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Screen-printed electrode based electrochemical detector coupled with ionic liquid dispersive liquid–liquid microextraction and microvolume back-extraction for determination of mercury in water samples



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ABSTRACT

A novel approach is presented, whereby gold nanostructured screen-printed carbon electrodes (SPCnAuEs) are combined with in-situ ionic liquid formation dispersive liquid–liquid microextraction (in-situ IL-DLLME) and microvolume back-extraction for the determination of mercury in water samples. In-situ IL-DLLME is based on a simple metathesis reaction between a water-miscible IL and a salt to form a water-immiscible IL into sample solution. Mercury complex with ammonium pyrrolidinedithiocarbamate is extracted from sample solution into the water-immiscible IL formed in-situ. Then, an ultrasound-assisted procedure is employed to back-extract the mercury into 10 μL of a 4 M HCl aqueous solution, which is finally analyzed using SPCnAuEs.

Sample preparation methodology was optimized using a multivariate optimization strategy. Under optimized conditions, a linear range between 0.5 and 10 $\mu\text{g L}^{-1}$ was obtained with a correlation coefficient of 0.997 for six calibration points. The limit of detection obtained was 0.2 $\mu\text{g L}^{-1}$, which is lower than the threshold value established by the Environmental Protection Agency and European Union (i.e., 2 $\mu\text{g L}^{-1}$ and 1 $\mu\text{g L}^{-1}$, respectively). The repeatability of the proposed method was evaluated at two different spiking levels (3 and 10 $\mu\text{g L}^{-1}$) and a coefficient of variation of 13% was obtained in both cases. The performance of the proposed methodology was evaluated in real-world water samples including tap water, bottled water, river water and industrial wastewater. Relative recoveries between 95% and 108% were obtained.

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1. Introduction

Mercury is one of the most well-known toxic elements and even the World Health Organization places it between the first ten chemicals or group of chemicals of major public health concern [1]. Mercury exists in different forms with different properties, namely elemental or metallic (i.e., Hg^0); inorganic (i.e., Hg^{2+}); and organic (i.e., MeHg^+ , EtHg^+ , PhHg^+). Several factors determine the adverse effects from mercury exposure including its chemical form, the dose, the age and health of the person exposed, and the duration and kind of exposure (e.g., inhalation, ingestion, etc.) [2]. Among the most relevant health effects we can mention damage to

the gastrointestinal tract, nervous system, kidneys, respiratory failures and problems during the development of organs in unborn.

Mercury enters in the environment through both biogenic and anthropogenic vias. However, human activities such as mining, burning of fossil fuels, agriculture, paper and electrochemical industries, and household wastes, are the main responsible of the concerning increase of mercury levels in air, soil and water of certain contaminated areas. Monitoring the presence of mercury in natural and drinking waters is of great interest due to its high toxicity and bioaccumulation factor [3]. Mercury concentrations are commonly in the range of low ng L^{-1} in environmental waters [3] whereas the permitted level of mercury in drinking water depends on the responsible authorities of each territory. For example, the Environmental Protection Agency (EPA) sets the threshold level at 2 $\mu\text{g L}^{-1}$ [4], but the European Union establishes the limit at 1 $\mu\text{g L}^{-1}$ [5].

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Electrochemical techniques have been widely employed to determine mercury in natural and drinking waters. Two excellent reviews have been recently published about the latest advances in electrochemical, mainly voltammetric, determination of mercury [6,7]. Electrochemistry offers sensitivity, simplicity, rapid response and inexpensive instrumentation with miniaturization and portable options. A major drawback to be considered results from the difficulty of removing mercury from electrode surface between measurements which leads to memory effect problems [6,7]. However, tedious and time consuming cleaning steps can be avoided with the use of screen-printed electrodes (SPEs), which can be disposable after a single use due to their high cost effectiveness. Several methods based on SPEs have been reported for the determination of mercury in different water samples, including the use of bare gold SPEs [8], and modified SPEs with carbon nanomaterials [9–11], gold films [12,13], gold nanoparticles [14,15], nanohybrid materials [14] and chelating agents [16]. As can be seen in Table 1, the vast majority of the reported works include a preconcentration step over the working electrode (i.e., deposition time) followed by anodic stripping voltammetry. Gold is commonly employed in working electrodes due to its high affinity for mercury which leads to an improvement in its preconcentration. In addition, mercury suffers from a process named underpotential deposition (UPD) on gold electrodes [7]. The presence of gold promotes the adsorption of mercury atoms on the surface once the ionic metal is reduced forming an amalgam (Au–Hg). The formation of this amalgam is energetically more favored with respect to pure mercury and makes the deposition of mercury on gold occur at a more positive potential than in normal conditions. As a consequence, the selectivity of the method is generally improved. In this work, screen-printed carbon electrodes modified with gold nanoparticles (SPCnAuEs) are employed as electrochemical transducers in the detection stage. The use of nanoparticles in electroanalysis is continuously growing due to its numerous advantages, related to the unique properties of nanoparticulate materials [17] (e.g., increasing surface area, enhanced mass transport and improving selectivity, catalytic activity and signal to noise ratio).

Liquid-phase microextraction (LPME) [18] appeared in the latest nineties offering undoubted advantages as miniaturized extraction techniques, such as simplicity, easiness to handle, low sample and solvent consumptions, and an important reduction of residues generated. One of the most popular LPME technique is dispersive liquid–liquid microextraction (DLLME) [19] which has even come to dominate LPME research publications in the recent

years [20]. DLLME is based on the complete dispersion of the small volume of extractant solvent into the sample, normally assisted by a disperser agent. During DLLME, there is a high contact between phases therefore the extraction is really rapid and effective. After the extraction, phases are separated normally by centrifugation and the enriched phase with analyte is analyzed. Numerous modifications of the original DLLME procedure [19] have been reported up to now [21] including the use of new extractant solvents such as ionic liquids (ILs) [22]. Within the use of ILs, a novel methodology called in-situ IL formation dispersive liquid–liquid microextraction (in-situ IL-DLLME) [23,24] has recently been developed. In-situ IL-DLLME is based on the formation of a water-immiscible IL using a metathesis reaction between a water-miscible IL and an ion exchange salt into sample solution. Thereby, the extractant phase is generated in-situ in form of homogeneously dispersed fine drops, the disperser agent is totally avoided and the extraction efficiency generally increases.

Different LPME techniques including single-drop microextraction [25,26], DLLME [27–29], in-situ IL-DLLME [23] and task-specific IL ultrasound-assisted DLLME [30] have been employed for the determination and speciation of mercury in water samples. In these works, bulky and expensive chromatographic systems [25,28,29], capillary electrophoresis [27], UV–vis spectrometry [23], cold vapor [30] and electrothermal vaporization atomic absorption spectrometry [26] were used as separation and detection techniques, respectively.

The approach presented here employs an in-situ IL-DLLME followed by an ultrasound-assisted microvolume back-extraction and SPCnAuEs as electrochemical transducers for the determination of mercury in water samples. This combination exploits the advantages of including a miniaturized sample preparation step with the high sensitivity and specificity that offers the electrochemical determination of mercury using SPCnAuEs. LPME provides a high preconcentration of the analyte and a clean-up step for dirty matrices employing low amounts of sample and chemicals. In addition, considering the low volume of sample needed for analysis with SPEs, they appear as an alternative and perfectly compatible detection methodology after miniaturized extraction techniques, thus avoiding classical and bulky analytical instrumentation [31]. A multivariate optimization strategy has been adopted for the optimization of the sample preparation and the applicability of the method has been tested studying real-world water samples.

Table 1
Comparison of different methods using SPEs for the determination of mercury in water samples.

Electrode	Lineal range	LOD	Real water samples	Comments/analytical technique (deposition time in parentheses)	Ref.
SPGE	5–30 ng mL ⁻¹	1.1 ng mL ⁻¹	Wastewater and rain water	SWASV (60 s)	[8]
SPE/carbon black	2.5×10^{-8} – 1×10^{-7} M (5–20 µg L ⁻¹)	5×10^{-9} M (1 µg L ⁻¹)	Drinking water	Indirect determination by amperometric measurements of thiols	[9]
SPBE/MWCNTs	0.2–40 µg L ⁻¹	0.09 µg L ⁻¹	Tap water	SWASV (180 s)	[10]
Carbon NPs-based SPEs	1–10 µg L ⁻¹	–	Seawater	Heated electrodes/SWASV (120 s)	[11]
SPE/gold film	2–16 µg L ⁻¹	1.5 µg L ⁻¹	Tap water	SWASV (120 s)	[12]
SPE/gold film	0.2–0.8 µg L ⁻¹	0.08 µg L ⁻¹	–	Preconcentration step using magnetic nanoparticles modified with thiols/SWASV (120 s)	[12]
SPCE/gold film	0–100 µg L ⁻¹	0.9 µg L ⁻¹	–	SWASV (120 s)	[13]
SPGOnAuEs	2–50 µg L ⁻¹	1.9 µg L ⁻¹	–	SWASV (200 s)	[14]
SPCNTnAuEs	0.5–50 µg L ⁻¹	0.2 µg L ⁻¹	Tap and river waters	SWASV (200 s)	[14]
SPCnAuEs	5–100 µg L ⁻¹	3.3 µg L ⁻¹	–	SWASV (240 s)	[14]
SPCnAuEs	5–20 ng mL ⁻¹	0.8 ng mL ⁻¹	Rain and river waters, industrial wastewater	SWASV (120 s)	[15]
CTS-SPE	20–80 ng mL ⁻¹	2 ng mL ⁻¹	–	DPASV (30 s)	[16]

SPGE, screen-printed gold electrode; SWASV, square-wave anodic stripping voltammetry; SPBE, screen-printed bismuth electrode; MWCNTs, multi-walled carbon nanotubes; NPs, nanoparticles; SPGOnAuEs, screen-printed graphene oxide/gold nanoparticles electrodes; SPCNTnAuEs, screen-printed carbon nanotubes/gold nanoparticles electrodes; DPASV, differential-pulse anodic stripping voltammetry; CTS-SPE, chitosan-modified screen-printed electrodes.

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