AN EFFICIENT IONIC LIQUID-BASED CLOUD POINT EXTRACTION TO PRECONCENTRATE MERCURY IN ENVIRONMENTAL SAMPLES AND HAIR OF OCCUPATIONAL WORKERS BEFORE SPECTROPHOTOMETRIC DETECTION

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ABSTRACT. Mercury preconcentration in environmental samples and hair of occupational workers prior to spectrophotometric detection was described using a unique, eco-friendly, and quick ionic liquid-based cloud point extraction method. The discovered method used an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with Triton X-114 as an extracting phase in the presence of a new chelating agent 3-(2-hydroxy-5-ethoxycarbonylphenyl)-1,2,4-triazole at pH 7.0 to separate mercury and measure the complex spectrophotometrically at wavelength 550 nm. The effects of several analytical factors on extraction performance were investigated. With a correlation coefficient of 0.9997. The calibration graph was linear in the range of 2.0–400 µg/L. The limit of detection and preconcentration factor, respectively, were 0.5 µg/L and 100. The relative standard deviation of 100 and 300 µg/L mercury (n = 10) was 1.5 and 2.2, respectively, indicating the precision and reliability of the new IL-CPE approach. The accuracy of the proposed approach confirmed through the certified reference materials analysis. The applicability of the established technique was demonstrated successfully by the estimation of trace mercury in environmental samples and hair of occupational workers.

KEY WORDS: Mercury, Ionic liquid-based cloud point extraction, Environmental and hair samples, Spectrophotometry

INTRODUCTION

Contamination of environmental (water and food) and biological samples with mercury (Hg(II)) ions is a long-term problem with serious public health repercussions all over the world. Hg(II) resulted from mineral breakdown in burning fossil fuels, rocks, dental fillings, soil withering, human activity sources, industrial catalysts, batteries, and thermometer production, among other things. Hg salts are present in some pharmaceutical antiseptic creams and ointments used in skin lightening creams. Hg(II) is an extremely hazardous metal pollutant that causes a wide range of neurological diseases [1, 2]. As a result, estimating and measuring the environmental consequences of tiny quantities of Hg(II) is essential for avoiding potential health concerns caused by it [3-5].

For estimation of Hg(II) in various samples, several instruments including inductively coupled plasma with mass spectrometry [6] or atomic emission spectrometry [7], gas chromatography-inductively coupled plasma-mass spectrometry [8], cold vapour atomic absorption spectrometry [7, 9], HPLC coupled to cold vapour atomic fluorescence spectrometry [10], graphite furnace atomic absorption spectrometry [11] and spectrophotometry [12-15], were used. Furthermore, these methods have several drawbacks, such as low sensitivity, significant matrix interference, and the necessity for highly experienced laboratory specialists to carry them out. Therefore, rapid, environmentally acceptable, validated approaches for separation of Hg(II) in environmental and biological samples in occupational environments are required.

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Different preconcentration-separation techniques have been utilized to preconcentrate Hg(II) ions in various samples such as solid phase extraction [1, 3, 6, 16-18], liquid-phase microextraction (LPME) [4, 5, 11, 19-23] and cloud point extraction (CPE) [24-30].

CPE is an efficient environmentally beneficial technology that uses a minimal amount of non-ionic surfactants rather than dangerous solvents. At the cloud point temperature (CPT), CPE can generate and remove non-ionic surfactant micelles from aqueous solutions, preconcentrating the analytes in a little amount of surfactant-rich phase [31, 32]. CPE has several advantages, including an elevated preconcentration factor, environmental friendliness, cost efficiency, increased safety, and simplicity.

Ionic liquids (ILs) were used as additive solvents with non-ionic surfactants to boost surfactant extraction efficiency and improvement factor of CPE [30]. ILs are a green and alternative solvent with great physicochemical features for diverse organic molecules and metal ions, including high thermal stability, non-volatility, economy, selective solubility, and superior extractabilities [31]. Because of these characteristics, ILs are ideal candidates for use as an adjuvant with nonionic surfactants in CPE separation procedures. Tetraethyleneglycol-bis(3-methylimidazolium) diiodide ionic liquid was utilized for enrichment of Hg(II) after complexation with 5,10,15,20-tetraakis(4-phenoxyphenyl)porphyrin prior to spectrofluorimetric determination [30].

To preconcentrate and assess trace Hg(II), a novel, easy, and green ionic liquid-based cloud point extraction (IL-CPE) approach combined with spectrophotometry was devised in the present study. A mixed-micellar system with 1-butyl-3-methylimidazolium hexafluorophosphate [C₄MIM][PF₆] as the IL, Triton-X114 nonionic surfactant as the extracting phase, and 3-(2-hydroxy-5-ethoxycarbonylphen-1-ylazo)-1,2,4-triazole (HECAT) as the complexing agent was employed in the devised approach. The impact of various operational circumstances has been investigated. The present approach has been utilized to estimate Hg(II) in environmental samples and hair of occupational workers.

**EXPERIMENTAL**

**Apparatus**

A Varian UV-Vis spectrophotometer (Cary 100 Conc., Australia) with a 10 mm quartz cell was utilized to measure absorbance. A glass electrode was utilized in conjunction with an Adwa AD1000 pH meter (Romania) for the pH readings. The phase separation was aided by a centrifuge (HERMLE, Germany). A thermostated water bath with good temperature control was utilized. To make solutions, a Milli-Q purification device (Millipore, USA) was used to get deionized/double distilled water. Before being utilized in this project, all glass and plastic wares were processed for at least 12 hours in HNO₃ (10% v/v), rinsed, and cleaned with double distilled water.

**Chemicals and solutions**

Analytical reagent grade chemicals and reagents were employed throughout. HgCl₂ (Merck, Darmstadt, Germany) was dissolved in bidistilled water to provide a stock solution of Hg(II) (1000 µg/mL). Appropriate dilutions with HNO₃ (0.01 mol/L) were prepared by working standard solutions used before daily use. High-quality concentrated HNO₃ (65%, w/w), HCl (37%, v/v), NH₄ (25%, v/v) and H₂O₂ (30%, w/v) (Merck) solutions were used. The IL, [C₄MIM][PF₆] was purchased from Across Organics (Geel, Belgium) and Triton X-114 as a non-ionic surfactant (Sigma–Aldrich, USA) was selected as the extraction solvent without further purification.

An aqueous solution of [C₄MIM][PF₆] (0.1 M) was provided by dissolving the correct weight of [C₄MIM][PF₆] in 100 mL of double distilled water with swirling. Triton X-114 (0.5%, v/v) solution was prepared by dissolving 0.5 mL of Triton X-114 in 100 mL of bidistilled water. Sodium chloride (NaCl) (2.0%, w/v) was prepared by dissolving 2.0 g of NaCl in 100 mL of bidistilled water.

Bull. Chem. Soc. Ethiop. 2022, 36(4)
The HECAT reagent was synthesised as described in the literature [33, 34]. A HECAT stock solution (1.0 × 10⁻³ mol/L) was made by dissolving an adequately weighed amount of purified azo (HECAT) in methanol in a 100-mL flask.

Specific buffer series have been used, like acetate (CH₃COONa-CH₃COOH) pH (3.0-5.5), phosphate (Na₂HPO₄- NaH₂PO₄) pH (6.0-7.0), ammoniacal (NH₄Cl) solution pH 8.0, and borate (sodium tetraborate and boric acid) pH (9.0-10). In particular, HCl and NaOH are used in adjusting the pH values as indicated in the literature [35].

Natural water (tap, mineral, or wastewater) samples were taken in Zagazig, Egypt; river water was gathered in Shobra, Egypt; and sea water was collected in the Red Sea. Samples of vegetables (tomato, potato, spinach, cabbage) and fish mussels were obtained from Makkah marketplaces in Saudi Arabia. Hair samples were taken from petrol station workers. 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 centrifuge tube (50 mL), a 30 mL sample solution containing 2.0-400 µg/L Hg(II) was combined with 4 mL of phosphate buffer (pH 7.0). After that, 2 mL of HECAT (1 × 10⁻³ mol/L), 200 µL [C₄MIM][PF₆] solution (0.1 mol/L), 300 µL of Triton-X114 (0.5%, v/v), and 1 mL of NaCl (2%, 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 min. The turbid solution was centrifuged at 4000 rpm for 5.0 minutes to achieve phase separation. To improve the viscosity of the extractant phase, the tube was chilled for 5 minutes in an ice bath. Following that, the IL-phase settled at the tube's bottom. With a pipette, the water supernatant was decanted. With ethanol, the viscous micelle-mediated extractant phase was diluted up to 500 µL. A spectrophotometer was utilized to measure the extracted Hg(II)-HECAT complex at 550 nm.

**Pretreatment of real samples and CRMs**

**Environmental samples**

Various samples were subjected to the suggested IL-CPE approach. The filtration of water samples via a cellulose membrane filter (0.45 µm pore size) occurred prior to dil. nitric acid acidification and stored at 4.0 °C. To homogenise the vegetable or fish samples, they were baked in a 90 °C oven for 24 hours before being pulverised in an agate mortar. A 15 mL combination of HNO₃ (65%, w/w) and H₂O₂ (30%, w/v) (2:1) was put into a Teflon beaker and evaporated at 150 °C on a hot plate for 2.0 h to near dryness for a wet acid digestion approach. After that, bidistilled water (10 mL) was added to the samples. A cellulose membrane filter (0.45 µm) was used to filter the resulting combination. The conventional addition process was employed after adding phosphate buffer to bring the pH to 7. The Hg(II) concentration in water, vegetable and fish samples, and CRM (NIST-1641d mercury in natural water) was preconcentrated and spectrophotometrically analysed using the developed IL-CPE technique.

**Hair samples**

The hair samples were cleaned in double distilled water and dried at 100 °C for one day in an oven. 0.1 g of hair samples or NCS ZC81002B human hair CRM were precisely weighed and subjected to a wet digestion process in a PTFE digestion vessel. The hair samples were prepared according to the literature.[19] Then, the Hg(II) content was determined using the developed IL-CPE technique.
RESULTS AND DISCUSSION

Effect of pH

When using the proposed IL-CPE technique, pH is a significant factor that affects the absorbance and development of metal-ligand complexes. When adding buffer solutions, it was investigated on a pH scale of 3.0–10. The results of this research are illustrated in (Figure 1). The extraction efficiency was enhanced with raising pH from 3.0-5.5 and maximum quantitative values were accomplished till the pH ranged from 5.5-7.0. A decrease in absorbance is obvious at higher pH values. In all subsequent trials, pH 7.0 was chosen as the optimal pH.

![Figure 1. Effect of pH on the absorbance of Hg(II)-HECAT complex through IL-CPE method.](image)

Effect of HECAT volume

The impact of HECAT (1.0 × 10^{-3} mol/L) volume has a major influence on the extraction efficiency of hydrophobic metal-chelate. The volume of HECAT (1.0 × 10^{-3} mol/L) solution was examined from 0.5 to 5.0 mL (Figure 2). The absorbance has been raised by raising the HECAT concentration to 2.0 mL and larger volumes of HECAT had no influence on the absorbance. In further tests, 2.0 mL of HECAT (1.0 × 10^{-3} mol/L) was utilised as the optimal volume for metal complexation.

Effect of extracting phase composition

It is crucial to choose the kind and volume of surfactant, as these factors have a major impact on Hg(II) extraction efficiency. Triton X-100, Tween-80, and Triton X-114 were explored as non-ionic surfactants. The findings showed that Triton X-114 was an excellent surfactant for quantitative recovery. The variance in Hg(II) extraction efficiency of Triton X-114 within the concentration range (0.1–1.0%, v/v) has been checked. At 0.5%, v/v surfactant concentration, the
maximum absorbance was observed (Figure 3). The impact of varying $[\text{C}_4\text{MIM}]\text{[PF}_6]$ concentrations as IL on extraction efficiency was next investigated by adding varied $[\text{C}_4\text{MIM}]\text{[PF}_6]$ volumes to the mixture (0.02-0.2 mol/L). The maximum extraction efficiency was observed, at (0.1 mol/L) $[\text{C}_4\text{MIM}]\text{[PF}_6]$, according to the results obtained (Figure 4). Furthermore, the addition of IL increases the phase separation, micellar size, and viscosity. Also, all experiments were conducted as salting-out agent in the existence of 1.0 mL of NaCl (2.0%, w/v).

**Figure 2.** Effect of HECAT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) volume on the absorbance of Hg(II)-HECAT complex through IL-CPE method.

**Figure 3.** Effect of Triton X-114 concentration on the absorbance of Hg(II)-HECAT complex through IL-CPE method.

**Effect of sample volume**

The sample volume is a crucial factor in the establishment of the IL-CPE approach, due to its direct relation with the preconcentration factor. Thus, various sample volumes ranging from 10 to 100 mL were studied. The IL-CPE approach boosted the quantitative output by 50 mL, according to the results. As a consequence, 50 mL was selected as the optimal volume for all following trials. A preconcentration factor (PF) of 100 was discovered as a result.

Bull. Chem. Soc. Ethiop. **2022**, *36*(4)
Effect of temperature and time

For a convenient phase separation and reliable pre-concentration, the equilibration temperature and time must be optimised. The effects of equilibration temperature and time on extraction efficiency and analytical signal were investigated at temperatures ranging from 30-70 °C and incubation times ranging from 1.0-15 min. Following the discovery, an equilibration temperature of 45 °C and an equilibration time of 5.0 min were chosen for future experiments.

Effect of centrifugation conditions

The impact of time and rate of centrifugation was investigated in the range of 2-10 min and 1000-5000 rpm. The best preconcentration conditions were found with a centrifugation time of 5 min and a rate of 4000 rpm in the presence of IL, followed by a cooling period of 5 min in an ice bath.

Effects of diluent

The elevated viscosity of surfactant-rich phase can be reduced by a diluent agent prior to spectrophotometric detection. The impact of different diluent solvents like methanol, ethanol, acetone, THF, and acetonitrile at concentrations ranging from 0.5 to 3.0 mL was studied. The findings confirmed ethanol as a diluent (0.5 mL).

Interference studies

The influence of the matrix was investigated by the proposed IL-CPE approach. The IL-CPE approach was used to introduce different amounts of matrix ions to 50 mL of the tested solution that contained 400 µg/L of Hg(II). Table 1 shows the findings of the tolerance limits, which were established as the concentration of interfering ions making absorbance change (5.0%). These findings revealed that, up to the tolerance values, the interfering ions evaluated had no appreciable interfering impact on the IL-CPE of Hg(II) in real samples.
An efficient ionic liquid-based cloud point extraction to preconcentrate mercury in

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                                   | 97 ± 2              |
| K\(^+\)         | KCl               | 10000                                   | 98 ± 3              |
| Ca\(^{2+}\)     | Ca(NO\(_3\))\(_2\)-4H\(_2\)O | 1000                                   | 100 ± 1             |
| Mg\(^{2+}\)     | Mg(NO\(_3\))\(_2\)-4H\(_2\)O | 1000                                   | 99 ± 2              |
| Cl\(^-\)        | KCl               | 10000                                   | 98 ± 2              |
| SO\(_4^{2-}\)   | Na\(_2\)SO\(_4\)  | 3000                                    | 96 ± 3              |
| CO\(_3^{2-}\)   | Na\(_2\)CO\(_3\)  | 1000                                    | 100 ± 3             |
| Cd\(^{2+}\)     | Cd(NO\(_3\))\(_2\)-4H\(_2\)O | 20                                     | 97 ± 2              |
| Pb\(^{2+}\)     | Pb(NO\(_3\))\(_2\) | 20                                     | 96 ± 2              |
| Fe\(^{3+}\)     | FeCl\(_3\)        | 20                                      | 97 ± 2              |
| Cu\(^{2+}\)     | Cu(NO\(_3\))\(_2\)-6H\(_2\)O | 10                                     | 98 ± 1              |
| Ni\(^{2+}\)     | Ni(NO\(_3\))\(_2\)-6H\(_2\)O | 10                                     | 95 ± 2              |
| Zn\(^{2+}\)     | Zn(NO\(_3\))\(_2\)-6H\(_2\)O | 10                                     | 98 ± 3              |
| Al\(^{3+}\)     | Al(NO\(_3\))\(_3\)-9H\(_2\)O | 10                                     | 97 ± 2              |
| Mn\(^{2+}\)     | Mn(NO\(_3\))\(_2\)-4H\(_2\)O | 10                                     | 98 ± 5              |
| Co\(^{2+}\)     | Co(NO\(_3\))\(_2\)-6H\(_2\)O | 10                                     | 97 ± 3              |

\(^a\)Mean ± standard deviations.

Analytical features

In the presence of IL-CPE within the detection range of 2.0-400 \(\mu\)g/L, the linear curve was constructed using the regression equation \(A_{Hg} = 0.0007C_{Hg} + 0.0007\) and the correlation coefficient \((R^2 = 0.9999)\). The detection (LOD) and quantification (LOQ) limits were set at 0.5 and 1.5 \(\mu\)g/L, respectively. LOD and LOQ were calculated by dividing the standard deviation of blank signals (3\(S_b\) and 10\(S_b\)) by the linear curve slope (m) [36]. The relative standard deviation (RSD) resulted from the IL-CPE method was examined at 100 and 300 \(\mu\)g/L Hg(II) and found to be 1.5 and 2.2, respectively \((n = 10)\) with a recovery percentage ranging from 95-102%, which showed an excellent precision of the approach. The enhancement factor (EF) was 14, which was obtained as the ratio between the calibration graph slopes with IL-CPE and without preconcentration.

Analytical applications

The suggested IL-CPE approach was examined for its validity and usefulness in assessing Hg(II) in CRMs (NIST 1641d mercury in natural water and NCS ZC81002B human hair). The certified values were 1.557 ± 0.02 \(\mu\)g/L and 1.06 ± 0.28 \(\mu\)g/g, respectively. The results revealed that the found and recovery values for Hg(II) were \((1.52 ± 0.03 \mu\text{g}/\text{L} and 1.05 ± 0.25 \mu\text{g/g})\) and \((97.62\% and 99.06\%\)) for NIST 1641d mercury in natural water and NCS ZC81002B human hair, respectively. The acquired results are quite close to the certified results. These findings demonstrate that the IL-CPE technique may be used to accurately and reliably quantify trace levels of Hg(II) in real samples.

The developed IL-CPE approach was used to determine Hg(II) in real water, vegetables, and fish mussels samples, and occupational workers' hair to evaluate the accuracy and reliability. The results are shown in Tables 2 and 3. Relative recoveries of Hg(II) in real samples were relatively satisfactory (95.0–100%). Also, the RSD as a precision was in the range of 1.21–2.41. The proposed IL-CPE method was appropriate and reliable for estimating trace levels of Hg(II) in real water, vegetables, fish mussels, and occupational workers' hair.

Bull. Chem. Soc. Ethiop. 2022, 36(4)
Table 2. Application of the proposed IL-CPE method for trace detection of Hg(II) ion in real water samples (N = 3.0).

| Samples       | Added (µg/L) | Found ± SD (µg/L) | Recovery (%) | RSD  |
|---------------|--------------|-------------------|--------------|------|
| Tap water     | 0            | BDL               | -            | -    |
|               | 100          | 95.0 ± 1.40       | 95.0         | 1.47 |
|               | 300          | 288.0 ± 3.70      | 96.0         | 1.28 |
| Mineral water | 0            | BDL               | -            | -    |
|               | 100          | 98.0 ± 2.0        | 98.0         | 2.04 |
|               | 300          | 291.0 ± 4.60      | 97.0         | 1.58 |
| River water   | 0            | BDL               | -            | -    |
|               | 100          | 99.0 ± 1.60       | 99.0         | 1.62 |
|               | 300          | 294.0 ± 3.90      | 98.0         | 1.33 |
| Wastewater    | 0            | BDL               | -            | -    |
|               | 100          | 208.0 ± 2.60      | 100          | 2.41 |
|               | 300          | 296.0 ± 4.80      | 96.0         | 1.62 |
| Sea water     | -            | 8.0 ± 0.24        | -            | -    |
|               | 100          | 106.0 ± 1.80      | 95.50        | 1.79 |
|               | 300          | 308.0 ± 4.0       | 99.0         | 1.30 |

*Mean ± standard deviation; ** BDL: Below detection limit; * Recovery% = [Observed value of Hg(II) / Expected value of Hg(II)] × 100.

Table 3. Application of the proposed IL-CPE method for trace detection of Hg(II) in real vegetables, fish mussels and hair samples (N = 3.0).

| Sample       | Added (µg/g) | Found ± SD (µg/g) | Recovery (%) | RSD  |
|--------------|--------------|-------------------|--------------|------|
| Tomato       | 0            | BDL               | -            | -    |
|              | 100          | 96.0 ± 1.90       | 96.0         | 1.98 |
|              | 300          | 291.0 ± 4.0       | 97.0         | 1.37 |
| Potato       | 0            | BDL               | -            | -    |
|              | 100          | 96.0 ± 2.10       | 96.0         | 2.19 |
|              | 300          | 297.0 ± 3.60      | 99.0         | 1.21 |
| Spinach      | 0            | BDL               | -            | -    |
|              | 100          | 96.0 ± 1.70       | 96.0         | 1.77 |
|              | 300          | 294.0 ± 4.30      | 98.0         | 1.46 |
| Cabbage      | 0            | BDL               | -            | -    |
|              | 100          | 95.0 ± 1.20       | 95.0         | 1.26 |
|              | 300          | 288.0 ± 5.20      | 96.0         | 1.81 |
| Fish mussels | 0            | BDL               | -            | -    |
|              | 100          | 95.20 ± 1.40      | 97.0         | 1.47 |
|              | 300          | 296.50 ± 4.70     | 98.0         | 1.59 |
| Hair         | 0            | BDL               | -            | -    |
|              | 100          | 97.0 ± 1.50       | 97.0         | 1.55 |
|              | 300          | 294.0 ± 6.0       | 98.0         | 2.04 |

Comparison with other preconcentration methods

For determining Hg(II) in various samples, the proposed IL-CPE process was compared to conventional preconcentration procedures combined with spectrophotometry (Table 4). The proposed technique's analytical performance is satisfactory. The LOD, RSD%, and PF were better than the published techniques.
Table 4. Comparison between the proposed IL-CPE procedure and reported methods for preconcentration of Hg(II) prior to spectrophotometric detection.

| Method         | Reagent                                      | Wave-length $\lambda_{abs}$ (nm) | Linear range (µg/L) | LOD$^a$ (µg/L) | RSD$^a$ | PF/EF$^a$ | Samples                  | References |
|----------------|----------------------------------------------|-----------------------------------|----------------------|-----------------|----------|-----------|---------------------------|-------------|
| SPE            | DPTC/neutral alumina/Polyethylene glycol.    | 520                               | NA$^*$               | 4.0             | 2.50     | 100       | Water                     | [16]        |
| SPE            | DMMDC/ microcrystalline naphthalene          | 490                               | 10-3000              | 5.0             | 2.70     | 187       | Water                     | [17]        |
| Ss-LLME        | ABTR/ C18 disks                              | 545                               | 10-3000              | 3.5             | 1.70     | 50        | Tobacco and tobacco additives | [18]        |
| IL-DLLME       | TMK/[Hmim][Tf$_2$N] and acetone              | 575                               | 12-140               | 3.9             | 1.7      | 18.8      | Water                     | [20]        |
| VA-LLME        | TOABr-coated Au NPs                          | 520                               | 4.9-120              | 0.8             | 4.7      | 100       | Water                     | [21]        |
| Sa-LLME        | PAN/1-decanol/THF                            | 560                               | 8.3-1000             | 1.80            | 2.44     | 20        | Water                     | [22]        |
| VA-LLME        | Astrazon red 6B                              | 550                               | 8.0-200              | 1.50            | NA       | 7.3       | Water                     | [13]        |
| SS-DLME        | TMK/1-octanol                                | 570                               | 5.0-400              | 1.60            | 1.57     | 120       | Water                     | [23]        |
| UA-CPE         | Thiophene-2,5-dicarboxylic acid/SDS and Tween 20 | 550                               | 1.0-700/10-250       | 0.27/0.12       | 2.8      | 100/85    | Fish                      | [24]        |
| CPE            | Iodide/H$_2$SO$_4$/Triton X-114              | 300                               | 10-400               | 3.0             | 0.76-2.51| 10.5/10   | Water                     | [25]        |
| CPE            | PAN/Triton X-114                             | 554                               | 10-1000              | 1.65            | 2.75     | 33.3      | Water                     | [26]        |
| CPE            | TAR/Triton X-114                             | 389                               | 50-2500              | 14.5            | 2.65     | 33.3      | Industrial effluent and water | [27]      |
| CPE            | TMK/Triton X-114                             | 570                               | 5.0-80               | 0.83            | 0.27     | 33.3/11   | Water                     | [28]        |
| CPE            | Rhodamine B hydrazide/Triton X-114           | 556                               | 10-100               | 1.40            | 0.35     | 5/24      | Industrial effluent and water | [28]      |
| CPE            | TAC/Ponpe 7.5                                | 556                               | 3.0-2200             | 0.86            | 3.2      | 33.3      | Water                     | [29]        |
| IL-CPE         | HECAT/Triton X-114-[C$_2$MIM] [PF$_6$]       | 550                               | 2.0-400              | 0.50            | 1.5-2.2  | 100       | Environmental samples and hair of occupational workers | Proposed work |

$^a$LOD: Limit of detection, RSD: Relative standard deviation, PF: Preconcentration factor and EF: Enrichment factor, NA: not available. $^*$SPE: solid phase extraction; DPTC: 1,5-Diphenylthiocarbazone; DMMDC: 2,6-dimethylmorpholine dithiocarbamate; ABTR: 5-(p-aminobenzylidene)-thiouronium; IL-DLLME: Ionic liquid-dispersive liquid–liquid microextraction; TMK: 4,4’-bis(dimethylamino) thio benzophenone; [Hmim][Tf$_2$N]: 1-hexyl-3-methylimmidazolium bis(trifluoromethylsulfonyl) imid; VA-LLME: vortex-assisted liquid–liquid microextraction; TOABr- coated Au-NPs: tetraoctylammonium bromide coated Au nanoparticles; Sa-UA-LPME: Ultrasonic-assisted supramolecular solvent-based liquid phase microextraction; PAN: 1-(2-Pyridylazo)-2-naphthol; THF: tetrahydrofuran; SS-DLME: syringe-to-syringe dispersive liquid-phase microextraction; UA-CPE: ultrasound-assisted cloud point extraction; SDS: sodium dodecyl sulphate; CPE: cloud point extraction; PAN: 1-(2-Pyridylazo)-2-naphthol; TAR: 4-(2-thiazoly)azo) resorcinol; TMK: Thio-Michler’s Ketone; TAC: 2-(2-Thiazoly)azo) p-cresol.
CONCLUSION

Without matrix interferences, a new, fast, low-cost, and environmentally friendly IL-CPE technique coupled with spectrophotometry has been developed for pre-concentration and estimation of Hg(II) in water, food and hair of occupational workers' samples. We used a selective reagent (HECAT) and a mixed-micellar system (Triton X-114/[C4MIM][PF6]). Other advantages of the presented IL-CPE approach are a decreased LOD (0.5 µg/L), a large PF (100), and excellent precision (RSD ≤ 2.2). Depending on these benefits, the proposed approach for determining Hg(II) in water, vegetables, fish samples, and occupational workers' hair is very efficient and reliable.

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