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Review

# Electrochemical determination of mercury: A review

Daniel Martín-Yerga, María Begoña González-García, Agustín Costa-García *

*Nanobioanalysis Group, Department of Physical and Analytical Chemistry, University of Oviedo, Spain*

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ABSTRACT

Mercury is a metal that has been extensively studied, in large part due to its high toxicity. Therefore, mercury levels must be monitored in different sample types using analytical methods. This review summarizes the electrochemical methods that have been used for mercury analysis in a variety of samples. A critical evaluation of the methods and electrode materials employed for mercury analysis is presented according to the following classifications: bare electrodes, chemically modified electrodes and nanostructured electrodes. The advantages and disadvantages of each type of electrode material regarding mercury analysis are also presented.



**Contents**



* Correspondence to: Nanobioanalysis Group, Department of Physical and Analytical Chemistry, University of Oviedo, 8 Julián Clavería St., Oviedo 33006, Spain. Tel.: +34 985103488.
*E-mail address:* costa@uniovi.es (A. Costa-García).

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## 1. Introduction

### 1.1. General aspects

Mercury is a metal with interesting properties, including low thermal conductivity and good electrical conductivity, and has several applications. Due to its low melting point, it is also a liquid metal at room temperature [1], which enables mercury to combine with other metals to form amalgams. Because of these characteristics, mercury has been used in lamps and measuring instruments as well as in the industrial manufacture of chemical compounds. The applications of various mercury compounds include its use as catalysts, fungicides, herbicides, pigments and even drugs [2].

The primary drawback of mercury is its high toxicity. The toxicology of each mercury species (elemental, inorganic, and organic mercury) is different, but every species poses a serious threat to human health and the environment. Mercury accumulates in the liver, brain, and bone tissue of organisms. Mercury can cause kidney failure, nervous-system disorders, intellectual impairment, and even death [3]. Mercury poisoning can occur in many different ways, including through the ingestion of fish that have been exposed to mercury in the environment. Even when an organism is not exposed to high doses of mercury, low doses can accumulate within the body over time, which can result in high metal concentrations and serious health problems.

The sources of mercury pollution are natural or anthropogenic, and the latter being the most relevant with regard to environmental contamination. Important sources of mercury pollution result its applications in fungicides or herbicides in agriculture, its use in the paper or electrochemical industry or disposal as industrial or household waste. However, approximately 25% of mercury pollution results from fuel combustion, and approximately 30% originates from industrial sources [4]. Through these modes of contamination, mercury is introduced into the water cycle. Although the predominant mercury species in water is $Hg^{2+}$, which is very soluble, other mercury species are also present in aqueous media and can be transformed through the actions of microorganisms and oxygen [5].

Mercury analysis is important due to its high toxicity, and water analysis is even more important because of the continuous contamination of natural waters by industrial waste. The level of mercury in water should be lower than a limit set by the authorities. That limit depends on the legislation of each country; for example, the USA Environmental Protection Agency has sets a maximum threshold of 2 $\mu g\, L^{-1}$ in drinking water [6]. This limit is lower in certain cases in the European Union, where a maximum of 1 $\mu g= L^{-1}$ is required by particular EU directives [7]. The World Health Organization recommends that mercury concentrations in drinking water not exceed 2 $\mu g\, L^{-1}$ [8].

With respect to health, high exposures to mercury can be determined by analyzing blood, urine and hair samples. Some mercury species are absorbed by organisms and transferred rapidly to the blood, while other species are excreted by urine. Thus, analyses of these samples should be performed to obtain information regarding exposure. Because mercury is capable of binding to cysteine and is absorbed by hair, the analysis of mercury in hair can be a useful measure of environmental exposure. For the mercury analysis of human samples, it is necessary to consider the half- life of mercury in the sample: from 3 to 30 days in whole blood, from 3 to 20 days in plasma and from 40 to 60 days in urine [9].

Therefore, considering the widespread use of mercury in industry, the high accumulation of mercury in the environment, and the high toxicity of mercury, the ability to routinely analyze different mercury species in various types of samples is critical.

### 1.2. Importance of electrochemical analysis

The most commonly used analytical methods for mercury determination are cold vapor atomic absorption spectroscopy (CVAAS) [10], cold vapor atomic fluorescence spectroscopy (CVAFS) [11] and inductively coupled plasma mass spectrometry (ICP-MS) [12]. Although these methods are well established, they have several significant drawbacks, such as lengthy analysis times and the use of expensive equipment. Furthermore, several complex steps must be performed, and these require specially trained personnel. Researchers continue to search for a method that overcomes these issues and is sensitive enough to replace the more established methods used for routine analysis.

Electrochemical methods are suitable for the routine analysis of mercury. These methods reduce the necessary expense and simplify the process because of the ease with which electrochemical instrumentation can be operated. Numerous electrochemical methods have been developed for mercury determination in different samples, especially water. Most of the reported electrochemical methods are based on the preconcentration of mercury on the working electrode and subsequent stripping, primarily using anodic stripping voltammetry (ASV). In fact, the U.S. Environmental Protection Agency has recommended the use of stripping voltammetry for mercury analysis [13].

The electrochemical analysis of mercury is sensitive, inexpensive, simple, and fast and can be performed with miniaturized, portable instrumentation [14]. However, a significant disadvantage results from memory effects resulting from the difficult removal of mercury from the working electrode. Therefore, reusing the electrode remains an important challenge. The goal is to obtain a working electrode that fulfills the ideal characteristics for routine analysis in laboratories accredited by the authorities.

### 1.3. Scope of this review

This review provides an overview of recently reported, novel electrode materials and procedures for the electrochemical analysis of mercury. The review focuses particularly on recent work in the field, and in particular, reports published since 2000. Voltammetric methods are emphasized because these are the most commonly reported, but some potentiometric methods are also reviewed. A related review on the subject by Clevenger et al. was previously published [15]. Therefore, several recent examples of electrode materials and the most important characteristics of the presented methods can be easily found.

The present review is organized by sections based on the different working electrode materials employed in the electrochemical mercury analyses. First, a review of methodologies using unmodified bare electrodes, especially those based on carbon and gold (Section 2), is provided. Then, studies using electrodes modified with chemical or biochemical species, chemically modified electrodes (CMEs), are presented (Section 3). Finally, the latest trend in electrode-surface development for mercury analysis, nanostructured electrodes, is introduced (Section 4). This organization is intended to provide an overview of how the development of new materials can improve the electrochemical analysis of mercury.

The text is accompanied by several tables highlighting pertinent information from the published works types of electrodes used, the analytes detected, the samples in which the analytes have been measured and analytical characteristics, such as linear ranges and limits of detection (LOD). Thus, with the help of these tables, the different methods can be compared.

Most of the works considered herein focus on the analysis of Hg(II) in aqueous media; however, studies involving different mercury species and samples (urine, soils) are also included.

## 2. Bare electrodes

Although the most commonly used methodology for electrochemical analyses of mercury involves modification of the electrodes with different substances, it is possible to successfully analyze mercury using bare electrodes composed of specific materials.

### 2.1. Carbon electrodes

In recent years, carbon has been the most typical material used to manufacture electrodes for electroanalysis, primarily because of the low cost and low chemical reactivity of this material. However, bare carbon electrodes have many properties that interfere with satisfactory mercury determination. The sensitivity of unmodified carbon electrodes is generally low, and the LODs and/or preconcentration times are not acceptable for routine analyses. Although many studies employing carbon electrodes were published before 2000, several studies have been reported recently. For instance, Muntyanu et al. employed a carbon fiber microelectrode to measure Hg(II). The addition of Au(III) to the solution, which is necessary to increase sensitivity and lower LODs, achieved detection of 1 μg/L [16]. With the same electrode, Afonso et al. were able to determine methylmercury in a chloride media employing fast scan voltammetry [17]. In other work, LODs as low as 0.1 ng/L have been obtained using a glassy-carbon macroelectrode process vessel as a working electrode with a deposition time of 10 min [18].

### 2.2. Gold electrodes

Gold has interesting properties, including high ductility and malleability, low reactivity to typical reagents and high electrical conductivity. In addition, gold can serve as a catalyst for chemical and electrochemical reactions. These features are responsible for the wide use of gold in electrochemical analyses. The main disadvantage of gold is its cost compared to other materials, such as carbon.

Because it exhibits a high affinity for mercury, thereby improving the effects of preconcentration, gold is an excellent material for a working electrode in electrochemical mercury analysis. In addition, metals such as mercury, arsenic or lead undergo a process called underpotential deposition (UPD) on gold electrodes [19]. UPD occurs as a result of the strong interaction between the metal and the gold electrode after the reduction of the ionic metal and results in the formation of an adsorbed layer. Because of this strong interaction and the resulting formation of the adsorbed layer, the reduction of the metal to produce the UPD occurs at a potential that is more positive than that for normal deposition. Because the first UPD process generates an adsorbed monolayer, this process only occurs at low metal concentrations, which makes it useful for achieving higher sensitivities for the electrochemical method . Moreover, because the reduction potential of the metal is shifted in the positive direction, the selectivity of the method is generally improved [20]. For these reasons, gold has been widely employed as a working electrode for electrochemical analysis.

The biggest concerns regarding the use of gold electrodes for mercury analysis pertain to the structural changes that are caused by the amalgam of the two metals after stripping [21,22]. Some authors have been unable to completely strip the mercury; thus, the electrode could not return to the original conditions until a cleaning step was preformed [23,24]. Other authors have reported that this situation is averted when only a few atoms of mercury are deposited on the gold electrode [25].

#### 2.2.1. Bare gold electrodes

Several studies employing gold rotating-disc electrodes for Hg(II) analysis in different samples have been published. For example, Bonfil et al. employed these electrodes to measure Hg(II) in urine after activating the electrode surface between measurements, possibly to remove deposited mercury. This activation improved the analytical signal, enabling detection levels as low as 0.04 μg/L [26]. This electrode was also used to analyze Hg(II) in seawater using potentiometric stripping. The study compared a rotating gold electrode with a static one and obtained higher sensitivity with the rotating electrode. This case also required electrochemical pretreatment to obtain reproducible signals [27]. Giacomino et al. studied different parameters and electrochemical techniques using gold rotating-disc electrodes for Hg(II) analysis in water and obtained the best results using square-wave voltammetry and a diluted HCl electrolytic media [28].

A 5-μm diameter gold microwire electrode was used to analyze Hg(II) in seawater. Chloride adsorption on the electrode surface worsened the analytical signal. This issue was fixed by applying a negative potential to desorb these anions, which improved the reproducibility of the analytical signal. Analysis of the used electrode by scanning electron microscopy (SEM) revealed degradation of the surface with continued use, and this degradation was likely due to stripping of the deposited mercury [29]. This type of electrode was employed for simultaneous quantification of $Zn^{2+}$, $Cu^{2+}$, $Hg^{2+}$, and $Pb^{2+}$ in different water samples [30] and was used in a remote system for in-situ analysis [24]. Using a heated gold microwire electrode (at 60 °C) significantly improves the preconcentration of mercury without requiring stirring [31]. Modification of the gold microwire electrode with mercaptoacetic acid prevented the formation of calomel in seawater, achieving the complete removal of mercury after every sweep [32].

Several gold microelectrode arrays were also employed for Hg(II) determination in different water samples, but the LOD of these electrodes (1 μg/L) is higher than that in most of the studies employing rotating gold or gold microwire electrodes [33,34].

Screen-printed gold electrodes (SPAuE) have also been used for the electrochemical determination of mercury. Commercially available, disposable screen-printed electrodes made with gold ink were used to analyze Hg(II) in water using a convective cell. The LOD obtained was 1.1 μg/L, and the low end of the linear range was 5 μg/L. Activation of the electrode was critical for obtaining an analytical signal demonstrating good behavior and shape [35].

As shown in Table 1, bare gold electrodes show significantly improved LODs compared to bare carbon electrodes, confirming the high interaction and improved preconcentration of mercury on gold.

#### 2.2.2. Gold film electrodes

Glassy carbon electrodes (GCE) modified with gold films were used for the analysis of total mercury in table salt samples. The high salt concentration in these samples hinders the stripping step, but this problem is solved by changing the medium after the deposition step; thus, stripping is performed in a medium with a lower salt concentration. This methodology can be useful when the sample matrix is complex and interferes with electrochemical measurements [36]. In related work, the thickness of the gold film was observed to affect the analytical signal. Thinner films were better able to detect low concentrations, and thicker films were better for measuring higher concentrations of mercury [37].

Interestingly, gold thin-film electrodes made from compact discs were employed successfully for mercury analysis. Stripping potentiometry using a polypropylene electrochemical cell showed good results for urine samples [38]. A similar electrode was used by Radulescu et al. for mercury determination in fish after a digestion step [39]. This type of electrode was also employed to determine total mercury in certified ground water samples, achieving a LOD of 0.008 μg/L [40], and in samples obtained from shrimp [41]. All of

**Table 1**
Analytical characteristics of bare electrodes published in the literature.

| Ref. | Electrode | Analyte | Sample | Linear range | LOD | Information |
|---|---|---|---|---|---|---|
| *Bare carbon electrodes* | | | | | | |
| [16] | Carbon fiber | $Hg^{2+}$ | Natural waters | 1–20 μg/L | *nda*[a] | DPASV (3.5 min deposition)<br>In presence of Au(III) |
| [17] | Carbon fiber | $CH_3Hg^+$ | Distilled water | 15–600 mg/L | *nda* | Fast scan voltammetry (10 V/s) |
| [18] | Glassy carbon vessel macroelectrode | $Hg^{2+}$ | Natural waters | 5–30 ng/L | 0.1 ng/L | PSA (10 min deposition) |
| *Bare gold electrodes* | | | | | | |
| [24] | Gold wire electrode | $Hg^{2+}$ | Natural waters | *nda* | 0.3 μg/L | PSA (5 min deposition)<br>150 Measurements (5% RSD) |
| [26] | Rotating GDE | $Hg^{2+}$ | Urine | 0.04–80.0 μg/L | 0.01 μg/L | SWASV (2 min deposition) |
| [27] | Rotating GDE | $Hg^{2+}$ | Seawater | *nda* | 0.005 μg/L | PSA (10 min deposition) |
| [28] | GDE | $Hg^{2+}$ | Distilled water | 1.0–5.0 μg/L | 0.40 μg/L | SWASV (2 min deposition) |
| [29] | Gold microwire | $Hg^{2+}$ | Seawater | *nda* | 0.0012 μg/L | SWASV (5 min deposition) |
| [30] | Vibrating gold microwire | $Hg^{2+}$ | Tap, river and sea waters | 0.2–20 μg/L | 0.2 μg/L | DPASV (30 s deposition) |
| [31] | Hot gold microwire | $Hg^{2+}$ | River water | 0.5–25 μg/L | 0.08 μg/L | PSA (2 min deposition) |
| [32] | Gold microwire/mercaptoacetic acid | $Hg^{2+}$ | Seawater | 0.4–7.5 μg/L | 0.2 μg/L | DPASV (3 min deposition) |
| [33] | Gold microelectrode array | $Hg^{2+}$ | Distilled water | 1.0–4.0 μg/L | 1 μg/L | SWASV (16 min deposition) |
| [34] | Gold microelectrode array | $Hg^{2+}$ | River water | 10–200 μg/L | *nda* | LSASV (30 s deposition) |
| [35] | SPAuE | Hg(II) | SRM and waste waters | 5.0–30.0 μg/L | 1.1 μg/L | SWASV (1 min deposition) |
| [36] | GCE/gold film | Total Hg | Table salt | 1.0–3.0 μg/L | 0.17 μg/L | DPASV (1 min deposition)<br>Medium exchange after deposition |
| [37] | GCE/gold film | Hg(II) | Hemodialysis concentrates | 0.5–2.5 μg/L | 0.12 μg/L | DPASV (1 min deposition) |
| [38] | Gold film from CDs | Total Hg | Urine | *nda* | *nda* | PSA (5 min deposition) |
| [39] | Gold film from CDs | Total Hg | Fish | 5–100 μg/L | 0.30 μg/L | PSA (10 min deposition) |
| [40] | Gold film from CDs | $Hg^{2+}$<br>$CH_3Hg^+$ | SRM groundwater | 0.02–200 μg/L | 0.008 μg/L | PSA<br>$CH_3Hg^+$ determination after UV degradation |
| [41] | Gold film from CDs | Total Hg | Fish and shrimps | *nda* | 5 ng/g | PSA (5 min deposition) |
| [42] | SPCE/gold film | $Hg^{2+}$ | Distilled water | 2.5–100 μg/L | 0.9 μg/L | SWASV (2 min deposition) |
| [43] | SPCE/gold film | Total Hg | Fish | 1–1000 μg/L | 0.9 μg/L | SWASV (2 min deposition) |
| [44] | SPCE/gold film | $Hg^{2+}$ | Tap water | 0.2–0.8 μg/L | 0.08 μg/L | SWASV (2 min deposition)<br>Preconcentration with magnetic particles |
| *Other bare electrodes* | | | | | | |
| [46] | BDD | $Hg^{2+}$ | Distilled water | 2–10 μg/L | *nda* | DPASV (2 min deposition) |
| [47] | Rotating BDD | $Hg^{2+}$ | Gas samples from a combustion system | 0.005–50 μg/L | 0.070 μg/L | DPASV (6 min deposition) |
| [48] | Iridium microdisks | $Hg^{2+}$ | Drinking water | 1–9 μg/L | 0.6 μg/L | SWASV (6 min deposition) |
| [49] | Gold-plated iridium nano-band array ultramicroelectrode | $Hg^{2+}$ | Soil | 10–180 μg/L | 0.5 μg/L | SWASV (4 min deposition) |
| [50] | SPAgE | $Hg^{2+}$ | Cosmetics | 500–4500 μg/L | 98 μg/L | Indirect determination of $Hg^{2+}$ by measuring the oxidation of $I^-$ |
| [51] | CPE/Bi film | $Hg^{2+}$ | Distilled water | 4–18 μg/L | 0.50 μg/L | SWASV (2 min deposition) |
| [52] | Pt/Sb film | $Hg^{2+}$ | Water sample | 2.5–80 μg/L | 0.39 μg/L | SWASV (2 min deposition) |

[a] *nda*: no data available.

these methods were performed using PSA as the electrochemical technique.

Screen-printed carbon electrodes (SPCEs) modified with gold films have also been employed. These methods require an activation step to obtain a stable baseline and have achieved LODs as low as 0.9 μg/L [42]. Additionally, this sensor has been used to determine the Hg(II) in fish samples after a digestion step [43]. Mandil et al. employed SPCEs modified with gold films to analyze $Hg^{2+}$ ions in tap water; notably, their methodology required a preconcentration step using magnetic nanoparticles ($Fe_3O_4$) modified with thiols. The preconcentration step improved the LOD by more than one order of magnitude, obtaining an optimal LOD of 0.08 μg/L [44].

Although mercury analysis using gold or gold-film electrodes may be the simplest method, improvements are necessary to enable the use of these types of electrodes for routine mercury analysis. The most important challenges pertain to the difficulty of cleaning the surfaces of conventional electrodes to enable their reuse. Unless the electrodes are activated, it is difficult to obtain stable baselines to enable straightforward determination of the analytical signals for disposable screen-printed working electrodes. Given the analytical characteristics presented in Table 1, it is not possible to determine whether bare gold electrodes and gold-film electrodes exhibit significant differences in analytical performance. However, these electrodes have been tested successfully with different sample types and used for the detection of different mercury species. Considering the sensitivity and selectivity afforded by UPD, the UPD of mercury on gold is very useful for the electrochemical analysis of mercury. Finally, the presence of a low and constant chloride concentration in the solution appears to improve the analytical signal when gold electrodes are used, although high concentrations of these ions may be detrimental to electrochemical measurements.

### 2.2.3. Other materials

Although they are not as common in the literature as carbon or gold, other bare electrodes have also been used for the electrochemical analysis of mercury.

Boron-doped diamond (BDD) electrodes have been used to obtain a higher sensitivity and lower background current compared to electrochemical techniques that employ GCEs [45]. Although nitrate and chloride ions have been shown to positively affect

analytical signals obtained with BDD electrodes, the formation of calomel on the electrode surface may be detrimental, and an LOD of only 2 μg/L has been obtained [46]. When a small concentration of ionic gold is added to the solution, calomel does not form on the electrode surface, and because mercury is reduced more easily, the analytical signal is shifted to a more positive potential. With this methodology, a Hg(II) concentration as low as 0.05 μg/L of has been measured. Several gold and mercury deposition processes may be occurring, which is most likely why the width of the analytical signal increases [47]. These two methods demonstrate the significant improvement that can be obtained even when the same electrode is employed.

Iridium microarray electrodes have also been used for Hg(II) determination, although the presence of $Cl^-$ ions in the electrolytic medium has a negative effect on the electrode and, therefore, on the sensitivity (LOD of 0.6 μg/L) and reproducibility [48]. Other work with iridium nano-band arrays plated with gold films has demonstrated their applicability in chloride media for the determination of mercury in several types of samples; however, lower sensitivity is obtained with this method [49].

The oxidation of $I^-$ ions at screen-printed silver electrodes (SPAgE) has been used for the indirect determination of $Hg^{2+}$ ions, particularly in the analysis of cosmetic samples [50] In this case, the analytical signal decreases as the mercury concentration increases. This methodology has demonstrated a high LOD (98 μg/L) and is not useful for routine analyses.

A bismuth-film electrode was employed for the simultaneous determination of $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ in tap water. The authors claim to have been able to analyze metals that are re-oxidized at potentials more negative and more positive than Bi using in-situ Bi-deposited films [51]. Glassy carbon electrodes have been modified similarly with antimony films [52]. Although the LODs of both methods appear to be similar (0.50 and 0.39 μg/L, respectively) when the same deposition time is used, the antimony-film electrodes exhibit excellent performance in more acidic media and demonstrate superior performance for mercury determination compared to bismuth-film electrodes.

For each of these materials, the interaction between mercury and the electrode surface is not as intense as it is with gold; therefore, less preconcentration is typically required. The LODs and linear ranges obtained using these electrodes (Table 1) demonstrate that, at least under the published conditions, these electrodes are not appropriate for routine analysis. Furthermore, platinum and diamond have the same high-cost drawback as gold; they are all expensive.

## 3. Chemically modified electrodes

Compared to bare electrodes, electrodes modified with chemical and biochemical compounds may possess advantages, such as improved sensitivity and selectivity, when used for the electrochemical determination of several analytes. Chemically modified electrodes (CME) have been used to analyze heavy metals at trace levels. These methods are based on the interaction of heavy metals with a functional group of the compound used to modify the electrode. Normally, this interaction is selective or only occurs with very specific metals, enabling discrimination depending on the potential employed for electrochemical measurements.

Some of the compounds used to modify electrodes are polymers, complexing agents, DNA and ion-imprinted polymers (IIP).

### 3.1. Polymer-modified electrodes

Conductive polymers are one of the materials most commonly used to modify electrode surfaces. These polymers typically contain groups that bind selectively to mercury or that can function as ion exchangers. Due to their polymeric character, they have a high number of reactive sites, allowing analyte preconcentration on the electrode surface. These polymers typically exhibit good electrical conductivity or electrocatalytic ability. Among the most typical strategies for modifying electrodes are 1) electropolymerization of the monomer onto the working electrode and 2) simple adsorption of the polymer onto the electrode surface. Different coatings are generated using different conditions, which can lead to analytical characteristics suitable for each specific application. Several polymers have been used with a diverse selection of working electrodes for electrochemical determination of mercury.

Some of the polymers used for this purpose are functionalized with groups that are able to bind Hg(II), either in cationic form ($Hg^{2+}$) or anionic form, in the presence of chlorides ($HgCl_3^-$ and $HgCl_3^{2-}$). The ability of these polymers to bind Hg(II) enables its preconcentration at the electrode surface and thus more sensitive detection. A GCE has been modified with an ethylenediamine tetra-N-(3-pyrrole-1-yl)-propylacetamide polymer with several pyrrole rings that confer a high capacity to bind Hg(II) and, to a lesser extent, other metals, such as Cu(II), Pb(II) and Cd(II). Preconcentration is performed at open circuit for the determination of Hg(II) and Cu(II) in water samples [53]. A film of methyl-red electropolymerized on GCE has also been employed for the Hg(II) analysis of lake water. Hg(II) is adsorbed onto the methyl-red film and is reduced at −1.2 V for 10 min. This polymer-modified electrode was shown to have the lowest LOD reported (0.009 μg/L) [54]. The resulting improvement in sensitivity may be due to high diffusion of chemical species to the polymeric film, which provides a high preconcentration effect. Rahman et al. have employed a GCE modified with a conductive polymer and EDTA and have shown that both the polymer and the EDTA can complex with mercury ions, making possible the sensitive determination of $Hg^{2+}$ (LOD of 0.1 μg/L) [55]. Furthermore, platinum electrodes have been modified with poly(3-hexylthiophene) for the determination of Hg(II) in fish samples [56], and SPCEs have also been modified with conductive polymers for Hg(II) determination. Electropolymerization of SPCEs has been obtained via cyclic voltammetry of aniline and 2,2′-dithioaniline, enabling the preconcentration of Hg(II) on the electrode surface, which can be measured electrochemically by ASV. However, the LOD obtained by this method is not useful for real water samples [57].

Other polymers that can operate as ion-exchangers, either cationic or anionic, are able to preconcentrate Hg(II). The structures of these polymers have an ion with a labile bond that may be exchanged with a Hg(II) ion, thereby forming a stronger bond and achieving Hg(II) preconcentration on the modified electrode surface. Electropolymerized polyviologen has been used to determine Hg(II) in tap water and seawater. After modifying a GCE with polyviologen, the electrode is able to exchange mercuric anions, such as $(HgCl_3)^-$ and $(HgCl_4)^{2-}$, complexes that are formed in chloride-containing media. This capacity to exchange anions improves the preconcentration and thus the sensitivity of the method and resulted in a LOD of 0.3 μg/L. Regeneration of the electrode was accomplished using a solution containing a high concentration of chloride ions [58].

Sol–gel electrodes constitute another type of polymer-based electrodes. These electrodes are made of a mixture of gel and carbon paste. Gold electrodes have been modified with functionalized sol–gel for mercury analysis [59]. A sol–gel carbon-composite electrode was modified with poly(vinylsulfonic acid) (PVSA), an anion exchanger that is able to preconcentrate mercuric anions onto the electrode surface. The preconcentration step is performed at open circuit. Regeneration of the electrode surface is obtained using a 3 M NaCl solution. The use of PVSA is crucial for the sensitive analysis of mercury because the unmodified electrode response is very low [60]. A type of sol–gel electrodes are the

sonogel electrodes, which are prepared using a high-energy ultrasonic bath composed of the mixture in which the electrode is fabricated. This method involves the generation of a gel with special features like high density, fine texture and homogenous structure. In one example from the literature, a sonogel electrode for mercury analysis was modified with electropolymerized 3-methylthiopene. This polymer can accumulate Hg(II) on the electrode surface at open circuit, after which electrochemical analysis is performed using DPASV. Several modifiers have been employed with the sonogel electrode, and 3-methylthiopene exhibits the best sensitivity [61]. However, these sol–gel electrodes exhibit higher LODs compared to other polymeric electrodes used for mercury analysis.

### 3.2. Electrodes modified with complexing agents

Other materials widely used for the modification of electrodes for the determination of heavy metals, particularly mercury, are compounds capable of forming complexes with metal ions. The species possessing this property are diverse and usually contain a functional group that participates in the complexation.

GCEs modified with monolayers of p-tert-butylthiacalix[4] arene (TCA) have also been used for Hg(II) determination in tap, lake and river water samples. Compared to bare GCE or GCE modified with a direct coating, electrodes modified with TCA monolayers demonstrate improved sensitivity and are able to detect 0.1 μg/L of Hg(II). This improvement in sensitivity may be due to a higher preconcentration of mercury ions in the monolayer, resulting in a higher stripping signal [62]. Manganese phthalocyanine (MnPht), a macrocyclic compound demonstrating high thermal and chemical stabilities, has been used to modify GCEs for the selective analysis of $Hg^{2+}$ cations. Although MnPht also binds $Ag^{+}$, the potential used for Hg(II) determinations enables high selectivity [63]. Additionally, GCEs have been modified with other macrocyclic compounds containing complexing groups, such as calyx[4]arene containing benzothiazole [64] and dithia-podands [65]. However, given the analytical performance reported by these studies (Table 2), modifying electrodes with macrocyclics does not appear to be a good methodology for mercury analysis because the sensitivity is not suitable for routine analysis.

Mercury analysis has also been performed using more complex systems, such as carbon ionic-liquid electrodes (CILEs) modified with aminoacids and gold, nanoparticles (AuNPs). In this case, fabrication begins by mixing a graphite paste, an ionic liquid and AuNPs, after which the electrode surface is modified with the aminoacid of interest. Aminoacid carboxyl groups are able to complex $Hg^{2+}$ ions. Three thiolated aminoacids, cysteine, glutathione and homocysteine, were used because they can easily attach to gold nanoparticles. The best results for $Hg^{2+}$ analysis in tap and waste water samples were obtained using cysteine and showed an LOD of 0.46 μg/L [66].

Carbon paste electrodes (CPEs) have been modified with several species that are able to complex and preconcentrate Hg(II) on the electrode surface. This is the case with nitro benzoyl diphenylmethylenphosphorane (N-BDMP). Because it also forms Cd(II) complexes, N-BDMP has been used to simultaneously determine Cd(II) and Hg(II) in different samples [67]. Cyclodextrins are another species that has been mixed into carbon paste for the purpose of mercury determination [68].

Different silica species functionalized with complexing groups have been employed for the modification of glassy carbon and carbon paste electrodes. Examples are mesoporous silica [69] or silica thin films [70] functionalized with thiol groups, which are able to preconcentrate mercury ions. In addition, mercury analysis has reportedly been performed using silica nanoparticles with a Schiff base [71] or mesostructured silica nanoparticles and a derivative of 5-mercapto-1-methyltetrazole, a complexing agent for $Hg^{2+}$ ions. Silica nanoparticles improve the $Hg^{2+}$ preconcentration, although the 100-mL sample size used is a disadvantage relative to other published methods [72].

Gold electrodes modified with complexing agents have also been used for mercury analysis. These include a gold disk electrode modified with 2-mercaptobenzimidazole [73], gold micro-/nanopore arrays modified with 2-mercaptobenzothiazole [74], and a gold-film electrode modified with Nafion and DTPA for the determination of methylmercury [75]. A gold nanopore array has demonstrated particularly good analytical performance, obtaining a low LOD (0.004 μg/L) and a linear range over two orders of magnitude. Due to the high porosity of the electrode structure, the electrode has a larger area, which facilitates mercury preconcentration.

Other electrodes employed for mercury determination are graphite tube electrodes modified with 2-mercaptobenzothiazole [76] or 2-mercaptobenzoxazole [77]. This type of electrode has been used in a flow system (for continuous-flow and flow-injection analysis) for the continuous analysis of $Hg^{2+}$ ions. Electrode regeneration was obtained by applying a positive potential for 60 s in a washing buffer (to eliminate mercury from the electrode). Although this system was successfully used for $Hg^{2+}$ determination, the LOD obtained is not sufficient for routine analysis, and the time required for preconcentration is high (600 s).

Disposable thick-film graphite electrodes modified with Au(III)/pyrrolidinedithiocarbamate (PDC) have also been used for mercury analysis. PDC works as a complexing agent for mercury ions, and Au(III) may be able to form a gold film in-situ after the electrochemical reduction step, thus combining the best features of each system to achieve a high sensitivity and a low LOD (0.005 μg/L) [78]. As previously discussed, in the presence of chloride ions, Hg(II) forms anionic complexes that are able to bind to the protonated amino groups of chitosan. This feature has been used to preconcentrate and electrochemically detect Hg(II) with screen-printed carbon electrodes modified with chitosan [79]. In addition, $Hg^{2+}$ detection has been obtained using SPCEs modified with a chelating resin containing dithiocarbamate groups [80].

Differences in LODs and in linear ranges for electrodes modified with complexing agents (Table 2) depend mainly on the compounds used as modifiers and the accumulation time. Published articles report both low and high LODs for GCEs, SPCEs and other electrodes. A study that compares these electrodes when the same modifier and similar conditions are employed would be interesting.

### 3.3. DNA-modified electrodes

Another material employed in chemically modified electrodes for the selective determination of $Hg^{2+}$ ions is DNA. DNA strands have different structures depending on their compositions, enabling the use of DNA for the selective detection of several analytes. $Hg^{2+}$ binds selectively to DNA strands whose structures contain several thymines by binding to T–T mismatches, thus stabilizing hybridization of the double strand. Strands that bind selectively to mercury are called mercury-specific oligonucleotides (MSO). Other cationic metals, such as $Ag^{+}$, $Cu^{2+}$, $Ni^{2+}$, $Fe^{2+}$, etc., presumably cannot achieve stabilization through T–T mismatches, resulting in the high selectivity observed for $Hg^{2+}$ ions [81].

Some of the published studies regarding mercury determination using poly-thymine oligonucleotides employed $Hg^{2+}$ preconcentration via the double strand and its subsequent reduction and stripping. Wu et al. modified a gold electrode with an oligonucleotide containing several thymines. After 15 min at open circuit, the $Hg^{2+}$ preconcentrated on the electrode surface due to the T–Hg–T interaction with the oligonucleotide and was measured electrochemically using ASV [82]. A gold disk electrode was modified with a DNA strand bound by hybridization to another strand

**Table 2**
Analytical characteristics of chemically modified electrodes published in the literature.

| Ref. | Electrode | Analyte | Sample | Linear range | LOD | Information |
|---|---|---|---|---|---|---|
| *Polymer coating electrodes* | | | | | | |
| [53] | Carbon disk/poly(ethylenediamine tetra-N-(3-pyrrole-1-yl) propylacetamide) | $Hg^{2+}$ | Distilled water | 2–1600 μg/L | 0.1 μg/L | DPASV (20 min open-circuit accumulation) (3 min deposition) |
| [54] | GCE/methyl-red film | Hg(II) | Lake water | 0.022–22 μg/L | 0.009 μg/L | CV-ASV (10 min deposition) |
| [55] | GCE/3′,4′-diamino-2,2′;5′, 2′′-terthiophene/EDTA | $Hg^{2+}$ | Urine | 0.15–20 μg/L | 0.1 μg/L | SWASV (10 min deposition) |
| [56] | Pt/poly(3-hexylthiophene) | Hg(II) | Fish | 20–1200 μg/L | 5 μg/L | DPASV (2 min deposition) |
| [57] | SPCE/poly(2,2′-dithiodianiline) | $Hg^{2+}$ | Distilled water | 2–2000 μg/L | 42 μg/L | DPASV (2 min deposition) |
| [58] | GCE/polyviologen | Hg(II) | Tap and sea waters | 1–100 μg/L | 0.3 μg/L | DPASV (5 min deposition) |
| [60] | Sol–gel carbon/PVSA | $Hg^{2+}$ | SRM and industrial waters | 10–10,000 μg/L | 3 μg/L | SWASV (8 min open-circuit accumulation) (1 min deposition) |
| [61] | Sonogel carbon/poly-3-methylthiophene | $Hg^{2+}$ | Wastewater | 10–780 μg/L | 1.4 μg/L | DPASV (30 min open-circuit accumulation) (12 s deposition) |
| *Electrodes modified with complexing agents* | | | | | | |
| [62] | GCE/TCA monolayer | $Hg^{2+}$ | Tap, lake, river water | 0.1–20 μg/L | 0.04 μg/L | DPASV (210 s deposition) |
| [63] | GCE/Nafion/MnPht | $Hg^{2+}$ | Distilled water | 0.4–2.4 mg/L | *nda* | Double potential step chronoamperometry |
| [64] | GCE/calix[4]arene functionalized with benzothiazole | $Hg^{2+}$ | Lake water and industrial wastewater | 25–300 μg/L | 5 μg/L | SWASV (6 min deposition) |
| [65] | GCE/1,8-bis(dodecylthio)-3, 6-dioxaoctane | $Hg^{2+}$ | Human urine | 14–200 μg/L | 6 μg/L | DPASV (25 min open-circuit accumulation) |
| [66] | CPE/carbon ionic liquid/AuNPs/ thiolated aminoacids | $Hg^{2+}$ | Waste and tap waters | 2–4000 μg/L | 0.46 μg/L | SWASV (10 min open-circuit accumulation) |
| [67] | CPE/N-BDMP | $Hg^{2+}$ | Tap water, fish and human hair | 10–2000 μg/L | 8.2 μg/L | SWASV (3.5 min deposition) |
| [68] | CPE/α-cyclodextrin | $Hg^{2+}$ | Distilled water | 40–800 μg/L | 10 μg/L | CVASV (20 s deposition) |
| [69] | CPE/mesoporous silica/thiol-terminated SAM | $Hg^{2+}$ | Distilled water | 20–1600 μg/L | 3 μg/L | SWASV (20 min open-circuit accumulation) |
| [70] | GCE/thiol-functionalized silica films | $Hg^{2+}$ | Lake water | 0.2–2 μg/L | 0.86 μg/L | SWASV (15 min open-circuit accumulation) (1 min deposition) |
| [71] | CPE/silica NPs/N,N′-bis(3-(2-thenylidenimino)propyl)piperazine | $Hg^{2+}$ | Tap and seawater, tobacco, fish and shrimps | 0.5–1000 μg/L | 0.05 μg/L | SWASV (1 min deposition) |
| [72] | CPE/mesostructured silica NP/5-mercapto-1-methyltetrazole | Hg(II) | River and ground waters | 20–200 μg/L | 20 μg/L | SWASV (10 min open-circuit accumulation) (1 min deposition) |
| [73] | Gold electrode/SAM/2-mercaptobenzimidazole | $Hg^{2+}$ | Distilled water | 0.5–3 mg/L | *nda* | CV-ASV (10 min deposition) |
| [74] | 3D gold nanopore array/2-mercaptobenzothiazole | $Hg^{2+}$ | Tap water | 0.01–2 μg/L | 0.004 μg/L | SWASV (5 min deposition) |
| [75] | GCE/gold film/Nafion | $CH_3Hg^+$ | Distilled water | 2–100 μg/L | 0.72 μg/L | DPASV (5 min deposition) |
| [76] | Epoxy-graphite tube/2-mercaptobenzothiazole | $Hg^{2+}$ | Water SRM and human hair | 2–1000 μg/L | 0.84 μg/L | DPASV (15 min open-circuit accumulation) (20 s deposition) Simultaneous detection of Bi(III), Hg(II) and Cu(II) |
| [77] | Graphite tube/2-mercaptobenzoxazole | $Hg^{2+}$ | Seawater and human urine | 2–200 μg/L | 0.38 μg/L | FIA-SWASV (10 min open-circuit accumulation) |
| [78] | Thick film graphite/Au(III)/PDC | $Hg^{2+}$ | River water | 0.2–50 μg/L | 0.005 μg/L | DPASV (2 min deposition) |
| [79] | SPCE/chitosan | Hg(II) | Distilled water | 20–80 μg/L | 2 μg/L | DPASV (30 s deposition) |
| [80] | SPCE/Sumichelate a10R | $Hg^{2+}$ | Seawater | 0.1–2 μg/L | 0.0024 μg/L | DPASV (20 min open-circuit accumulation) |
| *DNA-modified electrodes* | | | | | | |
| [82] | Gold/polythymine MSO | $Hg^{2+}$ | Distilled water | 0.04–0.2 μg/L | 0.012 μg/L | DPASV (15 min open-circuit accumulation) (1 min deposition) Medium exchange after deposition |
| [83] | GDE/polythymine MSO | $Hg^{2+}$ | Distilled water | 0.1–20 μg/L | 0.1 μg/L | SWASV (60 min open-circuit accumulation) Hybridization of $Hg^{2+}$ with oligos bound to AuNPs. |
| [84] | GDE/polythymine MSO hybridized with Fc-labeled strand | $Hg^{2+}$ | River water | 0.02–1000 μg/L | 0.012 μg/L | $Hg^{2+}$ displaces Fc from electrode DPASV of Fc (signal off detection) |
| [85] | Gold/polythimine MSO hairpin Fc-labeled | $Hg^{2+}$ | Sewage | 1–200 μg/L | 0.5 μg/L | $Hg^{2+}$ changes hairpin structure bringing Fc to the electrode DPASV of Fc (signal on detection) |

**Table 2** (*continued*)

| | | | | | | |
|---|---|---|---|---|---|---|
| [86] | Gold electrodes on chip/polythymine MSO hybridized | $Hg^{2+}$ | Sewage and tap water | 1.2–213.6 μg/L | 0.2 μg/L | $Hg^{2+}$ displaces hybridized strand and fewer RuHex are bound<br>Chronocoulometry of RuHex (signal off detection) |
| [87] | Gold/polythymine MSO Fc-labeled | $Hg^{2+}$ | Sewage | 0.2–400 μg/L | 0.1 μg/L | $Hg^{2+}$ displaces Fc from electrode<br>DPV of Fc (signal off) |
| [88] | Gold/polythymine MSO | $Hg^{2+}$ | Distilled water | *nda* | 2 μg/L | RuHex is bound to DNA-AuNPs. $Hg^{2+}$ binds the electrode with AuNPs<br>CV of RuHex (signal on detection) |
| [89] | Gold/polythymine MSO | $Hg^{2+}$ | River and tap waters | 0.1–400 μg/L | 0.1 μg/L | Similar to the previous system but with MB<br>DPV of MB (signal on) |
| [90] | Gold/polythymine MSO | $Hg^{2+}$ | Distilled water | 0.02–200 μg/L | 0.02 μg/L | Enzymatic relay between DNA labeled with GOx and Fc when $Hg^{2+}$ binds to the MSO<br>CV measurement |
| [91] | Gold/polythymine MSO | $Hg^{2+}$ | Tap water | 0.2–200 μg/L | 0.1 μg/L | $Hg^{2+}$ binds to an oligo labeled with hemin group<br>Enzymatic reaction of $H_2O_2$ with hemin group and amperometric detection |
| *Electrodes modified with IIP* | | | | | | |
| [93] | CPE/4-vinylpyridine IIP | $Hg^{2+}$ | Tap, river and lake waters | 0.5–1000 μg/L | 0.1 μg/L | DPASV (15 min open-circuit accumulation) (30 s deposition) |
| [94] | GCE/MWCNTs/AuNPs/poly(2-mercaptobenzothiazole) IIP | $Hg^{2+}$ | River and tap waters | 0.08–19.2 μg/L | 0.016 μg/L | DPASV (12 min open-circuit accumulation) (1 min deposition) |
| [95] | GCE/MWCNTs/5,10,15,20-tetrakis(3-hydroxyphenyl) porphyrin IIP nanobeads | $Hg^{2+}$ | Ground and waste waters | 2–140,000 μg/L | 1 μg/L | DPASV (5 min open-circuit accumulation) (100 s deposition) |
| *Other chemically modified electrodes* | | | | | | |
| [96] | CPE/silica particles | $Hg^{2+}$ | Distilled water | 40–2000 μg/L | 10 μg/L | SWASV (30 s deposition) |
| [97] | GCE/thiol-functionalized porous clay heterostructures | $Hg^{2+}$ | Distilled water | 0.8–4 μg/L | 0.1 μg/L | DPASV (20 min open-circuit accumulation) (15 s deposition) |
| [98] | CPE/vermiculite | $Hg^{2+}$ | Distilled water | 20–1600 μg/L | 11.4 μg/L | SWASV (15 min open-circuit accumulation ) (30 s deposition) |
| [99] | CPE/TZT-HDTA-clay | $Hg^{2+}$ | River and sea waters | 10–2000 μg/L | 0.1 μg/L | DPASV (5 min open-circuit accumulation) |
| [100] | CPE/montmorillonite | Hg(II) | Saline and bottled waters | 10–35 μg/L | 3.5 μg/L | DPASV (15 min open-circuit accumulation) |
| [101] | CPE/thiol-functionalized organo-clay | $Hg^{2+}$ | River water | 20–140 μg/L | 13.6 μg/L | DPASV (30 s deposition) |
| [102] | CPE/1,3,4-thiadiazole-2,5-dithiol-HDTA-montmorillonite | Hg(II) | River and seawaters | 10–1000 μg/L | 0.15 μg/L | DPASV (5 min open-circuit accumulation) |
| [103] | SPCE/urease | $Hg^{2+}$ | Leachate samples | 10–100 μg/L | 8.5 μg/L | Amperometric measurement of $Hg^{2+}$ by inhibition of urease activity (20 min incubation) |
| [104] | Pt/invertase/glucose oxidase/mutarotase | $Hg^{2+}$ | Distilled water | 2–200 μg/L | *nda* | Amperometric measurement of $Hg^{2+}$ by inhibition of invertase activity (20 min incubation) |
| [105] | CPE/water hyacinth fibers | $Hg^{2+}$ | Distilled water | 400–800 μg/L | 195 μg/L | DPASV (10 min open-circuit accumulation) |

attached to a gold nanoparticle. This nanoparticle had several strands that were capable of selectively binding $Hg^{2+}$ because their structure contained several thymines. The sensitivity obtained with this system was very high because each strand that modified the electrode could preconcentrate several $Hg^{2+}$ ions. After this preconcentration, an electrochemical measurement was performed, consisting of reducing $Hg^{2+}$ by square-wave voltammetry using a cathodic sweep.[83]. The LODs for these methods were 0.012 μg/L and 0.1 μg/L, respectively, but the accumulation time was long (15 min and 60 min, respectively). On the other hand, although electrode regeneration was not specifically discussed, the electrode likely required mechanical polishing and fresh modification with DNA strands in order to be reused.

Another widely used mechanism that employs DNA strands to detect $Hg^{2+}$ involves altering the distance between the electrode surface and a redox label via the conformational change, dissociation or hybridization of DNA strands. For example, gold disk electrodes can be modified with self-assembled monolayers and a MSO initially hybridized with a ferrocene-labeled DNA strand. If the solution contains $Hg^{2+}$ ions, the ions can bind to the MSO, and the ferrocene-labeled strand moves away the electrode. Therefore, the analytical signal corresponding to the electrochemical measurement of ferrocene decreases as the concentration of $Hg^{2+}$ in the sample increases (signal-off detection). Good performance has been achieved with this methodology, which demonstrated
a LOD of 0.012 μg/L and a linear range of over three orders of magnitude. Furthermore, electrode regeneration can be achieved by washing with ascorbic acid solution for 1 h and posterior hybridization with the ferrocene-labeled strand [84]. Zhuang et al. have used a similar system, but with strands that are able to form hairpin structures. When $Hg^{2+}$ ions are not present in the solution, the strand forms a structure that excludes ferrocene from the electrode surface, thereby inhibiting electron transfer. On the contrary, when $Hg^{2+}$ ions are present in solution, the MSO binds to the ion, and the strand structure positions the ferrocene close to the electrode, enhancing electron transfer. Therefore, the signal increases as the $Hg^{2+}$ concentration in the solution increases

(signal-on detection). Electrode regeneration was achieved after immersion for 10 min in a Tris–HCl (pH 7.4) solution containing 1 M NaCl and 1 M $I^-$ [85]. A gold chip on a silver electrode with a MSO that was initially hybridized with a DNA strand . In addition, a redox mediator, hexaminruthenium (III) chloride (RuHex), which can bind to the double strand , was utilized. When $Hg^{2+}$ cations are present in the solution, they bind to the MSO and inhibit the formation of the double strand; therefore, the amount of RuHex is lower than when no $Hg^{2+}$ ions are present in solution, and the analytical signal decreases (signal-off) [86].

Other authors have employed similar hybridization systems for $Hg^{2+}$ determination, employing the electrochemical reactions of ferrocene [87], RuHex [88] or methylene blue [89] as the analytical signals.

Other innovative systems employing DNA strands have been used for $Hg^{2+}$ determination. An example is a system in which DNA strands modified with ferrocene and glucose oxidase bind to $Hg^{2+}$ ions, thus nearing each other. They then function as an electric relay with the gold electrode, enabling sensitive electrochemical measurements of $Hg^{2+}$ with a LOD of 0.02 μg/L and a linear range of four orders of magnitude [90]. The electrocatalytic activity of the hemin group towards the reduction of $H_2O_2$ has been exploited in a DNA system for the specific and sensitive determination of $Hg^{2+}$. The hemin group is bound to the DNA probe after the reaction of $Hg^{2+}$ with a polythymine capture probe [91]. Park et al. used a hairpin-DNA adsorbed on the surface of an ITO-coated glass modified with reduced graphene. After the DNA strand reacts with $Hg^{2+}$ ions, any change in the electrode surface is measured using electrochemical impedance spectroscopy (EIS) [92].

Although most of the LODs obtained with DNA-modified electrodes are below 0.5 μg/L and show satisfactory sensitivity for routine analysis, other aspects, such as a long analysis time, particularly when a hybridization reaction is required, present significant disadvantages compared to other types of modified electrodes. Moreover, these electrodes are only applicable to $Hg^{2+}$ because this is the only species that binds to the DNA strands.

### 3.4. IIP-modified electrodes

Molecularly imprinted polymers (MIP) are synthetic receptors capable of binding specifically to a given analyte. These materials have a high capacity for preconcentration, high selectivity and often, high stability. MIP technology can also be used to prepare polymers containing ion-selective sites. The more specific terminology for this case is ion-imprinted polymers (IIPs). The method of fabrication generally uses a monomer in the presence of the ion of interest, and the polymerization is carried out either chemically, by use of an initiator, or electrochemically, by applying an electrical potential to the electrode. After polymerization, the ion is removed from the polymer using a washing solution, leaving cavities (imprinted sites) on the polymer structure with shapes and sizes that are similar to those of the employed ion.

Carbon-paste electrodes were modified with an IIP for $Hg^{2+}$ detection. This IIP was synthesized in the presence of $Hg^{2+}$ from 4-vinylpyridine, a cross-linker (ethylene glycol dimethacrylate) and an initiator (2,2-azobisisobutyronitrile). After the polymerization and washing steps, the carbon paste was modified with the IIP to fabricate the electrode. $Hg^{2+}$ was preconcentrated on the electrode surface at open circuit (15 min). The resulting IIP electrode exhibited enhanced sensitivity compared to an electrode having no specific IIP or that did not employ a polymer (CPE only). This method was employed to analyze $Hg^{2+}$ in water samples, and a LOD of 0.1 μg/L was calculated [93].

Another example is the modification of GCE with a nanohybrid of AuNPs/SWCNTs and a specific IIP for $Hg^{2+}$ ions, poly(2-mercaptobenzothiazole). The nanohybrid material provides a high number of surface sites, enhancing the total number of effective imprinted sites. After preconcentration at open circuit for 12 min, $Hg^{2+}$ is measured electrochemically using DPASV. A sensitive and selective method for $Hg^{2+}$ was developed, and a LOD of 0.016 μg/L was achieved [94]. A more recently reported example is the modification of GCE with multi-walled carbon nanotubes (MWCNTs) and an IIP for $Hg^{2+}$, which exhibited a comparatively higher limit of detection (1 μg/L) and a shorter accumulation time (5 min) [95].

Electrodes modified with IIPs possess very promising characteristics, such as high selectivity and good sensitivity. However, they have the disadvantage that attaining low LODs requires a large accumulation time, usually $>$ 10 min. Further improvement of materials and the development of new imprinted polymers will facilitate the development of an electrode with better performance and shorter analysis times.

### 3.5. Other electrodes

Other chemically modified electrodes have been published in the literature for the electrochemical analysis of mercury.

Preconcentration of Hg(II) via interaction of the metallic ion and the hydroxide groups of silica particles have also been reported.. Carbon paste electrodes were modified with silica particles and used to determine mercury in water. This electrode exhibited low sensitivity compared to other methods [96].

Tchinda et al. employed thiol-functionalized porous clay heterostructures (PCHs) from mesoporous organosilica. This material was deposited as a thin film on a GCE, and, after accumulation at open circuit, Hg(II) was electrochemically determined by DPASV. The wide, open, porous structure improved Hg(II) preconcentration, resulting in high sensitivity (LOD of 0.1 μg/L). These structures were shown to form robust thin films without the need for polymers [97].

Due to their ability to exchange anions, clay and mica minerals have also been used to preconcentrate mercury ions in chloride media. Examples include the modification of CPEs with vermiculite [98], montmorillonite [99] or biotite [100]. Modification of these types of minerals with complexing groups have also been reported [101,102]. However, the analytical performance of electrodes modified with these minerals is not sufficient for routine analysis because these electrodes are unable to detect $Hg^{2+}$ levels in water that are below the regulated limits (see Table 2).

Metallic ions can inactivate some enzymes, a characteristic that was exploited by Rodriguez et al. when they employed a SPCE modified with urease. $Hg^{2+}$ ions hinder the enzymatic reaction, which is measured by an amperometric assay [103]. A platinum electrode that was modified with a clay gel containing several enzymes (glucose oxidase, invertase and mutarotase) was employed for the indirect determination of several mercury species (inorganic mercury, methyl and phenylmercury). Silver interference was important because silver also inhibits the enzymatic reaction [104]. Although this was an innovative method, the limits of detection were fairly high (8.5 and 2 μg/L, respectively) in both cases. In addition, the incubation time required for the enzymatic reaction was very long.

The water hyacinth plant is able to uptake heavy metal ions, a characteristic exploited to determine Hg(II) via modification of CPEs with the fibers of this plant [105].

Although CMEs may have demonstrated some potential for use in the selective electrochemical analysis of mercury, there are important concerns regarding their application in routine analysis, including the low sensitivities exhibited by most of these electrodes and the high preconcentration times required to detect trace amounts of mercury. To use DNA as an electrode modifier requires a hybridization reaction between DNA strands, and this reaction

takes a significant amount of time and requires specific and careful conditions.

## 4. Nanostructured electrodes

An important trend in recent years is nanotechnology. Nanomaterials have excellent and novel properties that differ from macroscopic materials in two main ways: nanomaterials behave according to the laws of quantum chemistry instead of the laws of classical physics, and nanomaterials have a high surface area, which makes them sensitive to surface processes.

Due to their novel characteristics, nanomaterials are being used widely in electrochemical analyses. Some nanomaterial properties significantly affect electrochemical analyses, including the following: their high surface areas, which increase working electrode areas; their ability to catalyze electron transfer; their high adsorption capacities; and their ability to be modified with compounds of interest, including biomolecules.

The nanomaterials most commonly used for the electrochemical analysis of mercury can be classified into three main groups: metallic nanoparticles, carbon nanomaterials and nanohybrid materials.

### 4.1. Metal nanoparticles

Metal nanoparticles are clusters with nanometric dimensions and contain 100 and 1000 atoms. The physical and electronic properties of metal nanoparticles generally depend on their size. The use of metal nanoparticles has become popular in the field of electroanalysis in recent years due to the advantages that nanoparticles offer compared to unmodified electrodes. For instance, metal nanoparticles can improve electron transfer between the electrode and electroactive substances and can catalyze some electrochemical reactions, decreasing the overpotential required for these reactions to occur and thus causing the process to become reversible [106]. The major drawback of metal nanoparticles is their higher reactivity compared to macroscopic materials [107], which can be a disadvantage for specific applications. Nevertheless, due to the advantages they provide, metal nanoparticles have been used in a large number of electrochemical applications [108].

For example, Wu et al. employed a GCE modified with porous, tubular $Fe(OH)_3$ nanoparticles to fabricate a sensor that exhibited high amperometric responses to $Hg^{2+}$ ions due to the high surface area of the nanoparticles [109].

Gold nanoparticles have specific advantages, such as the capabilities for easy surface modification and high biocompatibility. The surface chemistry of gold nanoparticles enables them to bind thiol groups very effectively. Gold nanoparticles have been used as electrode materials for the analysis of several analytes, including mercury. Electrode modification with gold nanoparticles can be accomplished via adsorption from colloidal gold solutions [110] or via electrochemical deposition that controls for size and dispersion [111].

GCEs have been modified with gold nanoparticles for the determination of Hg(II) in various samples, such as drinking water, ocular gel and sediments, using ASV. Compared to gold and gold film electrodes, GCEs modified with AuNPs exhibited lower LODs and better repeatability [112]. The same authors extended the use of GCEs modified with AuNPs to the analysis of other certified samples, such as ashes, sea lettuce, tuna fish and wastewater [113]. Using this same electrode, the analysis of methylmercury and inorganic mercury was achieved using a methodology that involved the initial determination of inorganic mercury and, after acid digestion in a microwave oven, the determination of total mercury as inorganic mercury [114]. Other authors have employed different electrochemical techniques to modify GCEs with AuNPs. Hezard et al. synthesized AuNPs on the electrode by applying cyclic voltammetry to a solution containing $HAuCl_4$ and used the resulting electrode to determine Hg(II) using ASV. The best results were obtained with a high-density coating of small gold nanoparticles [115]. The same authors performed similar experiments using additional techniques to deposit AuNPs on the electrode surface: cyclic voltammetry, chronoamperometry and potentiostatic double-pulse. Of these, the best results were obtained with chronoamperometry, which generated smaller nanoparticles at high density on the electrode surface [116]. Thus, it appears that the density and size of gold nanoparticles have an important influence on the analytical signal for Hg(II) obtained by electrochemical methods. As shown in Table 3, the LODs for all these studies were below 0.2 μg/L but did show some differences. These differences may be due to the different methodologies employed to generate the AuNPs as well as the different characteristics of the AuNPs generated.

The analysis of Hg(II) using a GCE modified with PEDOT/AuNPs did not demonstrate any improvements compared to results obtained using the simpler GCE/AuNPs electrode. Although PEDOT contains sulfur atoms that may interact with metals like mercury, it appears that this effect does not influence Hg(II) determination. Furthermore, after each measurement, electrochemical treatment and EDTA are necessary to remove the mercury deposited on the electrode [117].

Commercial screen-printed carbon electrodes modified with gold nanoparticles have also been used for Hg(II) analysis in rain, river and industrial water samples [118]. Higher sensitivities and lower LODs (0.8 μg/L) were observed compared to commercial screen-printed gold electrodes [35]. Such gold-nanoparticle-modified screen-printed carbon electrodes have been successfully employed to analyze mercury in indoor dust samples after an ultrasonic extraction method [119,120].

Gold nanoelectrode ensembles (GNEE) are another system that employs gold nanoparticles to electrochemically analyze mercury. In this case, the modified gold electrode consists of a three-dimensional network of silicate into which gold nanoseeds (5–6 nm) have been added. The resulting electrode was able to measure 0.1 μg/L of Hg(II) using ASV and was able to detect Hg(II), As(III) and Cu(II) simultaneously [121].

Thus, gold nanoparticles appear to be an important electrode material for the electrochemical analysis of mercury. The UPD of mercury on gold is an adsorption process that depends largely on the electrode area; therefore, the use of AuNPs, which have high surface areas, improves the behavior of these processes and significantly enhances the analytical response of mercury. Moreover, as shown in some of the reviewed studies, mercury deposition on AuNPs is reversible at low concentrations, thus eliminating the memory effects observed with other methods and thus providing a renewable electrode surface. Electrodes made with gold nanoparticles for the purpose of mercury analysis have all the advantages of the aforementioned macroscopic materials as well as some additional advantages, making gold-nanoparticle-modified electrodes one of the most promising tools for electrochemical mercury analysis. However, it is important to recognize that the Hg(II) signals obtained using these electrodes tend to occur at potentials where a wide baseline exists in the *i–E* curve, making it necessary to perform blank (or background) subtraction to obtain good visual signals that are easy to measure. No clear explanation for this fact has been published to date.

### 4.2. Carbon nanomaterials

Carbon nanomaterials have been extensively used in electrochemical analyses. These nanomaterials have significant

**Table 3**
Analytical characteristics of nanostructured electrodes published in the literature.

| Ref. | Electrode | Analyte | Sample | Linear range | LOD | Information |
|---|---|---|---|---|---|---|
| *Electrodes modified with nanoparticles* | | | | | | |
| [109] | GCE/$Fe(OH)_3$NPs | Hg(II) | Tap and river waters | 0.2–16,000 μg/L | 0.06 μg/L | DPASV |
| [112] | GCE/AuNPs | $Hg^{2+}$ | Drinking water, sediments and ocular gel | 0.01–0.5 μg/L | 0.15 ng/L | SWASV (2 min deposition) |
| [113] | GCE/AuNPs | Hg(II) | Sediment, incineration ash, fish and sea lettuce CRMs, drinking water and pharmaceuticals | *nda* | *nda* | SWASV (2 min deposition) |
| [114] | GCE/AuNPs | $Hg^{2+}$ $CH_3Hg^+$ | Distilled water | 0.6–10 μg/L | 0.2 μg/L | SWASV (2 min deposition) |
| [115] | GCE/AuNPs | Hg(II) | Distilled water | 0.13–0.80 μg/L | 0.08 μg/L | SWASV (5 min deposition) |
| [116] | GCE/AuNPs | Hg(II) | Distilled water | 0.16–2.0 μg/L | 0.08 μg/L | SWASV (5 min deposition) |
| [117] | GCE/PEDOT/AuNPs | $Hg^{2+}$ | Distilled water | 0.5–11 μg/L | 0.83 μg/L | DPASV (2.5 min deposition) |
| [118] | SPCE/AuNPs | Hg(II) | Waste water | 5–20 μg/L | 0.8 μg/L | SWASV (2 min deposition) |
| [121] | GNEE | $Hg^{2+}$ | Distilled water | 0.1–14 μg/L | 0.02 μg/L | SWASV (100 s deposition) Simultaneous detection of As(III), Cu(II) and Hg(II) |
| *Electrodes modified with carbon nanomaterials* | | | | | | |
| [125] | MWCNTs paste electrode | $Hg^{2+}$ | Waste water | 1–25 μg/L | 0.42 μg/L | SWASV (3.5 min deposition) |
| [126] | CPE/MWCNTs | Hg(II) | Natural water and industrial wastewater | 1.3–16.6 μg/L | 0.48 μg/L | LSASV (4 min deposition) |
| [127] | CPE/MWCNTs/3-(4-methoxybenzylide-neamino)-2-thioxothiazolodin-4-one | Hg(II) | Sea and waste waters | 0.2–140 μg/L | 0.18 μg/L | SWASV (1.5 min deposition) |
| [128] | GCE/MWCNTs | $Hg^{2+}$ | Lake water | 0.16–10 μg/L | 0.004 μg/L | DPASV (5 min deposition) |
| [129] | GCE/MWCNTs-Fast Violet B | $Hg^{2+}$ | Tap and lake waters | 0.2–2.8 ng/L | 0.2 ng/L | DPASV (40 s deposition) |
| [130] | SPBiE/MWCNTs | Hg(II) | Tap water and human hair | 0.2–40 μg/L | 0.09 μg/L | SWASV (3 min deposition) |
| [131] | PDAN interdigitated array/MWCNTs | $Hg^{2+}$ | Distilled water | 0.4–2 mg/L | *nda* | SWASV (15 min min open-circuit accumulation) |
| [132] | SPE/carbon black film | $Hg^{2+}$ | Drinking water | 5–20 μg/L | 2 μg/L | Indirect detection of $Hg^{2+}$ by amperometric measurement of thiols |
| [133] | SPCNPsE | $Hg^{2+}$ | Distilled water | 1–10 μg/L | *nda* | SWASV (2 min deposition) Heated electrodes (40 °C) |
| *Electrodes modified with nanohybrid materials* | | | | | | |
| [134] | GCE/AuNPs/MWCNTs | $Hg^{2+}$ | Distilled water | 0.1–250 μg/L | 0.06 μg/L | DPASV (2 min deposition) |
| [135] | GCE/Au-PtNPs/TMB NF | $Hg^{2+}$ | Tap and river waters | 0.02–6 μg/L | 0.008 μg/L | SWASV (1.5 min deposition) |
| [136] | GCE/graphene/AuNPs | $Hg^{2+}$ | River water | 0.008–0.05 μg/L | 0.006 μg/L | SWASV (2 min deposition) |
| [137] | GCE/AuNPs/GO-IL | $Hg^{2+}$ | Tap and sea waters | 0.02–20 μg/L | 0.006 μg/L | DPASV (11 min deposition) |
| [20] | SPCE/MWCNTs/AuNPs | $Hg^{2+}$ | Tap and river waters | 0.5–50 μg/L | 0.2 μg/L | SWASV (3.5 min deposition) |
| *Electrodes modified with other nanomaterials* | | | | | | |
| [138] | GCE/layered titanate nanosheets | $Hg^{2+}$ | Mushrooms | 0.008–0.7 μg/L | 0.005 μg/L | SWASV (10 min open-circuit accumulation, 80 s deposition) |

adsorption capabilities, enabling mercury to preconcentrate over the electrode surface, resulting in higher sensitivity compared to that obtained using non-modified electrodes.

Carbon nanotubes constitute the most widely used carbon nanomaterial in recent years. Carbon nanotubes are cylindrical structures that have diameters of a few nanometers. A carbon nanotube can be viewed as a single sheet of graphite rolled onto itself. Among the different types of carbon nanotubes, the main two are single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). The most important properties exhibited by these nanomaterials are high electrical conductivity, high mechanical strength and high thermal conductivity. The advantages afforded by carbon nanotubes with regard to electrochemical analysis mainly pertain to improvements in performance, such as the higher reversibility of processes and,consequently, increases in the velocity of electron transfer [122], the reduction of overpotentials, higher selectivity [123], and increased sensitivity due to the increased electrode surface area. A negative consequence of modifying electrodes with carbon nanotubes could be the resulting capacitive current because this current also increases with the electrode area and can sometimes negatively affect the analytical signal [124].

Several types of electrodes have been modified with carbon nanotubes for the purpose of electrochemical mercury determination.

Compared to the performance of other carbon electrodes, including carbon fiber, glassy carbon and carbon paste, under the same experimental conditions, Ly et al. improved Hg(II) sensitivity

using a carbon-nanotube paste electrode [125]. The increased sensitivity was clearly due to the higher surface area of the latter electrode compared to the other carbon electrodes.

CPEs have also been modified with carbon nanotubes for Hg(II) analysis. Adding chitosan crosslinked with glutaraldehyde (GA) to carbon paste improves the sensitivity of the Hg(II) analysis, an effect that could be due to the complexation of the chitosan–GA system to with Hg(II) [126]. Another study reports the results of a MWCNTs–CPE that has been modified with a Schiff base. This compound can complex with metal ions, and the modified electrode can be used to simultaneously determine Pb(II) and Hg(II) in several samples, including tuna fish, shrimp, tobacco and human teeth. The use of carbon nanotubes improves the analytical signal and enhances the effect of modification with the Schiff base, resulting in a LOD of 0.18 μg/L, which is significantly lower than the LOD of 0.48 μg/L achieved in the previous example [127].

Yi modified a GCE with MWCNTs to analyze Hg(II) in lake water samples. The use of MWCNTs produced a significant improvement over the results obtained with bare GCEs. Furthermore, the addition of KI improved the stripping peak of Hg(II) and avoided Cu(II) interference due to $CuI_2$ precipitation [128]. The covalent functionalization of CNTs with Fast Violet B and the subsequent modification of the GCE enabled the selective determination of Hg(II) because Fast Violet B binds specifically to Hg(II) [129]. With respect to the low levels of the linear range, the electrode modified with Fast Violet B reached a value lower than three orders of magnitude compared to the electrode without modification. The chemical interaction between the modifier and mercury improved the preconcentration effect, which resulted in higher sensitivity.

Screen-printed electrodes made of carbon, bismuth and carbon nanotubes ink were used to determine Hg(II) in tap water and human hair. Adding Bi and CNTs, individually and in combination, to the carbon ink to fabricate the screen-printed electrode improved the sensitivity [130].

Nguyen et al. modified a silicon chip with an array of poly(1,8-diaminonaphthalene) (PDAN), a conductive polymer, and carbon nanotubes. Selective adsorption of $Hg^{2+}$ occurs at open circuit, after which the electrochemical analysis is performed. However, the sensitivity obtained by this electrode is inferior to that obtained for other electrodes [131].

Another carbon nanostructured material that has been applied to Hg(II) analysis is carbon black, a material with a high number of surface defects. This material has been used to obtain high-sensitivity measurements of thiol groups, which form stable complexes with Hg(II). Palleschi et al. have developed an amperometric sensor using screen-printed electrodes modified with carbon black for the indirect analysis of Hg(II) in drinking water. The sensor responds to the oxidation of thiols, and the analytical signal is lower when Hg(II) is present in the sample [132].

Heated screen-printed electrodes with carbon nanoparticles (SPCNPsE) have been employed for the determination of heavy metals in seawater. In this regard, the use of heated electrodes has been shown to increase the mobility of ions, achieving faster deposition and higher sensitivity, thus achieving an LOD of 1 μg/L [133].

The use of carbon nanomaterials for electrochemical mercury determination exhibits some important improvements compared to unmodified electrodes. The increased surface area of the working electrode increases the sensitivity, and low amounts of mercury can be detected. However, carbon nanomaterials particularly stand out when they are modified with other selective compounds, resulting in greater preconcentration and even higher sensitivity. Although graphene exhibits excellent properties with regard to its use in electrochemical analysis, there have been no published reports regarding mercury determination using electrodes modified only with graphene or its derivatives. All published studies regarding graphene-modified electrodes have involved the use of accompanying species that can interact with mercury, such as gold nanoparticles or species containing functional groups.

### 4.3. Nanohybrid materials

Although the use of single nanostructured materials appear to present advantages over the use of macroscopic materials, researchers are still working to develop innovative technologies that enhance these advantages. One such technology is the use of hybrid nanostructured materials. These hybrid systems can exhibit properties that amplify those of single nanostructured materials.

Several methodologies for modifying electrodes with nanohybrid materials currently exist. Similar to modifications using single nanomaterials, nanohybrid modification methods depend largely on the type of working electrode and the materials used. Several nanohybrid materials have been used in different electrochemical analyses, including the determination of mercury.

In one such instance, GCEs were modified with a nanohybrid of AuNPs/CNTs. The nanoparticles were chemically synthesized on the CNTs by citrate reduction in a microwave oven. After synthesizing the nanohybrid, each electrode was modified by placing a drop of the nanohybrid on its surface and waiting until the surface dried. This nanohybrid material enabled Hg(II) determination with high sensitivity (LOD = 0.06 μg/L) [134].

Gong et al. modified a GCE with a nanohybrid consisting of gold and platinum nanoparticles and 3,3′,5,5′tetramethylbenzidine (TMB) nanofibers. The nanoparticles were homogeneously distributed in the nanofibers, forming a three-dimensional nanoporous network. Analysis of Hg(II) employed ASV and exhibited great sensitivity, reaching a LOD of 8 ng/L [135]. The same authors also modified a GCE with a nanohybrid consisting of graphene and gold nanoparticles. The composite nanohybrid exhibited improved electron transfer and sensing behavior, reaching Hg(II) LODs of 6 ng/L (120 s deposition time) and 0.6 ng/L (300 s deposition time). This improvement was due to the combination of the excellent properties of graphene (unique electrical conductivity and high surface area) and the beneficial properties of AuNPs (high catalytic activity and good conductivity). The graphene/AuNPs nanohybrid exhibited higher sensitivity than a nanohybrid formed by CNTs/AuNPs [136].

Graphene oxide and gold nanoparticles have also been used to modify glassy carbon electrodes. With the help of an ionic liquid, such modified GCEs were used to determine Hg(II) in drinking and environmental water samples. When modified with the nanohybrid material, the electrode possessed a highly enhanced electron-conductive nanostructured membrane and a large electroactive surface area [137].

Screen-printed carbon electrodes have also been modified with nanohybrid materials such as graphene/AuNPs and MWCNTs/AuNPs. Modification of screen-printed carbon electrodes with carbon nanomaterials has been achieved by means of physical adsorption, after which the AuNPs have been generated by applying a constant current to a solution of $HAuCl_4$. The use of nanohybrid materials appear to have improved the sensitivity and lowered LODs compared to experiments where only AuNPs were obtained (0.2 and 3.3 μg/L, respectively). The results show that the nanohybrid formed by MWCNTs/AuNPs is more adequate for Hg(II) analysis. Moreover, reutilization of these nanohybrid-modified screen-printed electrodes was achieved for several measurements of Hg(II) in water samples [20].

As demonstrated by the studies above, nanohybrid materials are being used for electrochemical mercury analysis and have shown very interesting characteristics pertaining to measurements of mercury contamination, even at low levels. The ease of modification of these materials and the good stability they have demonstrated are particularly advantageous features. As shown in Table 3, the time required for analysis is short. Therefore, for a low

price and in a short amount of time, the analysis of mercury in water at sub-ppb levels can be performed. However, the electrodes developed thus far have only been used to determine $Hg^{2+}$ in aqueous samples. Thus, the performance of these methods with other media and for the determination of different mercury species remains to be studied.

### 4.4. Other nanostructured materials

Titanate nanosheets contain sodium ions between their layers that are exchangeable with other cations, such as heavy metal ions. This property has been used by Yuan et al. for Hg(II) determination in river water and mushroom samples employing a GCE modified with titanate nanosheets. A LOD of 5 ng/L was reported after 10 min of open-circuit accumulation. Electrode regeneration is carried out by performing multiple oxidation scans to remove all of the accumulated mercury [138]. Such materials exhibit interesting characteristics with regard to the preconcentration of ions, but a long accumulation time is still required for ionic exchange.

In addition, an alumina/gold-composite working electrode modified with bunch-like bismuth nanostructures has been used successfully to detect different heavy metal ions, including $Hg^{2+}$ [139].

## 5. Conclusions and future perspectives

The electrochemical analysis of mercury is of great interest and has been under investigation for many years. Continuous development of new materials has contributed to the advancement of mercury-determination techniques. In recent years, considerable research has been conducted with advanced materials, such as DNA, IIP and especially nanomaterials. As a result, a wide range of tools, ranging from bare electrodes of various materials to electrodes modified with compounds that can significantly improve the sensitivity, is now available for the electrochemical analysis of mercury.

Each electrode type reported in the literature and reviewed here has advantages and disadvantages. For example, bare carbon electrodes exhibit a low interaction with mercury, and the mercury preconcentration effect is small. On the other hand, this preconcentration effect is significant for gold electrodes, either bare or film, due to the UPD process, resulting in low LODs when sufficient preconcentration times are employed. The benefit of using gold film electrodes is that the cost of a thin layer of gold is substantially less than the cost of a full gold electrode. The performances reported for other bare electrodes in the literature depend on the materials used, but these performances are generally worse, showing higher LODs, than that exhibited by gold electrodes. Similarly, electrodes modified with polymers and complexing agents present differing results depending on the modification material and the accumulation time. Good results, in terms of sensitivity and LODs, are obtained with DNA-modified electrodes because of the ability of DNA strands to preconcentrate mercury as well as the innovative methodologies developed. However, DNA strands are difficult to work with, and the hybridization reaction time can be lengthy. Similar results are obtained with electrodes modified with IIP, for which the largest drawback is the accumulation time required for mercury preconcentration, which is comparatively higher compared to that for other electrodes. Excellent performance is exhibited by electrodes modified with AuNPs or CNTs, but the results obtained with nanohybrid-modified electrodes show even greater improvement. Nanohybrid-modified electrodes show very low LODs and have low analysis times, rendering nanohybrid electrodes the most promising method for electrochemical mercury analysis.

It is noteworthy that considering all the advantages of electrochemical instrumentation, the methods reviewed herein are still not used for routine analysis. For timely mercury analysis, screen-printed electrodes present certain advantages, such as low cost, ease of use, low sample volume and the possibility of using portable instrumentation. Although screen-printed electrodes have been reported for mercury analysis, the LODs are close to the regulated limits; thus, the analyses are unreliable. Modification of these electrodes with different nanomaterials may enable more sensitive detection, thereby fulfilling all of the requirements of routine analysis. The main advantage of the screen-printed electrodes with regard to mercury analysis is the fact that these electrodes are single-use and, therefore, avoid mercury memory effects as well as deposition-stripping steps and tedious cleaning steps. A completely unique application is the continuous analysis of mercury, of which only a few examples have been published. For this application, the electrode employed must be very stable and robust to successfully work under the same conditions and after repeated analyses. Currently, the most prominent concern is the regeneration of electrodes because mercury is strongly deposited on the surface and removal, can change the electrode surface, causing measurement conditions to deteriorate with continued use. To successfully address this issue, it is necessary to find an electrode that is stable, does not deteriorate with continuous use and is capable of detecting low mercury concentrations.

It is also important to highlight the lack of published works regarding the electrochemical analysis of mercury in blood samples, including whole blood, serum or plasma. Developing an electrochemical method for measuring mercury in blood would reduce the effort and time compared to the conventional methods currently implemented in hospitals. The main problem is the difficult extraction of mercury from blood, as mercury binds strongly to proteins that contain various sulfur-containing functional groups. Therefore, developing a reliable and easy method by which mercury can be extracted from blood to a simpler matrix remains an important area of research.

Although some issues remain unresolved with regard to the electrochemical analysis of mercury, recent advances in this field have brought us closer to replacing conventional methods with superior electrochemical methods. We are closer to using electrochemical methods for the routine analyses of mercury than we were 10 years ago, and this goal will certainly be achieved very soon.

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