeImCl (0.1 M) volume, 100 µL; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).
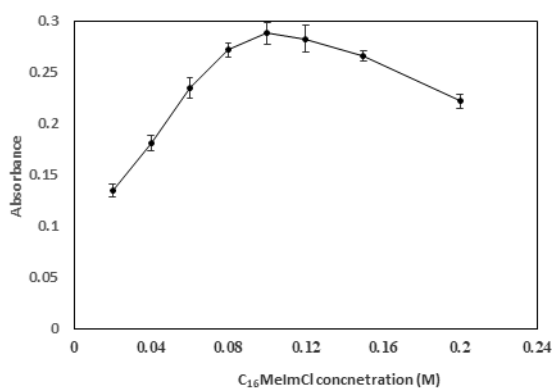
Figure 5. Effect of $C_{16}MeImCl$ concentration on the extraction efficiency of Ni(II) through SAIL-CPE method. Conditions: (Conditions: (Ni(II) concentration, 300 µg L^{-1}; pH 6.5; concentration of sunset yellow, 0.2% (w/v); $C_{16}MeImCl$ (0.1 M) volume, 100 µL; Triton X-114 (0.5% v/v), 200 µL; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

Influence of sample volume

The Ni(II) solution volume of is an important factor for achieving a high enrichment factor and maximum absorbance based on SAIL-CPE procedure. The sample volume effect was investigated using (10–100.0 mL) model solutions. Higher than 50 mL, Ni(II) ion recoveries were not quantitative. Hence, Ni(II) solution (50 mL) was chosen as the highest sample volume in all the subsequent studies.

Influence of equilibration temperature and time

To achieve easy phase separation and efficient preconcentration, it is imperative to optimize the equilibration temperature and time. It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient phase separation. The influence of the equilibration temperature was investigated by varying the temperature from 30 to 70°C. The results demonstrate that in the temperature at 45°C, the extraction efficiency for the Ni(II)–sunset yellow complex was constant. Therefore, an equilibration temperature of 45°C was chosen for further experiments. Higher temperatures lead to the decomposition of the

complex and the reduction of extraction yield. The dependence of extraction efficiency upon incubation time was studied in the range of 1.0–15 min. An incubation time of 5.0 min was enough for the separation process and quantitative extraction of analyte.

Influence of centrifugation conditions

Centrifuge rate and time has important impact on the separation of IL and aqueous phase. The centrifugation rate was tested in the range 1000 and 5000 rpm. The centrifugation rate was increased up to 4000 rpm which chosen as the optimum rate for complete separation of extracting phase either in the presence or in the absence of the SAIL. Also, the centrifugation time effect on the analytical signals was evaluated between 2.0 and 20 min. The maximum extraction efficiency was obtained at 5.0 min to ensure complete phase separation in the presence of SAIL, but 15 min centrifugation was necessary in the absence of SAIL. So, 4000 rpm and 5.0 min were chosen as optimum centrifuge rate and time for further studies.

Effects of diluent

High viscosity of the surfactant-rich phase is drastically decreased using diluting agents. For the spectrophotometric method, the addition of a diluent into the surfactant-rich phase is often needed to obtain a homogeneous solution with compatible viscosity. Methanol, ethanol, acetone, N, N-dimethylformamide, and acetonitrile were tested as diluent solvents. Surfactant-rich phase was found to be freely soluble in methanol. Therefore, acidic methanol was chosen to have appropriate amount of sample for transferring and measurement of the absorbance of the sample and a suitable preconcentration factor. Hence the surfactant-rich phase was completed to 0.5 mL by acidic methanol. Therefore, the preconcentration factor (PF) has been described as the sample volume ratio to the final dilute volume of surfactant-rich phase (0.5 mL). Therefore, PF was attained as 100.

Influence of matrix ions

The possible effect of the commonly present matrix constituents on the preconcentration and determination of the Ni(II) ions in different real samples were examined. The results obtained are shown in **Table 1.** The tolerance limit is defined as the highest amount of interfering ions creating a relative error $\leq \pm 5$ %. An advantage of this method was that the Ni(II) ions recovered from the multi-element real samples were quantitative ($> 95\%$) at the level of tolerance provided in Table 1. No obvious interference effect of matrix ions was observed in the determination of Ni(II) ions under the experimental conditions which confirm the applicability of SAIL-CPE method for Ni(II) determination in various real samples.

Table 1. Influence of coexisting matrix ions on the recovery of Ni(II) ions using the deveolped SAIL-CPE procedure (N=3).

Ion	Added as	Concentration (mg L^{-1})	Recovery (%) [a]
Na$^+$	NaCl	5000	97 ± 1
K$^+$	KCl	5000	95 ± 2
Ca^{2+}	CaCl$_2$	1000	96 ± 3
Mg^{2+}	MgCl$_2$	1000	96 ± 2
Cl$^-$	KCl	5000	98 ± 1
SO$_4^{2-}$	Na$_2$SO$_4$	2000	97 ± 2
NO$_3^-$	NaNO$_3$	3000	96 ± 3
Fe^{3+}	FeCl$_3$	500	97 ± 2
Mn^{2+}	MnSO$_4$. H$_2$O	500	98 ± 1
Cr^{3+}	Cr(NO$_3$)$_3$.9H$_2$O	200	96 ± 2
Co^{2+}	Co(NO$_3$)$_2$	50	97 ± 2
Cu^{2+}	Cu(NO$_3$)$_2$.3H$_2$O	30	95 ± 2
Cd^{2+}	Cd(NO$_3$)$_2$.6H$_2$O	30	96 ± 2
Zn^{2+}	Zn(NO$_3$)$_2$.6H$_2$O	50	98 ± 1

[a] Mean $\pm$ standard deviation.

Analytical features of the proposed method

Comparison of the analytical features of the proposed method in the presence and absence of SAIL (C$_{16}$MeImCl) was made, and the results are featured in **Table 2.** Using the optimized experimental conditions described above, a satisfactory linear relationship was obtained in the presence of SAIL in the micellar mixture in the concentration range of 2.0-600 µg L^{-1} with the following linear regression equation, $A = 5.0 \times 10^{-4}$ C $- 2.7 \times 10^{-3}$ with a correlation coefficient (R^2 0.9998, n=10), where A is the absorbance and C is the Ni(II) concentration (µg L^{-1}). The limits of detection (LOD) and quantification (LOQ) were calculated as $3s_b/m$ and $10s_b/m$, respectively, where s_b is the standard deviation from ten replicate measurements of blank samples and m is the

slope of the calibration curve. The LOD and LOQ were 0.60 and 2.0 µg L^{-1}, respectively. The lower detection limit of the present SAIL-CPE method indicates high sensitivity and suggests its efficient application for the determination of very low concentrations of Ni(II) in real samples.

The performance of the proposed SAIL-CPE procedure was assessed by calculating two parameters including; the enrichment factor (EF) and the consumptive index (CI). The enrichment factor (EF), defined as the ratio between the calibration graph slopes with and without preconcentration procedure. The consumptive index (CI) was determined using

the expression CI = Vs/EF, where Vs is the analyte solution volume. The reliability and precision of the proposed SAIL-CPE system as the relative standard deviation (RSD %) in the presence and absence of SAIL were examined by applying ten replicate determinations of 300 µg L^{-1} of Ni(II), and RSD % of the recoveries were found to be 1.40 and 2.9%, respectively which illustrate a good precision of the method and confirmed our belief about the effect of C_{16}MeImCl on the completeness of separation of extracting phase from the aqueous phase which directly affects the repeatability of the results (**Table 2**).

Table 2. Analytical characteristics of the proposed SAIL-CPE method.

Parameters	In the presence of SAIL	In the absence of SAIL
Calibration range (µg L^{-1})	2.0–600	10-400
Calibration equation [a]		
Slope (b)	5.0×10^{-4}	3.0×10^{-4}
Intercept (a)	2.7×10^{-3}	1.7×10^{-3}
Correlation coefficient (R^2)	0.9998	0.9990
LOD (µg L^{-1}) (3σ, n=10)	0.60	3.0
LOQ (µg L^{-1}) (3σ, n=10)	2.0	10
Relative standard deviation (RSD%; n=10, 300 µg L^{-1})	1.40	2.90
Enrichment factor (EF)	28.2	21.5
Consumptive index (CI)	1.754	2.326

[a] A = a+ bC, where C is the concentration of Ni(II) in µg L^{-1}, A is the absorbance units, a is the intercept, b is the slope.

Validation studies

Additionally, the applicability of the developed SAIL-CPE method was checked and validated for the estimation of Ni(II) concnetrations in two certified reference materials (TMDA-51.3 fortified water, TMDA-53.3 fortified water and spinach leaves SRM 1570a) through standard addition method at

three concentrations. The concordant resulting values of recoveries levels derived from the method developed were in good agreement with the CRMs certified values (Table 3). The application of the proposed method to the real samples and CRMs show that this method is highly accurate and reliable, is free of interference and validates the estimation of Ni(II) ion at trace levels in real samples (**Table 3**).

Table 3. The validation of the proposed SAIL-CPE procedure for Ni(II) estimation in CRMs (N= 3.0).

Certified reference materials	Certified value (µg L^{-1})	Found ± SD [a] (µg L^{-1})	RSD (%)	Recovery (%)
TMDA-53.3 fortified water	311	303 ± 0.90	2.50	97.43
TMDA-51.3 fortified water	68.3	65.8 ± 0.80	3.20	96.34
NIST 1570a Spinach Leaves	2.14 ± 0.1	2.08 ± 0.06	3.10	97.20

[a] Mean ± standard deviation based on three replicate determinations.

Analytical applications to real samples

The potential application of the developed SAIL-CPE preconcentration method to the identify and separate Ni(II) ion in different real water and acid digested samples including food and tobacco samples was tested. The sample solutions were spiked with known quantities of Ni(II) ion using the standard addition method to verify the reliability and accuracy of the developed process. **Table 4** shows the percentage of the analyte recovered from the spiked real sample and the RSD%. The quantitative recoveries for the Ni(II) analyte were great, in the range of 95.0–99.50 % with RSD < 3.0 %. Such results show that the approach is accurate and could therefore be used in to separate, preconcentrate and evaluate trace amounts of Ni(II) in real water, food and tobbaco samples.

Table 4. The results for the standard addition-recovery method for the preconcentration of Ni(II) in real samples using the developed SAIL-CPE method (N=3.0).

Sample	Added (µg L^{-1})	Found [a] ± SD (µg L^{-1})	Recovery (%)[b]	Sample	Added (µg g^{-1})	Found [a] ± SD (µg g^{-1})	Recovery (%)[b]
Tape water	0	3.28±0.09	-	**Cabbage**	0	8.50±0.13	-
	100	100.40±0.42	97.21		100	107.20±0.49	98.80
	200	196.0±0.73	96.42		200	198.50±1.05	95.20
Mineral water	0	< LOD[c]	-	**Spinach**	0	15.0±0.29	-
	100	95.60±0.50	95.60		100	112.10±0.74	97.50
	200	192.0 ±1.10	96.0		200	213.0±1.20	99.10
Sea water	0	40.0±0.31	-	**Tomato**	0	10.0±0.23	-
	100	134.80±0.96	96.30		100	105.80±0.65	96.20
	200	230.0±1.30	95.83		200	203.70±0.96	97.0
Well water	0	< LOD[c]	-	**Potato**	0	6.0.0±0.12	-
	100	99.50±0.42	99.50		100	103.0±0.54	97.20
	200	194.0±0.80	97.0		200	204.0±1.35	99.0
Waste water	0	34.0±0.28	-	**Tobacco**	0	19.0±0.23	-
	100	130.80±0.50	97.60		100	114.0±0.67	95.80
	200	222.30±0.97	95.0		200	215.50±1.10	98.40

[a] Mean ± standard deviation.

[b] Recovery% = [Observed value of Ni(II) / Expected value of Ni(II)] × 100

[c] LOD: limit of detection.

Comparison with other preconcentration methods

The proposed SAIL-CPE method was compared to the other extraction procedure documented in the literature [6-8, 12, 15-23]. Comparison allows better analysis, relative to other approaches, of the positive aspects of the proposed method. As can be seen in **Table 5**, the main advantages of the process were the large working ranges, low detection limits, better reliability (as recovery%) and repeatability/reproducibility (as RSDs%) and high PF, as well as the use of green chemicals. According to these properties, using conventional ILs and toxic organic solvents, the SAIL-CPE technique has the potential to be a good alternative to the extraction methods. Such results showed that the proposed SAIL-CPE protocol could be implemented successfully without any systematic error to analyse different real samples.

Table 5. Comparison between the proposed SAIL-CPE procedure and other reported extraction methods for Ni(II) determination in various samples.

Preconcentration method	Detection system	LOD[a] ($\mu g\ L^{-1}$)	Linearity ($\mu g\ L^{-1}$)	PF/EF[b]	Samples matrix	References
CPE [c]	FAAS	5.0	Up to 80	30	Peach leaves and Apple leaves- CRM	[6]
CPE	FAAS	1.0	10-500	30	Water samples	[7]
CPE	SP	2.0	10-250	50	Water samples	[8]
SPE	SP	3.0	10-370	-	Water, food, biological and soil samples	[12]
Coprecipitation	FAAS	1.05	250-5000	25	Food samples	[15]
ILDLLME	SP	9.8	30-1500	200	environmental and biological samples	[16]
DLLM-SFOD	FAAS	1.2	4.23-250	158	Water samples	[17]
DLLME	FAAS	1.59	10-250	51.8	Water samples and vitamin B12	[18]
DLLME	FAAS	12.5	50-500	40.2	Water samples	[19]
DLLME	FAAS	1.4	4.7-100	29	Water samples	[20]
SSLLME	FAAS	1.30	-	40	Water, tobacco and fertilizer samples	[21]
EADLLME	GFAAS	15	50-1000	196.4	Water and fruit juice samples	[22]
HLLME	GFAAS	2.2	5.0-125	-	Aqueous samples	[23]
SAIL-CPE	FAAS	0.60	2.0-600	100	Water, food and tobacco samples	Proposed work

[a] LOD: Limit of detection;

[b] PF: Preconcentration factor and EF: Enrichment factor.

[c] CPE: cloud point extraction; SPE: solid phase extraction; ILDLLME: ionic liquid dispersive liquid–liquid microextraction; DLLM-SFOD: dispersive liquid-liquid microextraction based on solidification of floating organic drop; DLLME: dispersive liquid-liquid microextraction; SSLLME: supramolecular solvent liquid-liquid microextraction; EADLLME: effervescence assisted dispersive liquid–liquid microextraction; SAE-DLLME: surfactant assisted emulsification dispersive liquid–liquid microextraction; HLLME: homogeneous liquid–liquid microextraction; FAAS: flame atomic absorption spectrometry; GFAAS: graphite furnace flame atomic absorption spectrometry; SP: spectrophotometry.

CONCLUSIONS

In the present study, green, efficient, simple, fast and environmentally friendly mixed-micellar system based on a SAIL-CPE technique was developed and validated to preconcentrate Ni(II) ions in real water, food and tobacco samples prior to FAAS determination. Good characteristics of the proposed method such as extremely high sensitivity with low LOD (0.60 µg L^{-1}), high preconcentration factors (100), simplicity, and green. Moreover, the developed procedure was successfully applied to preconcentrate and determine trace amounts of Ni(II) ions from real sample solutions without significant interference. Satisfactory repeatability and reproducibility (RSDs% lower than 3.0%). The new method was successfully applied to certified reference materials for trace Ni(II) determination.

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