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Recent advances in the electrochemical detection of mercury

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ABSTRACT

Electrochemical detection is one of the most important techniques for analysis of mercury. Electrodes with a high preconcentration capacity are employed to achieve a sensitive detection of mercury at concentrations harmless to health. The two most employed approaches in recent years are nanostructured electrodes and DNA-based assays. In the former case, electrodes with gold nanostructures, because their high affinity with mercury, and with carbon nanomaterials are the most reported. In the latter case, the strong bound between Hg(II) and thymine DNA bases allows the preconcentration of very small amounts of mercury. In this review, we critically evaluate the electrochemical detection of mercury reported in several works during the last few years.

KEYWORDS: Mercury, Electrochemistry, Electroanalysis, Nanotechnology, DNA

INTRODUCTION

Mercury is considered by the World Human Organization as one of the top ten chemicals of major public health concern since their exposure, even in small quantities, could cause serious health and environmental issues. Mercury is present naturally but it is also released through human activity, especially by industrial processes. It produces serious toxic effects in the nervous, digestive and immune systems and other parts of the organism. The Environmental Protection Agency (EPA) has established a maximum contaminant level for mercury of 2 µg/L in drinking water[1], similar to the value recommended by the World Human Organization[2]. The EPA has also defined that high mercury-concentrated samples contain more than 260 mg/kg for soil or more than 0.15 mg/L for wastewater[3]. For these reasons, the development of analytical methods for the detection of low concentrations of mercury in different samples is a very important matter, and numerous examples have been described in the literature. Electrochemical techniques are very suitable for the detection of low concentrations of mercury because of their ability to rapidly preconcentrate metals on the electrode surface using methods such as anodic stripping voltammetry. They also present other very interesting features such as the possibility of using modified electrodes and performing the measurements with user-friendly, low-cost and portable instrumentation. The electrochemical detection of mercury is a recurring and widely studied topic and several related reviews have been published in recent years. For instance, Martín-Yerga et al.[4] and Gao et al.[5] published almost simultaneously two reviews on electrochemical/voltammetric determination of mercury in 2013, Zaib et al. reviewed the state of the art on the electrochemical detection of mercury and arsenic in 2015[6], Li et al. published a review about biosensing detection of mercury[7], with some examples of electrochemical detection and other more general reviews[8,9] have also been published. Therefore, this review will focus on the most recent works published in the last two years (2015-2017). Practically in all cases, the authors used voltammetric detection, so the review will be organized in two main sections based on the electrode modification (nanostructured and DNA-based), whose most relevant aspects are shown in **Figure 1** in a summarized way.

[FIGURE 1]

NANOSTRUCTURED ELECTRODES

One approach to achieve a sensitive detection of mercury is using electrode materials capable to preconcentrate the metal from the sample on or near the electrode surface. Electrode materials used for mercury detection usually have a strong affinity for the metal or complexing properties. Gold shows a high affinity towards mercury and can form reduced mercury monolayers at potential higher than its redox potential, by the underpotential deposition process[10]. Therefore, gold-based nanomaterials have been widely used as electrode surfaces for mercury determination. For instance, glassy carbon electrodes (GCE) modified with gold nanoparticles (AuNPs) have been applied to the detection of mercury in fish samples[11]. A similar system but using a Nafion-modified electrode, a cationic exchanger polymer, has also been proposed for mercury detection in river and ground waters[12]. Other types of electrodes have also been modified with gold nanoparticles, such as indium-tin oxide (ITO) semiconductor electrodes, whose performance was compared to GCE[13*]. These authors found a higher sensitivity for ITO electrodes modified with AuNPs by electrostatic adsorption. ITO electrodes were also modified with nanoporous gold fabricated by sequential deposition of silver nanoparticles and AuNPs followed by silver etching with nitric acid (**Figure 2**), generating a porous nanostructure with high surface area[14**]. These devices were applied to different samples such as tap and lake water samples, soil and milk. A nanoporous carbon material modified with AuNPs was also described as electrode surface for the detection of mercury in water samples (tap, lake, groundwater) with high sensitivity[15], suggesting that the nanoporous materials present very interesting characteristics for this application.

[FIGURE 2]

Screen-printed electrodes (SPEs) modified with gold nanoparticles have also been widely used for the detection of mercury in groundwater[16]. Coupled to micro-extraction with ionic liquids, they can detect low concentrations of mercury (even sub-ppb levels) in different types of water[17] or urine[18*]. Gold nanoparticles-modified SPEs have also been used with other nanomaterials such as carbon black that provide an electroactive area superior to conventional graphite and were applied to soil and river water samples[19]. SPEs have ideal properties to be used in environmental detection or as point-of-care devices: they are low-cost, disposable, miniaturized and portable. These properties make them very interesting for a future commercial sensor for the detection of mercury. Paper-based electrodes are also a cost-effective alternative for the detection of numerous species, but they have not been widely used for the electrochemical detection of mercury. Within the last few years, only one publication reported the use of carbon paper electrodes modified with gold and selenium nanoparticles for the detection of both nitrate and mercury in lake water samples[20]. However, this electrode was only able to detect 14 ppb as the lower limit of the linear range, which is above the legal limits established in drinking water.

Carbon nanomaterials have also been employed for the fabrication of electrode surfaces applied to the mercury detection. However, these materials do not show a high affinity for mercury, so other materials with complexing capabilities are needed to achieve a more effective preconcentration. Graphene, as a trendy material, has been used in the last years in different configurations (as reduced or oxidised graphene): with proteins acting as sorbent for solid-phase extraction[21], grafted with carboimidazole[22], with pectin[23] or β-cyclodextrin[24], with PEDOT nanorods[25] or with an ion-imprinted polymer[26]. All these materials allow the complexation of mercury ions on the electrode surface before carrying out the electrochemical detection and were applied to mercury detection in tap, river or waste water samples. Other carbon nanomaterials such as multi[27] and single-walled nanotubes[28] or ultrathin g-C_3N_4 (with -NH and -NH_2 groups)[29] were also reported with similar environmental samples. It is surprising to note that the latter is the

only example of a two-dimensional layered material used for the electrochemical detection of mercury (besides graphene). 2D materials is a hot topic currently and it is expected that more examples of these materials for mercury detection could be described in the coming years.

Electrodes modified with other nanoparticles have also been reported for electrochemical determination of mercury in the last years, but they are not as common as gold or carbon-based nanomaterials. Some examples are: electrodes modified with lead nanoparticles with thiol-functionalized polysiloxane[30], platinum nanoparticles modified with polypyrrole[31], different configurations of nickel nanoparticles with carbon composites[32,33] or bismuth[34] and hydroxyapatite nanoparticles[35]. These nanostructured electrodes were applied to the detection of mercury in several environmental real samples such as tap, river, lake, waste or ground water samples.

DNA-BASED ELECTRODES

The interaction of metals with nucleic acids has been extensively studied and it has been found that strong thymine-Hg(II)-thymine bonds can be formed and stabilize double strand DNA without altering significantly their structure[36]. This bond is much stronger and more specific than other metallic interactions with DNA. DNA strands with a significant number of thymine bases can help to bind a large amount of mercury and preconcentrate on the electrode surfaces modified with this type of biomolecules. Different strategies have been described in recent years for the electrochemical detection of mercury using biosensors or bioassays based on the thymine-Hg-thymine (T-Hg-T) bonds or even using electrodes modified directly with thymine, which are able to detect low amounts of mercury with a limit of detection of 1.5 ng/L and successfully applied to tap water samples[37]. Sandwich-type biosensors have been reported using electrodes modified with a capture probe that binds a reporter probe (or an analogous system) by T-Hg-T bonds. For instance, an assay using a gold nanocarrier functionalized with methyl blue attached to the reporter probe was

described, which is able to achieve a limit of detection of 0.001 aM and a linear range between 1 aM and 100 nM. This sensor was applied to the detection of mercury in tap water, river water and landfill leachate samples. However, alike other cases in this section, the 8 orders of magnitude of the linear range are obtained with small current changes between 4.5 and 9 µA, suggesting a low sensitivity (slope of the calibration plot)[38]. A comparable sandwich biosensor was developed by Qiu et al. and applied to tap water samples[39**]. In this case, a signal probe functionalized with invertase-gold dendrimer nanospheres, which binds to a capture probe from the electrode through T-Hg-T bonds, was used (**Figure 3**). Glucose is generated after the addition of sucrose and it was detected by a commercial glucometer, avoiding the need of a potentiostat and simplifying the measurement system. This approach achieved a linear range from 10 pM to 100 nM with a LOD of 4.2 pM. Although it does not reach a detection limit as low as other cases described in the literature, it is a simpler system with typical analysis times of biosensors (about 2 hours), much lower than other cases described in this section. A different approach using a triple-helix DNA that leaves a free strand on the electrode surface after Hg(II) binding was described and evaluated in drinking and river water samples[40]. Then, a cytosine-rich reporter probe that can form C-Ag-C bonds is hybridized with the free strand and the silver signal can be measured electrochemically. This procedure takes several incubation and dryness steps increasing the analysis time above 3 h. A complex but novel system was described by Huang et al.[41]. After the binding of DNA strands with Hg(II), the formation of a G-quadruplex structure is initiated, which is able to self-assemble hemin to form a catalytic DNAzyme that catalyze the H_2O_2-mediated 3,3',5,5'-tetramethylbenzidine (TMB) oxidation. Furthermore, the detection is amplified by adding the c-myc telomeric oligonucleotide to form a guanine nanowire. Although this system is smart and was applied successfully to tap water samples, it takes several incubation reactions and temperature changes, making the system unsuited for fast and in situ testing as the complete analysis takes about 5 h.

[FIGURE 3]

Several strategies employed an Exonuclease-III assisted target recycling capable of breaking the double strand DNA formed by the T-Hg-T bonds and release some signaling species or some reagent for a subsequent reaction, which could be associated with the concentration of mercury. The recycling reaction can be carried out for several cycles thereby amplifying the signal and being able to obtain very low limits of detection. For instance, Shi et al.[42] used this system for mercury detection in lake and tap water samples with a 3D graphene/gold electrode and a reporter probe attached to gold nanoparticles obtaining an excellent linear range between 0.1 fM and 0.1 µM (although with a slight response change from 4 to 30 µA over the range). In this case, the preparation of the sensor surface and the functional reagents takes several days and complex steps, which decreases the possible applicability of this approach. In another work[43], the authors used a gold electrode modified with vertically-aligned single-walled carbon nanotubes for the detection of a reporter probe released from the recycling reaction. The linear range was also exceptional from 10 fM to 1 µM, but again 8 orders of magnitude with a low signal variation of 15 µA and a long analysis time with several steps and reactions of several hours. A hairpin capture probe which opens its structure in presence of Hg(II) was also used in this kind of recycling approaches and was tested with real samples such as tap and lake waters[44]. High-throughput detection could be performed by using a 96-well plate modified with a capture probe, which binds to a reporter probe functionalized with invertase that transforms sucrose in glucose and it is measured with a commercial glucometer in each well[45*]. The limit of detection in this case was 10^{-17} M, extremely low for mercury, but it takes several long-time reactions with a total time higher than 24 hours. This approach was applied to the detection of mercury in tap, river and sewage water samples.

Electrochemiluminescence (ECL) detection is widely used in DNA assays because it offers excellent detection limits so it is possible to detect DNA without carrying out amplification reactions. Some examples of ECL detection haven been described for the detection of mercury

using DNA-based assays. Cheng et al. used an electrode modified with $[Ru(bpy)_3]^{2+}$ and cyclodextrin that interacts with a DNA probe blocking part of the electrode surface and decreasing the ECL signal[46]. This sensor was tested with plant samples. In presence of Hg(II), the probe binds the metal, and the less-blocked electrode surface produces a larger ECL signal. A similar system but with a signal-off approach was used with luminol as ECL species and streptavidin as surface blocker and applied in river water samples[47]. An ECL system using a paper-based bipolar electrode has also been described for the detection of mercury in drinking and lake water samples[48]. Although the limits of detection are superior to those obtained with amplification or recycling reactions, they are usually in the order of low ppt, well below the legal limits in drinking water.

CONCLUDING REMARKS

The electrochemical determination of mercury has remained a hot topic for many years. Recent advances are mainly focused on the development of electrode surfaces capable of preconcentrating the lowest amounts of mercury in a sample using novel nanostructured materials or the strong interaction between Hg(II) and DNA strands by the formation of a thymine complex. Assays with oligonucleotides generally lead to the detection of extremely low mercury concentrations, but they present some issues inherent to some biomaterials: they only work in certain optimum conditions, being less stable than nanostructured materials, and the assays are complex and take longer times. Therefore, although they have excellent analytical characteristics, they are not ready for real-world use. On the contrary, the main drawback of nanostructured materials is that they do not lead to enough sensitive detection and in most cases the limit of detection is very close to the legal limits. It is a point that should be resolved in the coming years. In this sense, nanostructured electrode surfaces with high electroactive areas and excellent surface properties are well placed to achieve the sensitive detection of these species in a suitable analysis time. Among these materials, the nanoporous materials begin to stand out, and their improvement could be useful for future analytical

applications by fast and simple procedures. Because the high toxicity of mercury and the usefulness of *in situ* determination, low-cost disposable miniaturized devices such as screen-printed electrodes or the novel paper electrodes should play an important role in the coming years to get portable devices that can be used rapidly at the sampling point. Another aspect to consider in the electrochemical determination of mercury is the type of sample analysed. There are numerous examples of mercury determination in aqueous samples, but very few for other such as food or clinical samples. In this regard, the development of electrochemical devices capable of detecting low concentrations of mercury in samples such as blood or hair, useful for monitoring human contamination, would be very interesting and an important advance in this field.

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*45: Although a quite complex biosensing system is employed in this work, an extremely low limit of detection is obtained. Authors could detect mercury in the 10^{-17} M order, which is exceptional and could be useful in circumstances where the detection of very low mercury concentrations were neccesary.

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[47] Z. Guo, B. Chen, Z. Wang, X. Jiang, An electrochemiluminescence biosensor for mercury ion detection based on gamma-polyglutamic acid-graphene-luminol composite and oligonucleotides, Sensors Actuators, B Chem. 209 (2015) 579–585. doi:10.1016/j.snb.2014.12.028.

[48] H. Liu, X. Zhou, J. Shen, D. Xing, Sensitive Detection of Hg 2+ with Switchable Electrochemiluminescence Luminophore and Disposable Bipolar Electrode, ChemElectroChem. (2017). doi:10.1002/celc.201600912.

FIGURES

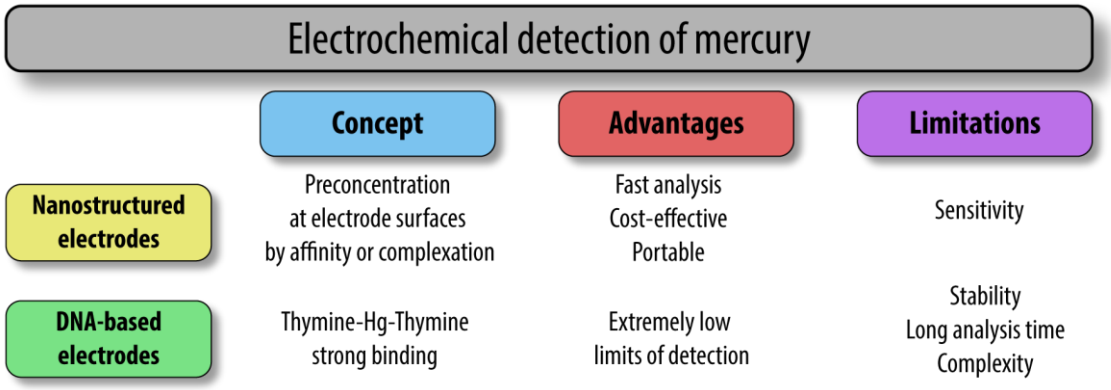

Figure 1. Most relevant aspects of nanostructured and DNA-based electrodes employed for the electrochemical detection of mercury.

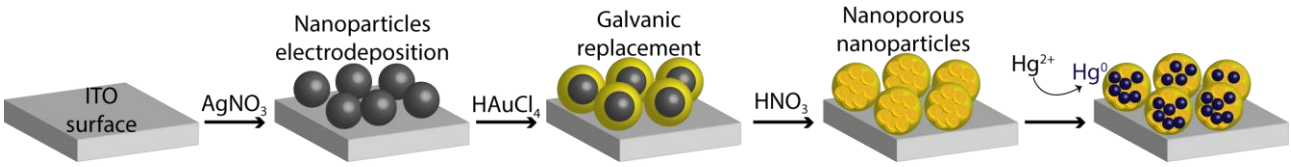

Figure 2. Scheme of the fabrication of nanoporous gold electrodes on ITO surfaces reported in reference 11 for the detection of mercury after preconcentration and stripping.

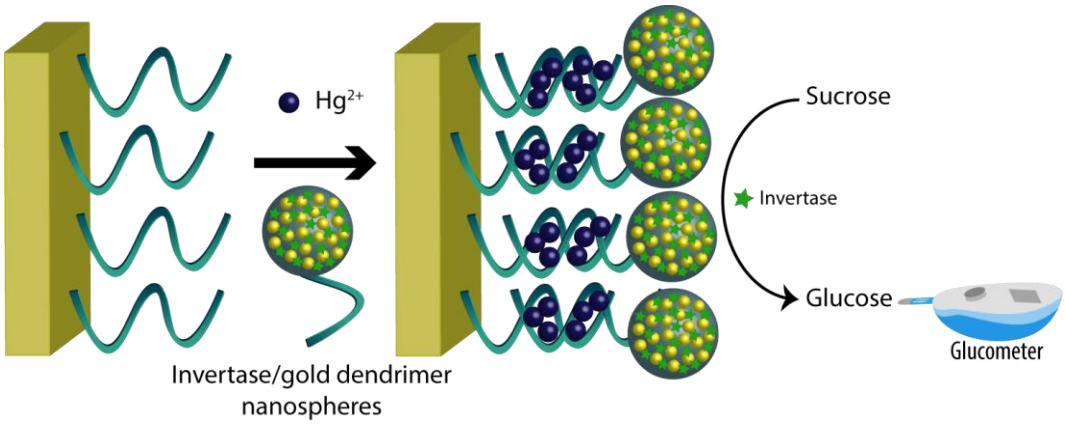

Figure 3. Scheme of the biosensor for mercury detection reported in reference 36. Invertase/gold dendrimer nanospheres bind to the capture probe by the T-Hg-T strong bonds and the generated glucose is detected by a commercial glucometer.