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Bulletin of Faculty of Science - Zagazig University

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FS-ZU

Preconcentration and spectrophotometric determination of mercury in water, food and hair samples through ionic-liquid induced micelle-mediated extraction

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ARTICLE HISTORY

Received: 6 June 2020

Revised: 20 June 2020

Accepted: 20 June 2020

KEY WORDS

Mercury; Cloud point extraction; ionic liquid; Triton X-114; Water, food and hair samples; Spectrophotometry.

ABSTRACT A new, eco-friendly, and rapid micelle-mediated preconcentration technique was described for trace mercury in water, food and hair samples prior to its spectrophotometric determination. The developed method depended on cloud point extraction supported with ionic liquid (IL-CPE) for extraction of mercury utilizing a nonionic surfactant (Triton X-114) and 1-hexadecyl-3-methylimidazolium chloride (C₁₆MeImCl) ionic liquid, as an extracting phase in the presence of 5-benzyl-4-[4-methoxybenzylideneamino)-4H-1,2,4-triazole-3-thiol (BMBATT) as a new chelating agent at pH 7.0. The influence of various analytical variables on improving the extraction performance was tested. In the range of 2.0-600 μg L⁻¹, the calibration curve was linear with correlation coefficient of 0.9997. The detection limit and preconcentration factor were 0.4 μg L⁻¹ and 100, respectively. The reliability and precision of the developed IL-CPE system as the relative standard deviation (RSD %) of 100 and 400 μg L⁻¹ mercury were in the range 1.0 and 2.4%, respectively (n=10). The validity of the developed IL-CPE approach was confirmed by the analysis of certified reference materials (NIST-1641d mercury in natural water and NCS ZC81002B human hair). The applicability of proposed IL-CPE technique was demonstrated successfully by estimation of trace mercury in real water, food and hair samples.

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INTRODUCTION

Mercury is the most dangerous metal contaminants in water, foods and biological samples. It occurs naturally as a consequence of normal mineral breakdown in rocks, volcanic eruption, soil withering, human activity sources, industrial catalysts, batteries and thermometers [1-3]. Mercury with toxic impact induces severe troubles in human beings e.g., blood pressure, glioma, intense mental disabilities, nervousness, depression, eyes problems and CNS dysfunction. The acceptable mercury level for water samples is $10 \mu\text{g L}^{-1}$ according to World Health Organization (WHO) [4]. Evaluating of the mercury amount in water and food has considerable importance for assessing their environmental effects and toxicity. Therefore, the development of an effective and accurate analytical procedure for separation, preconcentration and environmental determination of mercury is critical [1-3].

Distinct instrumental analytical technologies involving inductively coupled plasma mass spectrometry (ICP-MS) [5], ICP-atomic emission spectrometry (ICP-AES) [6], cold vapor atomic absorption spectrometry (CVAAS) [7-10], HPLC coupled to cold vapor atomic fluorescence spectrometry (HPLC-CVAAS) [11], and GFAAS [12] were advanced for determination of mercury in various samples. Moreover, these technologies have some disadvantages like operational costs, high interferences of the complex matrix and highly qualified laboratory specialists are needed to carry them out.

Due to their ease, minimal cost, and good accuracy, UV-Vis spectrophotometric procedures are still preferred and commonly included in mercury determination [13-15]. Nevertheless, UV-Vis spectrophotometry can't be utilized effectively for the estimation of the analytes without provisional chemical separations because of matrix interference. Until assessing low levels of Hg(II) these problems can be solved by the use of a specific separation and preconcentration procedure.

Certain common enrichment-separation techniques including liquid-liquid microextraction (LLME) [5, 7, 12, 15-17], solid

phase extraction [5, 9, 18-31], cloud point extraction [32-39], and coprecipitation [40] were utilized to preconcentrate minimal levels of mercury.

Cloud point extraction (CPE) is a potentially eco-friendly technique small volume of low toxicity non-surfactants instead of the hazardous solvents. CPE has some advantages like high preconcentration factor, green, low cost, higher safety and simplicity. CPE can form and separate non-ionic surfactant micelles from aqueous solutions at the cloud point temperature (CPT), which preconcentrate the analytes in a little volume of surfactant-rich phase [41, 42]. To improve the extraction capacity of surfactants and the enrichment factor, ionic liquids were added as a diluting solvent.

Ionic liquids (ILs) are a green and alternative solvents that has excellent physicochemical properties such as thermal stability, nonvolatile nature, economical, selective solubility, and good extractabilities for various organic compounds and metal ions [37, 41]. These properties of ILs make them most suitable candidates as an additive with nonionic surfactants in CPE separation processes.

In this work, a novel, easy and green IL-CPE procedure combined with spectrophotometry was developed to preconcentrate and evaluate trace mercury in water, food and hair samples. In the developed method, mixed-micellar system consisting of $\text{C}_{16}\text{MeImCl}$ as IL and Triton-X114 nonionic surfactant was used as extracting phase and 5-benzyl-4-[4-methoxybenzylideneamino]-4H-1,2,4-triazole-3-thiol (BMBATT) as complexing agent were selected. The effect of different operation conditions has been studied. The present procedure has been demonstrated successfully by estimation of trace mercury in real water, food and hair samples

EXPERIMENTAL

Apparatus

Used for the absorbance measurements was a Varian UV-Vis spectrophotometer (Cary 100 Conc., Australia) fitted with 10 mm quartz cell.

For the pH measurements, Adwa AD1000 pH-meter (Romania) was used conjunction with a glass-electrode. A Centrifuge (HERMLE, Germany) utilized to facilitate the phase separation. A thermostated water bath with good temperature control utilized for the CPE procedures. Milli-Q purification apparatus (Millipore, USA) utilized to acquire deionized/bidistilled water used to prepare solutions. All glass wares or plastic materials were processed for at least 12 h in HNO₃ (10%, v/v), rinsed and washed with bidistilled water before use in this project.

Chemicals and solutions

All chemical substances and reagents were of analytical reagent grade. Dissolving HgCl₂ (Merck, Darmstadt, Germany) in bidistilled water had produced a standard solutions of 1000 µg mL⁻¹ mercury. Appropriate dilutions with 0.01 mol L⁻¹ HNO₃ were prepared by working standard solutions used before daily use. High-quality concentrated HNO₃ (65 % m/m), HCl (37 % v/v), NH₃ (25% v/v) and H₂O₂ (30%, m/v) (Merck, Darmstadt, Germany) solutions were used. The IL, C₁₆MeImCl was purchased from Across Organics (Geel, Belgium) and the non-ionic surfactant Triton X-114 (1, 1,3,3-tetramethylbutyl)phenyl-polyethylene glycol) (Sigma–Aldrich, USA) were selected as the extraction solvent without further purification. Aqueous solution of C₁₆MeImCl (0.1 mol L⁻¹) was provided by dissolving the correct weight of C₁₆MeImCl in 100 mL of bidistilled water in 100 mL volumetric flask with swirling. Triton X-114's aqueous 1.0 % (v/v) solution was provided by dissolving 1.0 mL of Triton X-114 in 100 mL of bidistilled water in 100 mL volumetric stirring flask.

The new Schiff base reagent 5-benzyl-4-[(4-methoxybenzylidene) amine]-4H-1,2,4-triazole-3-thiol (BMBATT) was synthesized according to the literature [43]. A stock solution (1.0 × 10⁻³ mol L⁻¹) of BMBATT was produced by dissolving 0.032 g in ethanol in a 100-mL flask.

Specific buffer series have been used like acetate buffer solution (CH₃COONa-CH₃COOH) pH range from (3.0-5.5), phosphate buffer solution (Na₂HPO₄- NaH₂PO₄) pH range

from (6.0-7.0), ammoniacal buffer (NH₃-NH₄Cl) solution pH 8.0, and phosphate buffer solution (Na₂HPO₄-NaOH) pH range from (9.0-10) as indicated in the literature [44]. Samples of natural water (tap, mineral, or wastewater) were obtained from Zagazig, Egypt; river water was collected from Shobra, Egypt and sea water were obtained from Red sea, Egypt. Samples of vegetables (tomato, potato, onion, spinaach, cabbage) and fruits (apples) were gained from Makkah markets, Saudi Arabia. Hair samples were taken from our research group males. Certified reference materials (CRMs): (NIST-1641 d, National Institute of Standards and Technology, Gaithersburg, MD, USA) and (NCS ZC81002B human hair, China National Analysis Center) were used to validate the method's accuracy.

Preconcentration IL-CPE procedure

In a 50-mL centrifuge tube, 30 mL of mercury sample solution containing 2.0-600 µg L⁻¹ of mercury were put and 4.0 mL phosphate buffer (pH 7.0) was added. After that 2.0 mL of BMBATT (1.0 × 10⁻³ mol L⁻¹) 200 µL of C₁₆MeImCl solution (0.1 mol L⁻¹), 300 µL of Triton-X114 (0.5% v/v), and 1.0 mL of NaCl (2.0%, w/v) were added, respectively. With bidistilled water the solution was diluted to the level. After that, the tubes were transferred to a water bath at 45 °C for 5.0 min. To achieve phase separation, the turbid mixture was centrifuged at 4000 rpm for 5.0 min. The tubes were cooled in an ice bath for 5.0 min to increase the viscosity of the extractant phase. The IL-phase was subsequently sedimented at the bottom of the tube. The water supernatant was decanted with a pipette and discarded. The viscous preconcentrated analyte complex in micelle-mediated extractant phase was diluted up to 500 µL with ethanol. The mercury concentration was measured at λ_{max} = 568 nm using UV-Visible spectrophotometer.

Pretreatment of real samples and CRMs

Water samples

The proposed IL-CPE technique was applied to different water samples including tap, mineral, river, wastewater and sea water. The samples were filtered using a 0.45- μm pore size cellulose membrane filter before acidification with diluted HNO_3 and storing them at 4.0°C. Phosphate buffer solution was added to set the samples pH to 7.0 and then the standard addition method was applied. The mercury in water samples and CRM (NIST-1641d mercury in natural water) was preconcentrated using the proposed IL-CPE approach and evaluated by spectrophotometrically.

Food samples

The preconcentration IL-CPE procedure was repeated using different vegetables (tomato, potato, onion, spinach, cabbage) and fruits (apples) samples. The samples were dried at 90°C for 24 h in an oven and homogenized by grinding in an agate mortar. A 15 mL mixture of HNO_3 (65%, m/m) and H_2O_2 (30%, v/v) (2:1) were added in a Teflon beaker for a wet acid digestion procedure, evaporated to near dryness by heating at 150°C for 2.0 h on a hot plate. The samples were combined with 10 mL of bidistilled water after evaporation. The resulting mixture was filtered through a 0.45- μm pore size cellulose membrane filter, adjust the pH to 7.0 before dilution with deionized water to 50 mL, then packed in bottles of polyethylene. The mercury content were evaluated using the IL-CPE procedure.

Hair samples

The hair samples were rinsed with bidistilled water and dried for 24 h at 100°C in an oven. Hair samples (0.1 g) and NCS ZC81002B human hair certified reference material (0.1 g) were accurately weighed into a PTFE digestion vessel and exposed to a wet digestion process. About 10 mL of concentrated HNO_3 (65% m/m) and 5.0 mL of H_2O_2 (30% m/v) were added and the vessel closed for 20

min, and then complete digestion by heating on a hot plate at 100°C to near dryness. After cooling, 10 mL of HNO_3 (0.1 mol L^{-1}) was added to the residue, complete to 50 mL with bidistilled water, and then filter the solution. Phosphate buffer was utilized to adjust the pH to 7.0. A EDTA (0.05 mol L^{-1}) was utilized as masking agent for determination of mercury in CRMs [19]. After that the preconcentration IL-CPE procedure was completed as previously described.

RESULTS AND DISCUSSION

Effect of pH

The pH is a critical parameter that effect on the absorbance and formation of metal-ligand complex by applying the proposed IL-CPE approach. It was explored in the pH scale of 3.0–10 by adding buffer solutions. The findings obtained from this study are set out **Figure 1**. The extraction efficiency increased with increasing pH from 3.0-6.0 and maximum quantitative values are accomplished till the pH rang 6.0-8.0. at higher pH values a decrease in absorbance is obvious. So, pH 7.0 was selected as the best pH in all further studies.

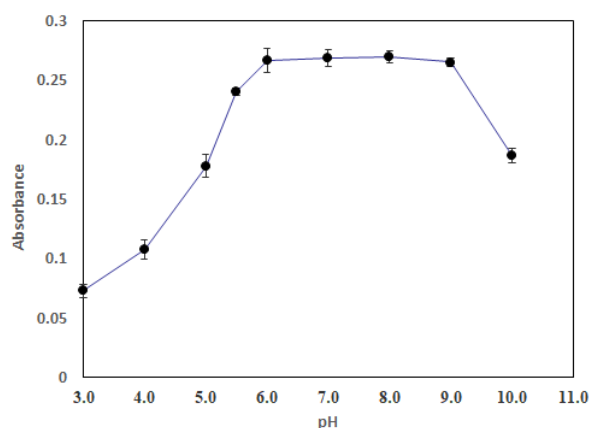


Figure 1. Effect of pH on the extraction efficiency of Hg(II) through IL-CPE method. Conditions: (Hg(II) concentration, 500 $\mu\text{g L}^{-1}$; concentration of BMBATT, (1.0×10^{-3} mol L^{-1}); $\text{C}_{16}\text{MeImCl}$ (0.1 mol L^{-1}) volume, 200 μL ; Triton X-114 (0.5% v/v), 300 μL ; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

Effect of BMBATT quantity

The impact of BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) volume has major influence on the extraction efficiency of hydrophobic metal-chelate. The volume of BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) solution was examined from 0.5 to 5.0 mL **Figure 2**. The absorbance has been increased by increasing the sunset yellow concentration up to 2.0 mL of BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) and higher volumes of BMBATT have no significant effect in the absorbance. In further tests, 2.0 mL of BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) was utilized as the optimal volume for metal complexation.

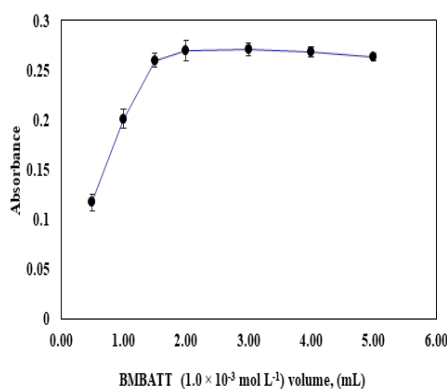


Figure 2. Effect of BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) volume on the extraction efficiency of Hg(II) through IL-CPE method. Conditions: (Hg(II) concentration, $500 \mu\text{g L}^{-1}$; pH 7.0; $\text{C}_{16}\text{MeImCl}$ (0.1 mol L^{-1}) volume, $200 \mu\text{L}$; Triton X-114 (0.5% v/v), $300 \mu\text{L}$; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

Effect of extracting phase composition

It is necessary to select the type and volume of surfactant which has a significant effect on the efficiency of mercury extraction. Various non-ionic surfactants (Triton X-114 Triton X-100 and Tween-80) were studied, and the results illustrated that the Triton X-114 was the perfect surfactant for the quantitative recoveries and extraction of mercury–BMBATT. The variance in mercury extraction efficiency within the concentration range of 0.1–1.0% v/v of Triton X-114 has been checked. The maximum absorbance was observed at 0.5% v/v Triton X-114 (**Figure 3**). The effect of $\text{C}_{16}\text{MeImCl}$ as IL concentration on the extraction efficiency was then tested by the addition of different

$\text{C}_{16}\text{MeImCl}$ amounts from ($0.02\text{--}0.2 \text{ mol L}^{-1}$) to the mixture. The maximum extraction efficiency was observed, at (0.1 mol L^{-1}) $\text{C}_{16}\text{MeImCl}$, according to the results obtained (**Figure 4**). Furthermore, addition of IL increases the phase separation, micellar size and viscosity. Also, all experiments were conducted as salting-out agent in the existence of NaCl (2.0% w/v).

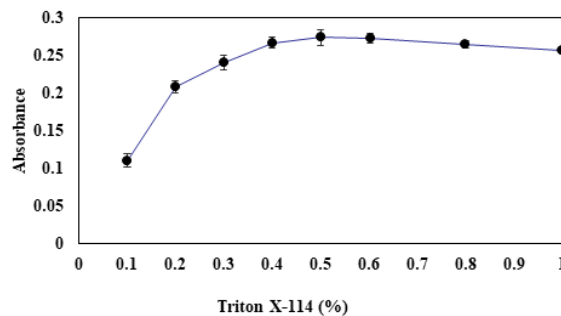


Figure 3. Effect of Triton X-114 concentration on the extraction efficiency of Hg(II) through IL-CPE method. Conditions: (Hg(II) concentration, $500 \mu\text{g L}^{-1}$; pH 7.0; BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$), 2.0 mL; $\text{C}_{16}\text{MeImCl}$ (0.1 mol L^{-1}) volume, $200 \mu\text{L}$; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

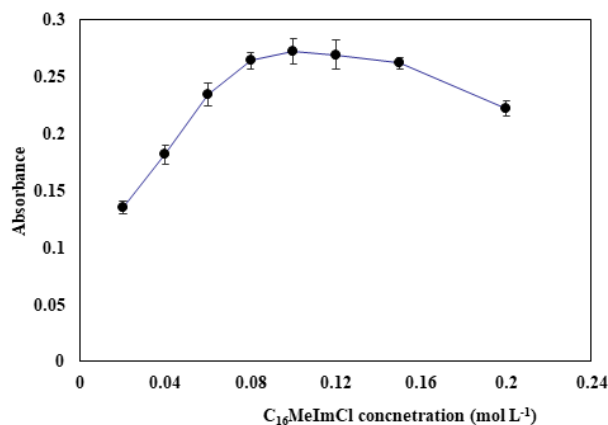


Figure 4. Effect of $\text{C}_{16}\text{MeImCl}$ concentration on the extraction efficiency of Hg(II) through IL-CPE method. Conditions: (Hg(II) concentration, $500 \mu\text{g L}^{-1}$; pH 7.0; BMBATT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$), 2.0 mL; Triton X-114 (0.5% v/v), $300 \mu\text{L}$; NaCl (2.0%, w/v), 1.0 mL; centrifugation time, 5.0 min; volume of sample, 50 mL).

Effect of sample volume

The sample volume is an important parameter for the development of IL-CPE method, due to the direct relation with the preconcentration factor. Thus, various sample volumes ranging from 10 mL to 100 mL were studied and other experimental conditions were remained constant. The results showed that the

quantitative analytical signal was increased up to 50 mL using the IL-CPE method. Therefore, 50 mL was chosen as the best sample volume for all subsequent studies. Hence, the preconcentration factor (PF) was detected to be 100 (the model solution volume :50 mL, and the final volume :0.5 mL).

Effect of equilibration temperature and time

To attain a convenient phase separation and reliable pre-concentration, it is essential to optimize the equilibration temperature and time. The impacts of the equilibration temperature and time on the extraction efficiency and analytical signal were tested the temperature range of from 30-70°C and incubation time range of 1.0–15 min. The finding showed that equilibration temperature 45°C and an equilibration time 5.0 min were chosen for subsequent experiments.

Effect of centrifugation conditions

The impact of the centrifugation time and rate were studied in the time range of 2.0-10 min at different rates from 1000-5000 rpm. The optimum separation conditions were achieved at centrifugation time of 5.0 min and 4000 rpm as a rate in the presence of IL and cooling for 5.0

min in an ice-bath leads to the maximum absorbance and sensitivity.

Effects of diluent

The elevated viscosity of surfactant-rich phase can be reduced utilizing a diluent agent prior to spectrophotometric detection. The impact of different diluent solvents like methanol, ethanol, acetone, THF and acetonitrile in range of 0.5-3.0 mL were investigated. The results confirmed that ethanol was selected as a diluent.

Study of interferences

The matrix effect on the extraction capability and determination of mercury by the developed IL-CPE method was studied. Different concentrations of interfering ions were added to 50 mL of the model solution containing 600 µg L⁻¹ mercury and the IL-CPE procedure was applied. The tolerance limit was defined as the concentration of matrix ions with a change in the sample absorbance > ±5.0% and the results showed in **Table 1**. These results elucidated that the matrix ions tested had no significant interference effect on the preconcentration and determination mercury in real samples up to the tolerance values.

Table 1. Influence of interfering ions on the percent recovery of Hg(II) using the proposed IL-CPE method (N = 3.0).

Interfering Ion	Added as	Tolerance Concentration (mg L ⁻¹)	Recovery (%) ^a
Na ⁺	NaNO ₃	10000	96 ± 2
K ⁺	KCl	10000	97 ± 2
Ca ²⁺	Ca(NO ₃).4H ₂ O	1000	98 ± 1
Mg ²⁺	Mg(NO ₃) ₂ .4H ₂ O	1000	95 ± 2
	O		
Cl ⁻	KCl	10000	98 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	3000	97 ± 4
CO ₃ ²⁻	Na ₂ CO ₃	1000	98 ± 5
Cd ²⁺	Cd(NO ₃) ₂ .4H ₂ O	20	97 ± 3
Pb ²⁺	Pb(NO ₃) ₂	20	97 ± 4
Fe ³⁺	FeCl ₃	20	98 ± 2
Cu ²⁺	Cu(NO ₃) ₂ .6H ₂ O	10	100 ± 2
Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	10	99 ± 3
Zn ²⁺	Zn(NO ₃) ₂ .6H ₂ O	10	98 ± 2

Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	10	96 ± 4
Mn ²⁺	Mn(NO ₃) ₂ ·4H ₂ O	10	100 ± 3
	O		
Co ²⁺	Co(NO ₃) ₂ ·6H ₂ O	10	97 ± 2

^a Mean ± standard deviations.

Analytical features of the proposed IL-CPE method

Different analytical criteria for estimating mercury under the optimum experimental conditions were evaluated. The linear calibration graph was obtained with regression equation of $A_{\text{Hg}} = 0.0004C_{\text{Hg}} + 0.0023$ and correlation coefficient (R^2 0.9997, $n=10$) in the presence of IL within the detection range of 2.0–600 $\mu\text{g L}^{-1}$ at $\lambda_{\text{max}} = 568$ nm. The limit of detection, LOD, was defined the ratio of three times standard deviation of seven blank absorbances to the slope of the calibration graph ($3S_b/m$) was 0.4 $\mu\text{g L}^{-1}$. The limit of quantification, LOQ, was found as the ratio of ten times standard deviation of seven replicate measurements of blank absorbances to the slope of the calibration graph ($10S_b/m$) was 1.33 $\mu\text{g L}^{-1}$. The relative standard deviations percentage (RSDs%) as the precision of the proposed method were examined at 100 and 400 $\mu\text{g L}^{-1}$ mercury and found to be 1.0 and 2.4%, respectively ($n=10$) with a recovery ranging from 97–101%, which illustrate a good precision of the method. Due to measuring the amount of mercury in sample solution (50 mL) in surfactant-rich phase final volume (0.5 mL) after preconcentration by IL-CPE. Therefore, PF was 100. The enhancement factor (EF) was obtained as the ratio of the slopes of the calibration graphs of mercury with and without preconcentration was 36.

Validation studies

The validity and applicability of the proposed IL-CPE procedure were evaluated for estimating mercury in CRMs; (NIST 1641d mercury in natural water; certified value ($1.557 \pm 0.02 \mu\text{g L}^{-1}$) and NCS ZC81002B human hair; certified value ($1.06 \pm 0.28 \mu\text{g g}^{-1}$)). The results obtained showed that the found values and the recoveries for mercury in NIST 1641d mercury in natural water and NCS ZC81002B human hair were ($1.51 \pm 0.04 \mu\text{g L}^{-1}$ and $1.04 \pm 0.23 \mu\text{g g}^{-1}$) and (97 and 98), respectively. The obtained values are in good agreement with the certified values. These results confirmed that the IL-CPE technique can be successfully utilized to estimate mercury at trace levels in real samples with high accuracy and validity.

Analytical applications to real samples

The developed IL-CPE technique was applied for determining mercury in real (tap, mineral, river, wastewater and sea) water, vegetables (tomato, potato, onion, spinach, cabbage), fruits (apples) and hair samples to evaluate the accuracy and reliability of the developed method by applying the standard addition method. The obtained results provided in **Table 2** shows that the relative recoveries of mercury in real samples were quite good (95.0–100%). Also, the relative standard deviation (RSDs %) were evaluated as a precision and were in the range of 0.70%–1.95%. The proposed IL-CPE approach was suitable and reliable for estimating mercury at trace levels in real water, food and hair samples.

Table 2. Application of the proposed IL-CPE method for trace detection of Hg(II) ion in real water, food and hair samples (N=3.0).

Samples	Added ($\mu\text{g L}^{-1}$)	Found \pm SD ^a ($\mu\text{g L}^{-1}$)	Recovery (%) ^c	RSD (%)	Sample	Added ($\mu\text{g g}^{-1}$)	Found ^a \pm SD ($\mu\text{g g}^{-1}$)	Recovery (%) ^c	RSD (%)
Tap water	0	BDL	-	-	Tomato	0	BDL	-	-
	200	190.0 \pm 2.50	95	1.32		200	194.0 \pm 1.40	97	0.72
	400	384.0 \pm 4.73	96	1.23		400	392.0 \pm 4.80	98	1.22
Mineral water	0	BDL	-	-	Potato	0	BDL	-	-
	200	194.0 \pm 2.38	97	1.23		200	190.0 \pm 2.90	95	1.53
	400	380.0 \pm 4.85	95	1.28		400	388.0 \pm 4.10	97	1.06
River water	0	BDL	-	-	Onion	0	BDL	-	-
	200	200.0 \pm 2.69	100	1.35		200	192.0 \pm 1.90	96	0.99
	400	392.0 \pm 3.97	98	1.01		400	396.0 \pm 4.60	99	1.16
Wastewater	0	7.8 \pm 0.15	-	-	Spinach	0	BDL	-	-
	200	206.0 \pm 1.44	99	0.70		200	196.0 \pm 3.40	98	1.73
	400	396.0 \pm 2.87	97	0.72		400	388.0 \pm 4.80	97	1.24
Sea water	-	10.0 \pm 0.1	-	-	Cabbage	0	BDL	-	-
	200	202.0 \pm 3.38	96	1.67		200	192.0 \pm 2.50	96	1.30
	400	402.0 \pm 4.90	98	1.22		400	400.0 \pm 6.70	100	1.68
					Hair	-	BDL	-	-
						200	198.0 \pm 3.1	99	1.57
						400	380.0 \pm 7.40	95	1.95

^a Mean \pm standard deviation.

^b BDL: Below detection limit.

^c Recovery% = [Observed value of Hg(II) / Expected value of Hg(II)] \times 100

Comparison with other preconcentration methods

The presented IL-CPE procedure was compared with the other preconcentration techniques [1-3, 14-16, 19, 20, 34-40] coupled

with UV-Vis spectrophotometer for determining mercury in various real samples (Table 3). The analytical performance proposed method is good the LOD, RSD% and PF or EF were better than the reported methods in literature.

Table 3. Comparison between the proposed IL-CPE procedure and other reported methods for Hg(II) preconcentration and determination.

Preconcentration method	Reagent	Detection system	LO D ^a ($\mu\text{g L}^{-1}$)	RS D % ^b	PF/E F ^c	Samples	References
Ss-LPME	Dithizone/ N,N-Dimethyl-cyclohexyl-amine/protonated N,N-dimethyl-cyclohexyl-amine carbonate	SP ($\lambda_{\text{max}}=574.5 \text{ nm}$)	0.19	0.8	40	water and hair samples	[1]
UA-Ss-LPME	(PAN/1-decanol/THF)	SP ($\lambda_{\text{max}}=560 \text{ nm}$)	1.80	2.4 4	20	Water samples	[2]
IL-DLLME	TMK/1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imid	SP ($\lambda_{\text{max}}=575 \text{ nm}$)	3.9	1.7	18.8	Water samples	[3]
EME/SP	PAN/ (DEHP in 1-octanol)	SP ($\lambda_{\text{max}}=554 \text{ nm}$)	0.7	5.2- 6.1 12 5.6 6.4	176 130	Water samples Fish Samples	[14]
SPE	Diphenylthiocarbazon/ a cellulose column.	SP ($\lambda_{\text{max}}=520 \text{ nm}$)	2.0	3.5	33	Water samples	[15]
VA-LLME	TOABr-coated Au NPs	SP ($\lambda_{\text{max}}=520 \text{ nm}$)	0.8	4.7	ND ^a	Tap and mineral water	[16]
SPE	Dithizone/ activated carbon xerogel	SP ($\lambda_{\text{max}}=490 \text{ nm}$)	7.6	1.3 6	25	Water samples	[19]
SPE	1,5-Diphenylthiocarbazon/ neutral alumina/ Polyethylene glycol,	SP ($\lambda_{\text{max}}=520 \text{ nm}$)	4.0	2.5 0	100	Water samples	[20]
US-CPE	thiophene-2,5-dicarboxylic acid/ Tween 20 and SDS	SP ($\lambda_{\text{max}}=550 \text{ nm}$)	0.27	2.8	85	Fish samples	[34]
CPE	Iodide with Triton X-114	SP ($\lambda_{\text{max}}=300 \text{ nm}$)	3.0	0.7 6- 2.5 1	19.5	water samples	[35]
CPE	PAN/ Triton X-114	SP ($\lambda_{\text{max}}=554 \text{ nm}$)	1.65	2.7 5	33.3	Environmental water samples	[36]
	TAR/ Triton X-114	SP ($\lambda_{\text{max}}=380 \text{ nm}$)	14.5	2.6 5	33.3		

CPE	TMK/Triton X-114	9 nm) SP (λ_{\max} =57 0 nm)	0.83	0.2 7	33.3	Water samples	[37]
IL-CPE	TPPP/ TEGII	SPF (λ_{ex} = 570 nm and λ_{em} = 658 nm)	0.08	2.4	45	water samples	[38]
CPE	Rhodamine B hydrazide /Triton X- 114	SP (λ_{\max} =55 6 nm)	1.40	0.3 5	5	industrial effluent sample	[39]
CPE	TAC/ Ponpe 7.5	SP (λ_{\max} =55 6 nm)	0.8	3.2	33.3	water samples	[40]
IL-CPE	BMBATT /Triton X- 114- C16MeImCl	SP (λ_{\max} =56 8 nm)	0.4	2.4	100	Water, food and hair samples	Proposed work

^a LOD: Limit of detection. ND: not detected.

^b RSD: Relative standard deviation.

^c PF: Preconcentration factor and EF: Enrichment factor.

^d UA-Ss-LPME: Ultrasonic-assisted supramolecular solvent-based liquid phase microextraction; SP: spectrophotometry; PAN: 1-(2-Pyridylazo)-2-naphthol; THF: tetrahydrofuran; IL-DLLME: Ionic liquid-dispersive liquid-liquid microextraction; TMK: 4,4'-bis(dimethylamino) thiobenzophenone; EME: Electromembrane; DEHP: bis(2-ethylhexyl) phosphate; SPE: solid phase extraction; VA-LLME: vortex-assisted liquid-liquid microextraction; TOABr- coated Au-NPs: tetraoctylammonium bromide coated Au nanoparticles; Ss-LPME: supramolecular solvent liquid phase microextraction; CPE: cloud point extraction; US-CPE: ultra-sonic cloud point extraction; SDS: sodium dodecyl sulphate; TAR: 4-(2-thiazolylazo) resorcinol; TMK: Thio-Michler's Ketone; IL-CPE: Ionic liquid-cloud point extraction; TPPP: 5,10,15,20-tetra-(4-phenoxyphenyl)porphyrin; TEGII: tetraethyleneglycol-bis(3-methylimidazolium) diiodide; SPF: spectrofluorimetry; TAC: 2-(2'-Thiazolylazo)-p-cresol, IL-CPE: ionic liquid-cloud point extraction.

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 ($0.60 \mu\text{g L}^{-1}$), 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.

REFERENCES

- [1] D. Schaumlöffel, Nickel species: analysis and toxic effects. *J. Trace Elem. Med.* **26**, 1 (2012).
- [2] R. Galbeiro, S. Garcia, I. Gaubeur, *J. Trace Elem. Med. Bio.* **28**, 160 (2014).
- [3] C. Zeng, X. Xu, N. Zhou, Y. Lin, *Spectrochim. Acta A.* **94**, 48 (2012).
- [4] H. Abdolmohammad-Zadeh, E. Ebrahimzadeh, *J. Braz. Chem. Soc.* **22**, 517 (2011).
- [5] S.M. Shah, H.N. Wang, X. Su, *Chem. Res. Chinese U.* **27**, 366 (2011).
- [6] S.G. Silva, P.V. Oliveira, J.A. Nóbrega, F.R.P. Rocha, *Anal. Methods*, **1**, 68 (2009).

- [7] Q. Han, Y. Huo, L. Yang, X. Yang, Y. He, Wu J., *Molecules*, **23**, 2597 (2018). doi:10.3390/molecules23102597.
- [8] R. El Sheikh, A.A. Gouda, A.H. Mostafa, N. Salah Eldin, *Int. J. Pharm. Pharm. Sci.* **7**, 176 (2015).
- [9] J. Song, W. Zhen, Z. Li, Y. Lian, Y. Yang, *Water. Sci. Technol.* **66**, 792 (2012).
- [10] S. Garcia, R. Galbeiro, S.G. Silva, C. Nomura, F.R.P. Rocha, I. Gaubeur, *Anal. Methods*, **4**, 2492 (2012).
- [11] Naeemullah, T.G. Kazi, M. Tuzen, *J. Ind. Eng. Chem.* **35**, 93 (2016).
- [12] A.S. Amin, A.S. AL-Attas, *J. Saudi Chem. Soc.* **16**, 451 (2012).
- [13] H. Ciftci, M.M. Temuz, E. Ciftci, *J. AOAC Int.*, **96**, 875 (2013).
- [14] M. Tuzen, M. Soylak, D. Citak, H.S. Ferreirara, M.G.A. Korn, M.A. Bezerra, *J. Hazard. Mater.* **162**, 1041 (2009).
- [15] D. Citak, M. Tuzen, M. Soylak., *Food Chem. Toxicol.* **47**, 2302 (2009).
- [16] S.M.N. Moallaa, A.S. Amin, *Anal. Methods*, **7**, 10229 (2015).
- [17] Y. Wang, J. Zhang, B. Zhao, X. Du, J. Ma, J. Li, *Biol. Trace. Elem. Res.* **144**, 1381 (2011).
- [18] M.H. Sorouraddin, L. Khoshmaram, *J. Chin. Chem. Soc.* **57**, 1346 (2010).
- [19] S. Dadfarnia, A.M.H. Shabani, M.S. Bidabadi, A.A. Jafari, *J. Hazard. Mater.* **173**, 534 (2010).
- [20] V.A. Lemos, E.V.S. Vieira, E. Santos, L. Santos, *CLEAN - Soil Air Water*, **40**, 268 (2012).
- [21] Z.A. ALOthman, M.A. Habila, E. Yilmaz, M. Soylak, S.M. Alfadul, *J. Mol. Liq.* **221**, 773 (2016).
- [22] S.M. Sorouraddin, M.A. Farajzadeh, H.N. Qarajeh, *Anal. Bioanal. Chem. Res.*, **6** 365 (2019).
- [23] S.M. Sorouraddin, M.A. Farajzadeh, H. Nasin, *Anal. Methods*, **11**, 1379 (2019).
- [24] E.K. Paleologos, D.L. Giokas, M.I. Karayannis, *Trends Anal. Chem.* **24**, 426 (2005)
- [25] N. Altunay, A. Elik, R. Gurkan, *Microchem. J.* **147**, 277 (2019).
- [26] J.A. Barreto, R.S. de Assis, R.J. Cassella, V.A. Lemos, *Talanta*, **193**, 23 (2019).
- [27] P. Singla, O. Singh, S. Chabba, R.K. Mahajan, *J. Mol. Liq.* **249**, 294 (2018)
- [28] A. Bera, H. Belhaj, *J. Mol. Liq.* **224**, 177 (2016)
- [29] A. Pal, A. Yadav, *J. Mol. Liq.* **251**, 167 (2018)
- [30] V.G. Rao, S. Mandal, S. Ghosh, C. Banerjee, N. Sarkar, *J. Phys. Chem. B* **117**, 1480 (2013)
- [31] V.G. Rao, S. Ghosh, C. Ghatak, S. Mandal, U. Brahmachari, N. Sarkar, *J. Phys. Chem. B* **116**, 2850 (2012)
- [32] J. Łuczak, J. Hupka, J. Thöming, C. Jungnickel, *Colloids Surf. A* **329**, 125 (2008)
- [33] H. Ma, H. Ke, T. Wang, J. Xiao, N. Du, L. Yu, *J. Mol. Liq.* **240**, 556 (2017)
- [34] C. Jungnickel, J. Łuczak, J. Ranke, J.F. Fernández, A. Müller, J. Thöming, *Colloids Surf. A* **316**, 278 (2008)
- [35] R. Vanyór, L. Biczók, Z. Miskolczy, *Colloids Surf. A* **299**, 256 (2007)
- [36] P.D. Galgano, O.A. El Seoud, *J. Colloid Interface Sci.* **345**, 1 (2010)
- [37] M.A. Rather, G.M. Rather, S.A. Pandit, S.A. Bhat, M.A. Bhat, *Talanta* **131**, 55 (2015)
- [38] H.T.S. Britton, *Hydrogen Ions*, 4th ed., Chapman and Hall, London, (1952).
- [39] A.A. Gouda, *Int. J. Environ. Anal. Chem.* **94**, 1210 (2014).
- [40] A.A. Gouda, A.M. Summan, A.H. Amin, *RSC Adv.* **6**, 94048 (2016).
- [41] E.M.Hafez, R. El Sheikh, M. Fathalla, A. Sayqal, A.A. Gouda, *Microchem. J.* **150**, 104100 (2019).