A pocket-size device for monitoring gaseous elemental mercury by passive sampling on a Nano-Au screen-printed electrode and detection by single drop smartphone-controlled voltammetry

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ABSTRACT

We report a novel strategy for decentralized monitoring of gaseous elemental mercury (GEM), Hg(0), in ambient air by a pocket-size low-cost analytical device. The essential components of the system are a gold nanoparticles-modified screen-printed carbon electrode (AuNPs-SPCE) for passive or active sampling by the amalgamation of mercury from the air and a miniaturized potentiostat (pen drive size). The potentiostat was connected to a smartphone for the determination of the amount of amalgamated Hg(0) during sampling, by voltammetry on a single 50 μL drop placed onto the AuNPs-SPCE. The method greatly benefits from the nano structuration of the gold electrode, providing a significant analytical improvement in terms of sensitivity and instrumental simplification, compared with a previously reported method based on a gold-sputtered screen-printed electrode. We report the exploration of the electrode surface by SEM, showing efficient adsorption on the nanoparticles due to the higher surface/volume ratio. Inter-electrode reproducibility using a set of three AuNPs-SPCE exposed to a GEM concentration of 5.78 ng dm^{-3} for sampling times from 0 to 360 min gave an average RSD of 16%. Passive and active sampling gave a similar performance for sampling times higher than 60 min. After 10 min passive sampling, the calibration gave adequate determination coefficients ($R^2 = 0.990$) for the range 5.88–56.39 ng dm^{-3}, with a detection limit of 2.41 ng dm^{-3}. A high sensitivity calibration using 180 min passive sampling for the range 0.23 – 5.69 ng dm^{-3} of GEM gave $R^2 = 0.986$, with a detection limit of 0.24 ng dm^{-3}.

1. Introduction

Mercury (Hg) is one of the most dangerous heavy metals emitted into the atmosphere due to its high toxicity and potential for bio-accumulation in terrestrial and aquatic biosystems [1,2]. Emission sources for mercury include both natural processes (volcanic activity and rock erosion) and anthropogenic sources, mainly from coal combustion in power plants, industrial processes (e.g., cement production, iron and steel production, nonferrous metal smelting, gold production and Chlor-alkali industry), waste disposal and incineration and artisanal gold mining [345]. Gaseous or particle-bound mercury readily spreads in the air, affecting heavily industrialized areas and remote regions far from emission sources [6]. Mercury exists in several physical states and chemical forms depending on temperature and pressure [7]. Among the

different forms of atmospheric mercury are gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM). GEM is the most stable and abundant one (~90%) [8,9], with atmospheric background levels of approximately 0.0015 ng dm^{-3} [8,10]. Approximately 80% of inhaled GEM is retained in the body. Once absorbed, it is distributed throughout the body and can even cross the blood-placenta and blood–brain barriers [11].

Current methodologies developed for the quantification of GEM in ambient air generally include active or passive collection on suitable materials (mainly gold) and Hg detection mainly based on standard techniques such as cold vapour atomic absorption spectrometry (CVAAS) [7,12], cold vapour atomic fluorescence spectrometry (CVAFS) [7,10,12,13] or inductively coupled plasma mass spectrometry (ICPMS) [8,14]. The standardized methods for in-situ GEM surveillance are
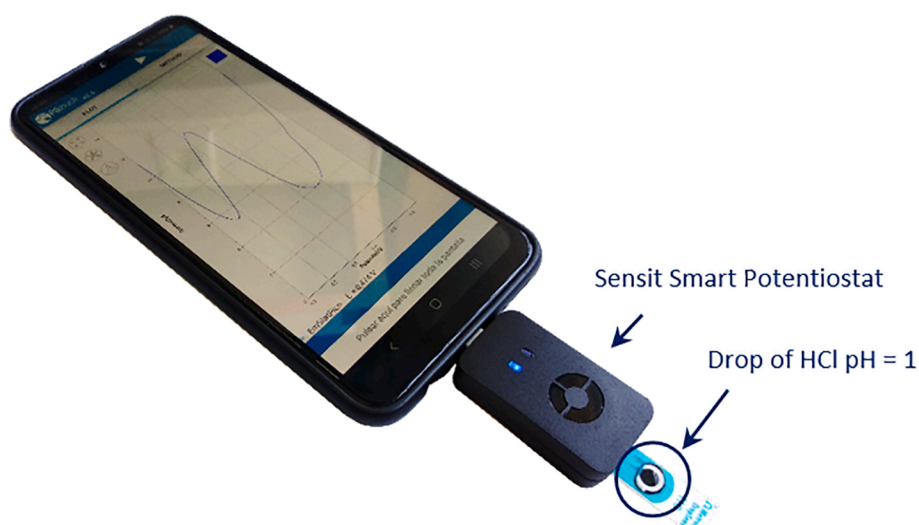
Fig. 1. Image of the portable voltammetric detection system for GEM determination by SWASV after sampling on AuNPs-SPCE.
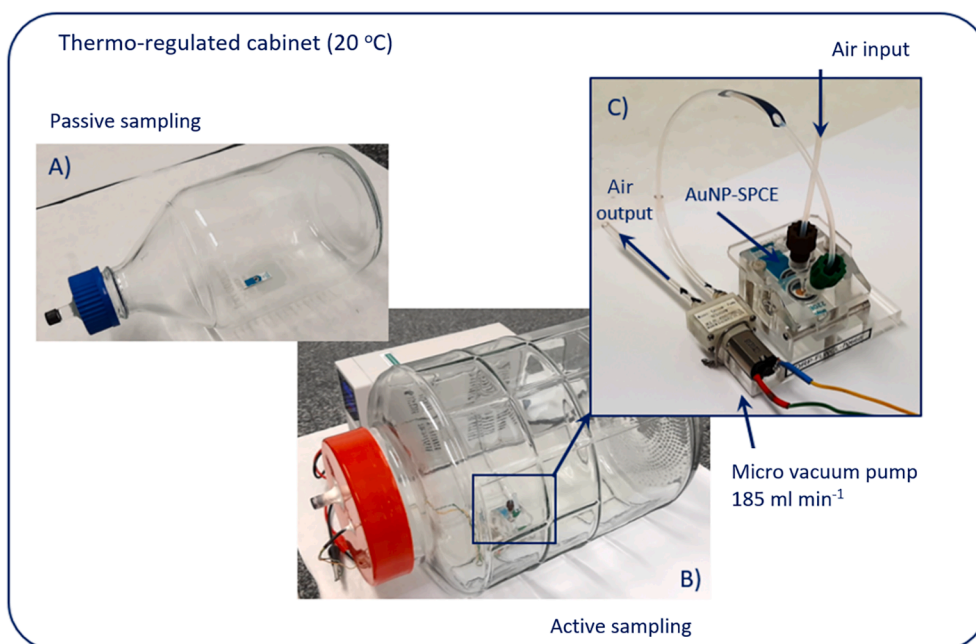

Fig. 2. Homemade system for the sampling of GEM on AuNPs-SPCE A) Passive system. B) Active system. C) Diagram of the flow cell containing AuNPs-SPCE electrode and the micro vacuum pump.

highly sensitive and fully automatic equipment but require high maintenance costs, depends on the power supply and require specialized personnel [9]. Passive sampling systems contribute to the simplification of the equipment. They are designed to uptake GEM by diffusion onto an adsorbent material according to Fick's Law [13,15]. Many adsorbent materials have been used in passive samplers for the GEM sampling, such as carbon treated with sulfur, iodine, chloride, alumina and zeolites [14,15]. However, noble metals, such as gold, is the most commonly used due to their strong chemical affinity for Hg by amalgamation [16]. Nanostructured materials have been tested for GEM sampling. As reported by McLagan et al. [17], nanostructured gold and silver sorbents could mitigate passivation effects due to the sheer abundance of available binding sites. E.g. Macagnano et al. have developed a conductive sensor based on composite nanofibrous electro-spun layers of titania easily decorated with gold nanoparticles (AuNPs) [10]. Santos et al. reported a GEM sampling device based on gold nanoparticles (AuNP)

forming a film on thiol-modified glass slides before CVAAS [8]. Using these materials allows building particular three-dimensional nanostructures with a large surface/volume ratio, resulting in faster and more efficient adsorption [16,18]. Passive samplers are inexpensive, quickly and easily deployed in field conditions. Their independence from power supplies allows them to be installed in remote areas, providing a high sampling spatial resolution [16,19]. However, after sampling, Hg needs to be desorbed and quantified in specialized laboratories using some of the analytical techniques mentioned above [8,20].

Voltammetric techniques are a low-cost alternative for on-site Hg analysis due to their easy handling and portability of the instrumentation [21]. Moreover, the use of low-cost disposable screen-printed electrodes (SPEs) avoids the need for tedious electrode pre-treatment and cleaning steps, facilitating their handling by unskilled personnel [22]. Stripping voltammetric determination of Hg (II) using screen-printed gold electrodes (SPGEs) is widely reported [23–25].
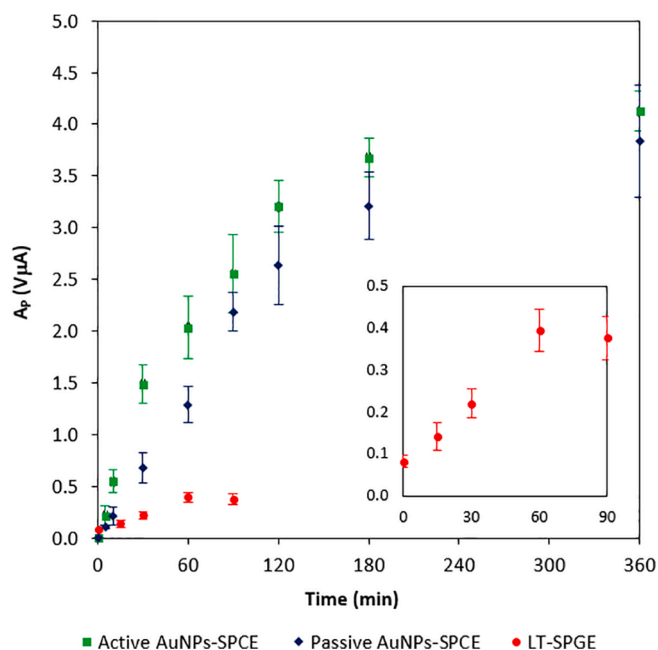
Fig. 3. Peak area (A_p) obtained for AuNPs-SPCE (active and passive) and LT-SPGE exposed to a GEM mass of 12.88 ng for times in the range from 5 to 360 min and from 10 to 90 min, respectively. Step potential 6 mV, amplitude 40 mV, initial potential 0.1 V, final potential 0.65 V, frequency 30 Hz (AuNPs-SPCE) and 10 Hz (LT-SGE).
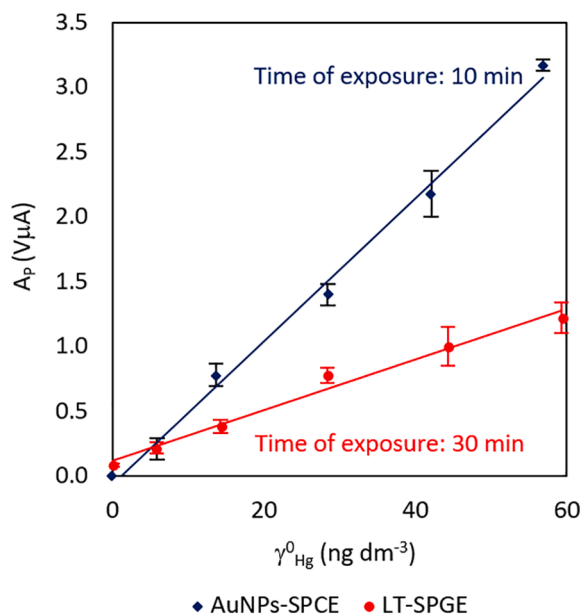
The application of nanomaterials in the electrochemical sensing field has been increasing over the years because they present more attractive physical, chemical and electronic properties than bulk material [21,26,27]. In particular, metallic nanoparticles (NPs) offer a larger active surface, an increased rate of mass transport and a rapid transfer of electrons, increasing the sensitivity of the measurement [21,27,28]. AuNPs have been successfully used for Hg (II) voltammetric detection. They can be directly integrated into printing ink or deposited on the working electrode surface. E.g. Bernalte et al. [28] used commercial AuNPs-SPCE to determine Hg (II) in water samples by SWASV. Sánchez-Calvo et al. [29] developed a methodology to determine Hg(II) in river water using a paper working electrode modified with a combination of carbon nanomaterials and AuNPs deposited on the SPCE platform.

The recent use of electrochemical devices coupled to smartphones has enabled the development of faster, low-cost, compact, miniaturized and portable detection systems [30]. This type of instrumental hybridization has been previously used in different fields, such as food safety [31] and environment [32,33] and point-of-care medical diagnostics [34,35].

The combination of passive sampling with voltammetric detection is a novel strategy for decentralized GEM analysis. Our group has recently reported the only tested method for voltammetric detection of GEM on SPGEs as a passive sampler and voltammetric detector [36]. In this work, we have taken advantage of the benefits of using AuNPs-SPCE to improve sensitivity and achieve a more efficient Hg adsorption in a shorter time. After sampling, the amalgamated Hg was stripped from the AuNPs-SPCE surface by SWASV, operating with only a 50 μL drop of HCl as the electrolyte solution. Using a pen drive size potentiostat controlled from a smartphone completes a pocket-size device that is fully portable and easily deployable in field conditions, without the need for a power source to work, facilitating in-situ GEM analysis.

Fig. 4. Calibration for 5.88 – 56.39 ng dm^{-3} GEM solutions on the AuNPs-SPCE exposed for 10 min and on LT-SPGE exposed for 30 min minutes. Step potential 6 mV, amplitude 40 mV, initial potential 0.1 V, final potential 0.65 V, frequency 30 Hz (AuNPs-SPCE) and 10 Hz (LT-SGE).
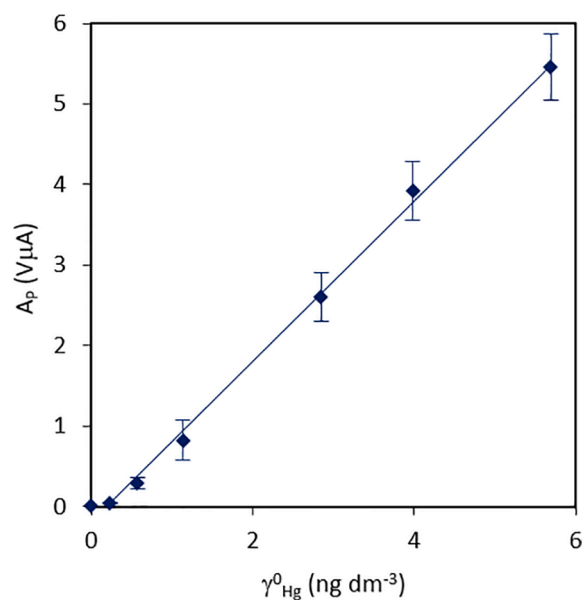

Fig. 5. Calibration for 0.23 to 5.69 ng dm^{-3} GEM solutions on the AuNPs-SPCE exposed for 180 min. Step potential 6 mV, amplitude 40 mV, initial potential 0.1 V, final potential 0.65 V and frequency 30 Hz (AuNPs-SPCE).

Table 1

Analytical data of the calibration curve for the determination of GEM (5.88 – 56.39 ng dm^{-3}) on an AuNPs-SPCE (10 min sampling time) and LT-SPGE (30 min sampling time) [36] in 0.1 M HCl.

Electrode	Slope (b)	Intercept (a)	S_b	S_a	$S_{x/y}$	Analytical resolution (ng dm^{-3})	R^2	Linearity (%)	LOD (ng dm^{-3})
AuNPs-SPCE	0.055	0.055	0.001	0.045	0.120	2.162	0.9897	97.450	2.41
LT-SPGE	0.020	0.120	0.001	0.034	0.092	4.722	0.9573	94.722	5.57

Table 2
Analytical data of the calibration curve for the determination of GEM (0.23–5.69 ng dm^{-3}) on an AuNPs-SPCE in 0.1 M HCl. 180 min sampling time.

Electrode	Slope (b)	Intercept (a)	S_b	S_a	$S_{x/y}$	Analytical resolution (ng dm^{-3})	R^2	Linearity (%)	LOD (ng ·dm^{-3})
AuNPs-SPCE	0.995	−0.176	0.027	0.078	0.250	0.251	0.986	97.270	0.236

2. Materials and methods

2.1. Reagents and solutions

Mercury metal (Panreac, Spain) was used as the source of GEM. HCl (hyperpure grade, Panreac, Spain) was used to prepare a 0.1 M solution for adjusting the samples to pH 1. The material used was washed by immersion in a 10% sub-boiled HNO$_3$ solution for one week. The sub-boiled HNO$_3$ was obtained from a quartz sub-boiling system (Kürner, Rosenheim, Germany). All solutions were prepared from ultra-pure water (18.2 MΩ cm) obtained from a Wasserlab Ultramatic system (Navarra de Tratamiento de Agua S.L., Pamplona, Spain).

2.2. Apparatus

A Sensit Smart potentiostat (Palm Instruments BV, The Netherlands) was used to perform voltammetric measurements. PStouch v.2.86 Android app, provided by PalmSens, controls the instrument. Disposable screen-printed electrode strips AuNPs-SPCEs (ref. DRP-110 GNP) were supplied by Methrom-DropSens (Spain). AuNPs-SPCEs consist of a working electrode (dispersion of gold nanoparticles on carbon of 4 mm of diameter), a counter electrode (made of carbon) and a silver pseudo-reference electrode. The three electrodes are printed on a ceramic surface. Also, screen-printed gold electrodes (sputtered gold) cured at low temperature (LT-SPGEs, ref. 220BT), supplied by Metrohm-DropSens (Spain), were used for comparison. The voltammetric experimental setup is shown in Fig. 1. The surface images of the AuNPs-SPCE were obtained by Scanning Electron Microscope (SEM) using an FE-SEM Quanta 3D FEG (FEI Company, Oregon, EE.UU).

2.3. Sampling of GEM on AuNPs-SPCE

As described in detail in Frutos-Puerto et al. [36], a standard, thermodynamically controlled GEM concentration was generated inside a "bell-jar" device (stock bottle), and working concentrations of GEM were generated by dilution. The relationship between sampling time and the amount of mercury adsorbed over the AuNPs-SPCE surface was studied by taking 1.0 cm^3 from the GEM stock bottle (1.0 cm^3 gas-tight syringe, SGE Analytical Science, Melbourne, Australia) and injected into another bottle containing the electrode (sampling bottle). A general schematic of the GEM sampling procedure is shown in Fig. S1. Two sampling methodologies were tested:

1. *Passive sampling.* The AuNPs-SPCE was placed face-up inside the bottle as described in Frutos-Puerto et al. [36] (Fig. 2A).
2. *Active sampling.* We used a homemade flow system as depicted in Fig. 2B. It consists of a 12.5 L volume hermetically sealed glass bottle containing a flow cell (FLWCL, Methrom-Dropsens, Oviedo, Spain). The air is forced to pass onto the AuNPs-SPCE electrode by a micro vacuum pump model SC3131PM powered by a power supply Peak-Tech model 6226 (Germany) (Fig. 2C), also placed inside the bottle. The pump operation voltage was fixed at 0.9 V to obtain an airflow of 185 mL min^{-1}.

2.4. Voltammetric detection of GEM at AuNPs-SPCE

As shown in Fig. 1, the AuNPs-SPCE was inserted in the potentiostat connection after the GEM sampling step. The electrochemical measurements were carried out by squared wave anodic stripping voltammetry (SWASV) as in [36]. Briefly, a 50 μL drop of 0.1 M HCl solution (pH 1) was pipetted onto the electrodes platform. Then the amalgamated Hg(0) atoms were stripped as Hg(II) to the solution (giving the analytical signal as oxidation current) under the following conditions: 5 s of equilibrium time at 0.1 V followed by a potential sweep between 0.1 and 0.65 V. The step potential was 6 mV, the amplitude 40 mV and the frequency 30 Hz.

3. Results and discussion

3.1. Surface characterization of AuNPs-SPCE

SEM was employed to explore the surface of the working electrode of the commercial AuNPs-SPCE and LT-SPGE, Fig. S2A and Fig. S2B, respectively. LT-SPGE shows a granular and rough structure with a grain diameter ranging from 0.6 to 2.5 μm approximately, allowing efficient superficial interaction between the gold surface and the gaseous mercury. For AuNPs-SPCE, the SEM image shows a base carbon structure containing the homogeneously distributed gold nanoparticles. The nanoparticle density is 133 ± 18 particles μm^2. The high density of gold nanoparticles on the carbon surface of the electrode and its small size may lead to a better performance of the mercury diffusion process, which may allow a better collection of the mercury atoms than in LT-SPGEs.

3.2. Voltammetric response on AuNPs-SPCE and inter-electrode reproducibility

The general voltammetric response of the AuNPs-SPCE to monitor the Hg(0) stripping process is presented in Fig. S3, showing the well-defined peaks of three replicates ($A_P = 0.058$; 0.048; 0.038 VμA). The electrodes were discarded after each measurement. It should be noted that since AuNPs-SPCE is not affected by the presence of dissolved oxygen, it was not necessary to deaireate the samples. The relative standard deviation (RSD) was evaluated using a set of 3 new unexposed AuNPs-SPCE electrodes, giving 6% for the peak heigh (I_P) and a 7% considering the peak area (A_P) (measured to baseline). The A_P RSD of AuNPs-SPCE electrodes (measured in triplicate) after they were exposed for the different times (0 – 360 min range) to 5.78 ng dm^{-3} of GEM was in the range of 7 to 14% (16% average). The reproducibility values were acceptable considering the disposable nature of these low-cost electrodes. The RSD value obtained for I_P was slightly lower than the value obtained for A_P. However, A_P was chosen as the analytical signal because the sensitivity is better as the peak shape tends to widen.

3.3. Influence of sampling time: Active sampling.

The sampling strategy employed in this work can be considered Hg-specific, since Hg is the only gaseous element present in ambient air capable of amalgamating to the gold nanoparticles sampling surface. The influence of sampling time on the GEM mass amalgamated by active sampling on the AuNPs-SPCE was first studied. A fixed concentration of GEM, γ_{Hg}^0, was obtained by taking a volume of 1.0 cm^3 of air from the GEM stock bottle (mass of GEM 12.88 ng) and injecting it into the sampling bottle containing the AuNPs-SPCE. The injected volume corresponds to a GEM concentration of 1.06 ng dm^{-3}. AuNPs-SPCEs were exposed in triplicate for 5, 10, 30, 60, 90, 120, 180 and 360 min. The experimental results of A_p (VμA) vs exposure time are shown in Fig. 3

(green line). For comparison, the red line show the results obtained with LT-SPGE electrodes, taken from [36] after sampling times 10, 30, 60 and 90 min using a GEM concentration of 5.78 ng dm^{-3} (12.88 ng). The mercury adsorption on the electrode surface follows an almost linear behaviour until the sorbent becomes saturated (equilibrium phase). This behaviour was also observed when LT-SPGE is employed as a passive sampler, in that case, also for different γ_{Hg}^0 concentrations [36], according to the expected behaviour of adsorption on a passive sampler of airborne gaseous substances [17].

The results show that values of A_p obtained by sampling-detection on the AuNPs-SPCEs are higher than those obtained for LT-SPGE [36], and the signal differences are more pronounced as exposure time increases. In LT-SPGE, the electrode saturation is reached much earlier (~60 min) than in AuNPs-SPCE (~300 min).

3.4. Influence of sampling time: Passive sampling.

The influence of sampling time on the GEM mass amalgamated by passive sampling on the AuNPs-SPCE was also studied. A fixed concentration of GEM, γ_{Hg}^0, was obtained by taking a volume of 1.0 cm^3 of air from the GEM stock bottle (GEM mass 12.88 ng) and injecting it into the sampling bottle containing the AuNPs-SPCE. The injected volume corresponds to a GEM concentration of 5.78 ng dm^{-3}. As in the active sampling experiments, AuNPs-SPCEs were exposed in triplicate for 5, 10, 30, 60, 90, 120, 180 and 360 min. The experimental results are presented in Fig. 3 (blue line). The behaviour of the voltammetric signals after passive sampling follows a similar trend to the active sampling (green line). Probably, convection enhances mercury's interaction with the electrode surface. However, when the electrode surface starts to be saturated and the GEM mass in the air is depleted, convection does not significantly improve over diffusion because the air flowing through the electrode is very diluted. Moreover, active sampling implies using more sophisticated instrumentation (pump, tubing and flow cell), so we decided to use passive sampling for calibration.

3.5. Calibration of the GEM passive sampling – Voltammetric detection system

According to the results showed in Fig. 3, 10 min of sampling is enough for calibration at the GEM concentration range selected. Therefore, for the calibration of the proposed method (passive sampling with voltammetric detection), increasing volumes of 1.0, 2.4, 5.0, 7.4 and 10 cm^3 air were taken from the GEM stock bottle and injected into the sampling bottle in separate experiments, resulting in final GEM concentrations ranging from 5.88 to 56.39 ng dm^{-3}. Three AuNPs-SPCEs were exposed for 10 min in each experiment (triplicate measurements).

The results, presented in Fig. 4, show the calibration line obtained (blue line). The calibration line obtained by LT-SPGE after 30 min sampling [36] is included for comparison. The results demonstrated that using AuNPs-SPCEs samplers provides a much more efficient sampling and voltammetric measurement of GEM. The detailed calibration parameters are given in Table 1. The detection limit obtained by using the AuNPs-SPCE, 2.41 ng dm^{-3}, would allow assessing some GEM regulatory levels, e.g. the mercury vapour time-weighted average (TWA) published by National Institute for Occupational Safety and Health (NIOSH), as the level to which a worker can be exposed per shift in the worktime without adverse effects. NIOSH has fixed a TWA of 50 ng dm^{-3} for mercury vapour during a 10-hour working day [37]. However, these detection limits are not enough to monitor GEM concentrations in the vicinity of the minimum risk level (0.2 ng dm^{-3}) established by the Agency for Toxic Substances and Disease Registry (ATSDR) [38].

A high sensitivity calibration was performed by applying a longer sampling time. Increasing volumes of 0.1, 0.2, 0.5, 0.7 and 1.0 cm^3 of air were taken from the GEM stock bottle and injected into the sampling bottle in separate experiments, resulting in final GEM concentrations ranging from 0.23 to 5.69 ng dm^{-3}. Three AuNPs-SPCEs were exposed for 180 min in each experiment (triplicate measurements). The calibration line obtained is shown in Fig. 5.

Table 2 summarizes the analytical parameters of the calibration curve in the range from 0.23 to 5.69 ng dm^{-3}. In this case, the detection limit was improved to 0.24 ng dm^{-3}. This value is appropriate for GEM monitoring in workplaces and even to assess GEM in ambient air at levels close to the 1 ng dm^{-3} annual mean guideline established by the World Health Organization (WHO) [39].

Table S1 shows the analytical characteristics obtained in the present work and in similar works described in the literature based on GEM passive sampling. The detection limits obtained in the present work for a sampling time of 10 and 180 min are better than the one reported in the literature by Frutos-Puerto et al. [36], whose value is 5.57 ng dm^{-3} for a sampling time of 30 min. Other works using CVAAS as an analysis technique have reported lower detection limits, e.g. Wängberg et al. [40] found a detection limit of 0.009 ng dm^{-3}, and recently, Snow et al. [19] reported a detection limit of 0.007 ng dm^{-3}. The main disadvantages of these two methods are the longer sampling times and that the analysis technique has high cost, on-site analysis limitations and the need for highly skilled technicians.

4. Conclusions

Gold nanoparticles-modified screen-printed electrodes (AuNPs-SPCE) have proven helpful as inexpensive, selective, sensitive and miniaturized samplers (active or passive) and voltammetric detectors for monitoring gaseous elemental mercury (GEM), with potential applicability to workplace ambient air. After GEM collection, the AuNPs-SPCE was connected to a portable, miniaturized smartphone-controlled potentiostat for SWASV measurement of amalgamated Hg. The electrodes showed an acceptable reproducibility value (16%) considering the disposable nature of these electrodes. There were no significant differences in analytical signal values between the active and passive sampling systems after 60 min of exposure, so the last one is preferred for simplicity. Laboratory calibration with GEM standards showed that the AuNPs-SPCE are suitable for monitoring GEM concentrations with detection limits of 2.41 and 0.24 ng dm^{-3} for exposure times of 10 and 180 min, respectively. These preliminary results are very promising for application in working environments and even in outdoor ambient air, allowing on-site analytical measurements using inexpensive and portable instrumentation after strict control of the influence of the relevant environmental parameters.

CRediT authorship contribution statement

Samuel Frutos-Puerto: Conceptualization, Methodology, Software, Validation, Investigation, Data curation, Writing – review & editing, Visualization. **M.C. Hurtado-Sanchez:** Investigation, Writing – review & editing, Visualization. **Maria Cerrato-Alvarez:** Conceptualization, Methodology, Software, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Conrado Miró-Rodríguez:** Writing – review & editing, Visualization, Supervision. **Eduardo Pinilla-Gil:** Conceptualization, Validation, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2022.107642.

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