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Electrochemical determination of mercury: a review

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23 **Abstract**

24 Mercury is a metal that has been extensively studied, being the high toxicity one of its most important
25 characteristic. Therefore, the level of mercury has to be controlled in different samples using analytical
26 methods. In this review many articles where electrochemical methods for the analysis of mercury in a
27 variety of samples are described. Here is presented a critical evaluation of the methods and electrode's
28 materials employed in the analysis of mercury according to the following classification: bare
29 electrodes, chemically modified electrodes and nanostructured electrodes. The advantages and
30 disadvantages of each type of material used are commented.

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34 **Keywords:** Mercury, Electrochemistry, Electroanalysis, Nanotechnology, Real samples

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43 **1. Introduction**

44 **1.1. General aspects**

45 Mercury is a metal with interesting properties employed in several applications. Some of this
46 features are: low heat conductivity, good electrical conductivity, and being a liquid metal at room
47 temperature, due to its low melting point.[1] This last property allows mercury to combine with other
48 metals to form amalgams. These characteristics are useful for the application of mercury in lamps,
49 measuring instruments, and in the industrial manufacture of chemical compounds. Different mercury
50 compounds are used in several situations such as catalysts, fungicides, herbicides, pigments, and even
51 drugs.[2]

52 The major drawback of this material is its high toxicity. The toxicology of each mercury species
53 (elemental, inorganic, and organic mercury) is different, but they all cause serious issues to the human
54 health and the environment. Mercury is accumulated in parts of the organism such as the liver or brain,
55 and tissues as bones. It can cause kidney failure, nervous system disorders, intellectual impairment, and
56 even death.[3] Mercury poisoning could come from different ways, for example, fish intake if the fish
57 has been in contact with a mercury environment. Although, even if a person is not exposed to high
58 doses of mercury, low doses could be accumulated in the organism and reach a high amount of the
59 metal causing important health problems.

60 Sources of mercury pollution are natural or anthropogenic, being the latter the most relevant for the
61 environment contamination. The most important sources are: use of mercury as a fungicide or herbicide
62 in agriculture, paper or electrochemical industry, and industrial or household waste, nonetheless about
63 25% of mercury pollution comes from fuel combustion and about 30% comes from industrial
64 sources.[4] Due to these contaminations, mercury is introduced into the water cycle. The predominant
65 specie in water is Hg^{2+} , very soluble, but other species of mercury are available in aqueous medium and
66 are transformed by the action of microorganisms and oxygen.[5]

67 Mercury analysis is important due to their high toxicity, and is even more important in water
68 analysis due to the continuous contamination of natural waters by industrial waste. The level of
69 mercury in water should be lower than a limit determined by the authorities. That limit depends on the
70 legislation of each country, for example, the USA Environmental Protection Agency sets a maximum
71 of $2 \mu\text{g L}^{-1}$ in drinking water.[6] For instance, this limit is lower in the specific case of the European
72 Union, where a maximum of $1 \mu\text{g L}^{-1}$ is set on the particular EU directive.[7] The World Health
73 Organization recommends that the mercury concentration in drinking water does not exceed $2 \mu\text{g L}^{-1}$.
74 [8]

75 In terms of health, a high exposure to mercury could be analyzed in blood, urine and hair samples.
76 Some mercury species are absorbed by the organism and transferred rapidly to the blood, while that
77 other species are excreted by the urine, thus, an analysis of these samples should be performed to
78 obtain information about the exposure. Mercury analysis in hair can be useful in the case of
79 environmental exposure because mercury is capable of binding to the cysteine and therefore be
80 adsorbed in the hair. For the analysis of mercury in human samples is necessary take into account the
81 half life of mercury in these samples: between 3 and 30 days in whole blood, between 3 and 20 days in
82 plasma and between 40 and 60 days in urine.[9]

83 Therefore, considering the high use of mercury in the industry, the high accumulation in the
84 environment, and the high toxicity shown, the importance of the routine analysis of different mercury
85 species in several kinds of samples it is extremely necessary.

86 **1.2. Importance of mercury electrochemical analysis**

87 The most used analytical methods for the determination of mercury are cold vapor atomic
88 absorption spectroscopy (CVAAS),[10] cold vapor atomic fluorescence spectroscopy (CVAFS)[11]
89 and also inductively coupled plasma mass spectrometry (ICP-MS).[12] These methods are well

90 established however have several significant drawbacks such as the long time consumed for the
91 analysis and the high cost of the equipment. Moreover, it is also necessary to perform several complex
92 steps which requires specialist personal. For these reasons, researchers are still searching for a method
93 that can overcome these issues and be sensitive enough to replace the more established methods in
94 routine analysis.

95 Electrochemical methods are well-placed to carry out routine analysis of mercury saving costs and
96 simplifying the process due to the easy operation of electrochemical instrumentation. Numerous
97 methods have been developed for mercury determination in different samples, especially water,
98 employing electrochemical techniques. Among the several examples of different electrochemical
99 methods reported, most of them are based on the preconcentration of mercury on the working electrode
100 and its subsequent stripping, predominating the anodic stripping voltammetry (ASV). Even the U.S.
101 Environmental Protection Agency has recommended the use of stripping voltammetry for the analysis
102 of mercury.[13]

103 Electrochemical analysis of mercury has the advantage of being sensitive, inexpensive, simple, fast
104 and can be performed with miniaturized and portable instrumentation.[14] The most significant
105 disadvantage is the memory effects due to the difficult removal of mercury from the working electrode.
106 Therefore, reusing the electrode still remains an important challenge. The key issue is to obtain a
107 working electrode that fulfills the ideal characteristics to be used in routine analysis at laboratories
108 accredited by the authorities.

109 **1.3. Scope of this review**

110 This review aims to give an overview of novel electrode materials and procedures published in the
111 literature for the electrochemical analysis of mercury in the last years. The review is focused on recent
112 work done in this field, especially considering the articles published since the year 2000 to present.

113 Moreover, voltammetric methods are mainly addressed because they are the most reported but some
114 potentiometric methods are also reviewed. A related review on the subject by Clevenger et. al. have
115 appeared in the literature in the past.[15] Therefore, the reader can readily find several recent examples
116 of electrode materials and the most important factors of the methods presented.

117 The review is organized by sections according with the different working electrode materials
118 employed in the electrochemical analysis. First, a revision of methodologies using bare electrodes
119 without modification, especially carbon and gold based (section 2) is provided. Then, the works using
120 electrodes modified with chemical or biochemical species, chemically modified electrodes (CMEs), are
121 presented (section 3). Finally, the latest trends in electrode surfaces for mercury analysis,
122 nanostructured electrodes, is introduced (section 4). This organization is intended to give the reader an
123 overview of how the development of new materials can improve the electrochemical analysis of
124 mercury.

125 The text is accompanied with several tables highlighting some information of the published works:
126 kind of electrode used, analyte detected, sample where the analyte is measured, as well as analytical
127 characteristics such as the linear range and the limit of detection (LOD). Thus, with the help of these
128 tables, the reader can compare the different works published.

129 Furthermore, most of the works commented focus in the analysis of Hg (II) in aqueous media, but
130 other works where different mercury species are determined as well as different samples (urine, soils)
131 are also reported.

132 **2. Bare electrodes**

133 Although the modification of electrodes with different substances is the most used methodology
134 for the electrochemical analysis of mercury, it is possible to perform successfully the analysis with bare
135 electrodes of specific materials.

136 **2.1. Carbon electrodes**

137 Carbon is the most typical material for the manufacture of electrodes used for electroanalysis in the
138 recent years because its low cost and low chemical reactivity. However, bare carbon electrodes do not
139 have good properties for the determination of mercury. The sensitivity of these unmodified carbon
140 electrodes is generally low and the LODs or the time of preconcentration are not acceptable for routine
141 analysis. Many articles employing this kind of electrodes were published before the year 2000, but also
142 some works have been reported recently. For instance, Muntyanu et. al. employed a carbon fiber
143 microelectrode to measure Hg (II). The use of Au (III) in the solution is essential to achieve an
144 improvement of the sensitivity and lower the LOD, achieving the detection of 1 µg/L.[16] With the
145 same electrode, Afonso et al. were able to determine methylmercury in a chloride media employing fast
146 scan voltammetry.[17] In other work, a LOD as low as 0.1 ng/L is obtained but using a macroelectrode
147 glassy carbon process vessel as a working electrode and a deposition time of 10 min.[18]

148 **2.2. Gold electrodes**

149 Gold has interesting properties: high ductility and malleability, low reactivity to typical reagents
150 and high electrical conductivity. Also, it could work as a catalyst for chemical and electrochemical
151 reactions. These features make gold a material widely used in electrochemical analysis. Its main
152 disadvantage is the cost compared to other materials like carbon.

153 For the analysis of mercury, gold is an excellent material as a working electrode with high affinity
154 for the analyte improving the preconcentration effect. Also, some metals such as mercury, arsenic or
155 lead have a process called underpotential deposition (UPD) on gold electrodes.[19] The UPD is
156 produced due to the strong interaction between the metal and the gold electrode after the reduction of
157 the ionic metal, resulting in the formation of an adsorbed layer. Due to the strong interaction and the
158 formation of the adsorbed layer, the reduction of the metal to produce the UPD occurs at a potential

159 more positive than the normal deposition. Since the first UPD process generates an adsorbed
160 monolayer, this fact only occurs when there is a low concentration of the metal, being a useful process
161 to achieve a higher sensitivity of the electrochemical method. Moreover, since the reduction potential
162 of the metal is shifted to positive potentials, it normally improves the selectivity of the method[20]. For
163 these reasons, gold as a working electrode for electrochemical analysis of mercury has been widely
164 employed.

165 The biggest issue for the analysis of mercury with gold electrodes is the structural change that
166 occurs after the stripping caused by the amalgam formed between both metals.[21,22] Some authors
167 report that mercury could not be completely stripped and the electrode could not return to the original
168 condition, thus requiring a cleaning step.[23,24] Whereas other authors report that this fact does not
169 occur when only few atoms of mercury are deposited on the gold electrode.[25]

170 **2.2.1. Gold bare electrodes**

171 Several works where authors used gold rotating disc electrode for analysis of Hg (II) in
172 different samples have been published. For example, Bonfil et al. employed these electrodes to measure
173 Hg (II) in urine after an activation of the surface between measurements, possibly to remove deposited
174 mercury. This activation improved the analytical signal until being able to detect 0.04 µg/L.[26] Also,
175 this electrode was used for the analysis of Hg (II) in seawater using potentiometric stripping,
176 comparing a rotating gold electrode with a static one. The rotating electrode exhibited higher
177 sensitivity. In this case, it was also necessary an electrochemical pretreatment to obtain a reproducible
178 signal.[27] Giacomino et al. studied different parameters and electrochemical techniques using gold
179 rotating disc electrodes for analysis of Hg (II) in water and the best results were obtained using square
180 wave voltammetry and a diluted HCl electrolytic media.[28]

181 A gold microwire electrode with a diameter of 5 μm was used for analysis of Hg (II) in
182 seawater. The adsorption of chloride on the electrode worsened the analytical signal. This issue was
183 fixed by applying a negative potential to desorb these anions, obtaining an improvement in the
184 reproducibility of the analytical signal. After observing the used electrode by scanning electron
185 microscopy (SEM), it was found that the surface was degrading with the use, probably due to the
186 stripping of the deposited mercury.[29] This kind of electrode was employed for simultaneous
187 quantification of Zn^{2+} , Cu^{2+} , Hg^{2+} , and Pb^{2+} in different water samples[30] and used in a remote system
188 for in-situ analysis.[24] The use of a heated gold microwire electrode (at 60 $^{\circ}\text{C}$) improves significantly
189 the preconcentration of mercury without the necessity of stirring.[31] The modification of the gold
190 microwire electrode with mercaptoacetic acid prevented the formation of calomel in seawater,
191 achieving the complete removal of mercury after every sweep.[32]

192 Several gold microelectrode arrays were also employed for the determination of Hg(II) in
193 different water samples, but the LOD of these electrodes is higher (1 $\mu\text{g/L}$) than most of the works
194 employing rotating gold or gold microwire electrodes.[33,34]

195 Screen-printed gold electrodes (SPAUE) have also been used for the electrochemical
196 determination of mercury. Disposable screen-printed electrodes made with gold ink, commercially
197 available, were used to analyze Hg (II) in water with a convective cell. The LOD obtained was 1.1
198 $\mu\text{g/L}$ and the low end of the linear range was 5 $\mu\text{g/L}$. The activation of the electrode was the key to
199 obtain an analytical signal with a good behavior and shape. [35]

200 As seen in the Table 1, gold bare electrodes improves significantly the LOD obtained for the
201 carbon bare electrodes, confirming the high interaction and better preconcentration of mercury on gold.

202 **2.2.2. Gold film electrodes**

203 Glassy carbon electrodes (GCE) modified with gold film were used for the analysis of total
204 mercury in table salt samples. Such samples have a high salt concentration that hinders the stripping
205 step, but this problem is solved by a medium change after the deposition step, doing the stripping in a
206 medium with a lower salt concentration. This methodology can be useful when the sample matrix is
207 complex and interferes with the electrochemical measurement.[36] In other related work, it was
208 observed that the thickness of the gold film has a relation with the analytical signal. The use of thinner
209 films worked better for low concentrations while the use of thicker films was better for higher
210 concentrations of mercury.[37]

211 Even, gold thin-film electrodes made from compact discs were employed successfully for the
212 analysis of mercury. Some authors employed stripping potentiometry and a polypropylene
213 electrochemical cell, obtaining good results in urine samples.[38] A similar electrode was used by
214 Radulescu et al. applying the method to the determination of mercury in fish after a digestion step.[39]
215 It was also employed in the determination of total mercury in certified ground water samples achieving
216 a LOD of 0.008 µg/L[40] and in shrimps samples.[41] All these methods were performed employing
217 PSA as electrochemical technique.

218 Screen-printed carbon electrodes (SPCEs) modified with a gold film were also employed, and
219 the activation step is again necessary to obtain a stable baseline achieving a LOD of 0.9 µg/L.[42]
220 Additionally, this sensor is used to determine Hg (II) in fish samples after a digestion method.[43]
221 Mandil et al. employed SPCEs modified with a gold film to analyze Hg²⁺ ions in tap water, following a
222 preconcentration step with magnetic nanoparticles (Fe₃O₄) modified with thiols. The preconcentration
223 step improved the LOD in more than one order of magnitude, finally being 0.08 µg/L.[44]

224 Although the analysis of mercury using gold or gold film electrodes could be the simplest
225 method, there are challenges ahead to make this kind of electrodes useful for the routine analysis of
226 mercury. The most important challenges lie ahead in the difficult of cleaning the surface of

227 conventional electrodes in order to be reused. Regarding disposable screen-printed electrodes, seems
228 necessary the activation of the working electrode, since it is difficult to get a stable baseline allowing
229 an easy measurement of the analytical signal. Considering the analytical characteristics presented in the
230 Table 1 is not possible to reach the conclusion that gold bare electrodes and gold film electrodes
231 present a significant difference on the analytical performance. A positive factor is that these electrodes
232 were tested successfully with different kinds of samples and used for the detection of different mercury
233 species. The UPD of mercury on gold is an electrochemical process very useful for the analysis of
234 mercury considering the sensitivity and selectivity provided by the UPD as explained previously.
235 Finally, it needs to be noted how the presence of a low and constant chloride concentration in the
236 solution appears to improve the analytical signal when gold electrodes are used, although a high
237 concentration of these ions may present issues in the electrochemical measurements.

238 **2.3. Other materials**

239 Other bare electrodes, which are not common in the literature as carbon and gold, were used for
240 electrochemical analysis of mercury.

241 Boron-doped diamond (BDD) electrodes have been used obtaining a higher sensitivity and
242 lower background current compared to GCE.[45] A positive effect on the analytical signal due to
243 nitrate and chloride ions was observed with this electrode, but the formation of calomel on the surface
244 may be detrimental and only 2 $\mu\text{g/L}$ of LOD was obtained.[46] When adding a small concentration of
245 ionic gold to the solution, the formation of calomel on the surface does not occurs, and the analytical
246 signal is shifted to more positive potential because the mercury is reduced more easily. With this
247 methodology, a concentration as low as 0.05 $\mu\text{g/L}$ of Hg (II) was measured. Several deposition
248 processes of gold and mercury may be happening, probably being the reason why the analytical signal
249 is wider.[47] There is a significantly improvement between these two methods employing the same
250 electrode.

251 Iridium microarray electrodes have also been used for Hg(II) determination, although a
252 electrolytic medium containing Cl^- ions has a negative effect in the electrode and, therefore, in the
253 sensitivity (LOD of $0.6 \mu\text{g/L}$) and reproducibility.[48] Other work with iridium nano-band arrays
254 plated with a gold film has shown its applicability in a chloride medium for the determination of
255 mercury in several kinds of samples, but the sensitivity obtained with this method is lower.[49]

256 The oxidation of I^- ions at screen-printed silver electrodes (SPAgE) has been used for the
257 indirect determination of Hg^{2+} ions. The analytical signal decreases in presence of increasing mercury
258 concentrations. The method was applied to cosmetic samples.[50] This methodology showed a high
259 LOD ($98 \mu\text{g/L}$), not useful for routine analysis.

260 A bismuth film electrode was employed for simultaneous determination of Hg^{2+} , Cd^{2+} , Pb^{2+} ,
261 Zn^{2+} and Cu^{2+} in tap water. Authors claim to be able to analyze metals re-oxidized at potentials more
262 negative and more positive than Bi using in-situ deposited Bi film.[51] Similar to the previous work
263 was the modification of a GCE with antimony film.[52] This film showed an excellent performance in
264 more acidic media and it worked better for mercury determination than the bismuth film electrode,
265 even though the LOD of both methods were similar (0.50 and $0.39 \mu\text{g/L}$) with the same deposition
266 time.

267 For these materials, the interaction between mercury and the electrode material is not as intense
268 as gold; thus, the preconcentration can normally be lower in this type of materials. The LOD and the
269 linear range obtained for these electrodes (Table 1) shows that, in the published conditions, they are not
270 appropriate for routine analysis. Furthermore, platinum and diamond present the same drawback as
271 gold, its high price.

272 **3. Chemically modified electrodes**

273 Compared to bare electrodes, the electrodes modified with chemical and biochemical
274 compounds may have advantages such as improved sensitivity and selectivity in the electrochemical
275 determination of several analytes. An application of chemically modified electrodes (CME) is the
276 analysis of heavy metals at trace levels. These methods are based on the interaction of a functional
277 group of the compound employed in the modification of the electrode with heavy metals. Normally,
278 this interaction is selective or only occurs with some metals, which could be discriminated depending
279 on the potential employed for their electrochemical measurement.

280 Some of the compounds used to modify electrodes employed in the electrochemical analysis of
281 mercury are polymers, several complexing agents, DNA and ion imprinted polymers (IIP).

282 **3.1. Polymer modified electrodes**

283 One of the most used materials for the modification of electrodes is conductive polymers. These
284 polymers typically contain groups that bind selectively to mercury, or can function as ion exchangers.
285 Due to the polymeric character, they have a high number of reactive sites, allowing the
286 preconcentration of the analyte on the electrode surface. Some characteristics of these polymers are
287 good electrical conductivity or the ability to work as an electrocatalyst. Between the most typical
288 strategies to modify electrodes can be found: the electropolymerization onto the working electrode
289 from the monomer, or the simple adsorption of the polymer on the electrode surface. Different coatings
290 are generated using different conditions, which can lead to more suitable analytical characteristics for
291 each specific application. Several polymers have been used on diverse working electrodes for the
292 electrochemical determination of mercury.

293 Some of these polymers are functionalized with groups able to bind Hg(II), either in cationic
294 form (Hg^{2+}) or anionic form in the presence of chlorides (HgCl_3^- and HgCl_4^{2-}). The ability of these
295 polymers to bind Hg(II) allows its preconcentration at the electrode surface achieving a more sensitive

296 detection. GCE was modified with a polymer of ethylenediamine tetra-N-(3-pyrrole-1-yl)-
297 propylacetamide. This polymer has several pyrrole rings that confer a high capacity to bind Hg(II) and,
298 to a lesser extent, other metals such as Cu(II), Pb(II) and Cd(II). Preconcentration is performed at open
299 circuit for the determination of Hg(II) and Cu(II) in water samples.[53] A film of methyl-red
300 electropolymerized on GCE was employed for the analysis of Hg (II) in lake water. Hg(II) is adsorbed
301 onto the methyl-red film and is reduced using -1.2 V during 10 minutes. The LOD obtained was very
302 low, 0.009 µg/L, being the polymer-modified electrode with the lower LOD reported.[54] This
303 improvement of the sensitivity may be due to the high diffusion of chemical species to the polymeric
304 film reaching a high preconcentration effect. Rahman et al. employed a GCE modified with a
305 conductor polymer and EDTA, both the polymer and the EDTA can complex mercury ions, achieving
306 the possibility of the sensitive determination of Hg²⁺ obtaining a LOD of 0.1 µg/L.[55] Platinum
307 electrodes were modified with poly(3-hexylthiophene) for the determination of Hg(II) in fish
308 samples.[56] SPCEs have also been modified with conductive polymers for the determination of
309 Hg(II). Electropolymerization by cyclic voltammetry of aniline and 2-2'-dithioaniline was carried out
310 on the SPCEs. With this system, Hg(II) was preconcentrated on the electrode surface and was
311 measured electrochemically by ASV. However, the LOD obtained is not useful for real water
312 samples.[57]

313 Other polymers having an ion-exchanger effect, either cationic or anionic, are able to
314 preconcentrate Hg(II). The structure of these polymers have an ion with a labile bond that may be
315 exchanged with a Hg(II) ion forming a stronger bond, achieving the preconcentration of Hg(II) in the
316 surface of an electrode modified with this polymer. Electropolymerized polyviologen has been used in
317 the determination of Hg(II) in tap and seawater. After modifying a GCE with polyviologen, the
318 electrode was able to exchange mercuric anions such as (HgCl₃)⁻ and (HgCl₄)²⁻, which are complexes
319 formed in a medium containing chloride. This capacity to exchange anions improves the

320 preconcentration and the sensitivity of the method. A LOD of 0.3 $\mu\text{g/L}$ was obtained. The regeneration
321 of the electrode was done with a solution containing a high concentration of chloride ions.[58]

322 Other polymer-based electrodes are the sol-gel electrodes. These electrodes are made of a
323 mixture of gel and carbon paste. Gold electrodes have been modified with functionalized sol-gel for the
324 analysis of mercury.[59] A sol-gel carbon composite electrode was modified with poly(vinylsulfonic
325 acid) (PVSA). PVSA is an anion exchanger able to preconcentrate mercuric anions onto the electrode
326 surface. The preconcentration is done at open circuit. The regeneration of the electrode is performed
327 with a 3 M NaCl solution. The use of PVSA is crucial for the sensitive analysis of mercury because the
328 unmodified electrode response is very low.[60] Between the sol-gel electrodes are also the sonogel
329 electrodes, which are prepared by applying a high-energy ultrasonic bath to the mixture to fabricate the
330 electrode. It involves the generation of a gel with special features such as high density, fine texture and
331 a homogenous structure. An example of sonogel electrode for mercury analysis is presented in the
332 literature. This electrode is modified with electropolymerized 3-methylthiopene. This polymer can
333 accumulate Hg(II) on the electrode at open circuit, then the electrochemical analysis is performed using
334 DPASV. Several modifiers of the sonogel electrode were employed, and the most sensitivity was
335 obtained with 3-methylthiopene.[61] However, the LODs for the sol-gel electrodes were higher than
336 other polymeric electrodes reported for the analysis of mercury.

337 **3.2. Electrodes modified with complexing agents**

338 Other materials widely used in the modification of electrodes for the determination of heavy
339 metals, in particular mercury, are compounds capable of forming complexes with metal ions. Species
340 possessing this property are diverse, usually have a functional group that performs the function of
341 complexing.

342 GCE modified with monolayers of p-tert-butylthiacalix[4]arene (TCA) has also been used for
343 determination of Hg(II) in tap, lake and river water samples. A more sensitive method is obtained
344 modifying with these monolayers than using bare GCE or GCE modified with a direct coating, being
345 able to detect 0.1 $\mu\text{g/L}$ of Hg(II). The improvement of the sensitivity may be due to an higher
346 preconcentration of mercury ions on the monolayer, resulting in a higher stripping signal.[62]
347 Manganese phthalocyanine (MnPht), macrocyclic with a high thermal and chemical stability, has been
348 used to modify GCEs and employed for the selective analysis of Hg^{2+} cations. MnPht also binds Ag^+
349 but the measurement potential allows a high selectivity on the method.[63] Also, GCEs have been
350 modified with other macrocycles containing complexing groups such as calix[4]arene containing
351 benzothiazole,[64] or dithia-podands.[65] Nonetheless, considering the analytical performance
352 obtained by these works (Table 2), the modification of electrodes with macrocycles does not seem a
353 good methodology for the analysis of mercury because the sensitivity is not suitable for routine
354 analysis.

355 More complex systems have also been employed such as the fabrication of carbon ionic liquid
356 electrode (CILE) modified with aminoacids and gold nanoparticles (AuNPs). The fabrication is carried
357 out mixing a graphite paste, ionic liquid and AuNPs, and then the electrode surface is modified with the
358 aminoacid of interest. Carboxyl groups of aminoacids are able to complex Hg^{2+} ions. Three
359 aminoacids thiolated were used because they may be easily attached to gold nanoparticles: cysteine,
360 glutathione and homocysteine. The best results for the analysis of Hg^{2+} in tap and waste water samples
361 were obtained using cysteine, achieving a LOD of 0.46 $\mu\text{g/L}$.[66]

362 Carbon paste electrodes (CPEs) have been modified with several species able to complex and
363 preconcentrate Hg (II) on the electrode surface. This is the case of nitro benzoyl
364 diphenylmethylenphosphorane (N-BDMP), which also form Cd(II) complexes, so it was used for the

365 simultaneous determination of Cd(II) and Hg(II) in different samples.[67] Other species mixed in
366 carbon paste for mercury determination are cyclodextrins[68].

367 Different silica species functionalized with complexing groups have been employed for the
368 modification of glassy carbon and carbon paste electrodes. For example, mesoporous silica[69] or silica
369 thin film[70] functionalized with thiols groups, which are able to preconcentrate mercury ions. Also, it
370 was reported the use of silica nanoparticles with a Schiff base[71] or mesostructured silica
371 nanoparticles and a derivative of 5-mercapto-1-methyltetrazole, complexing agent for Hg^{2+} ions. Silica
372 nanoparticles improve the preconcentration of Hg^{2+} , although the use of 100 ml of sample is an
373 important disadvantage comparing with other published methods.[72]

374 Gold electrodes modified with complexing agents have also been reported in the literature. For
375 example, a gold disk electrode modified with 2-mercaptobenzimidazole[73], gold micro-/nanopore
376 arrays modified with 2-mercaptobenzothiazole,[74] or a gold film electrode modified with Nafion and
377 DTPA for the determination of methylmercury.[75] It is worth noting the good analytical performance
378 of the gold nanopore array obtaining a low LOD (0.004 $\mu\text{g/L}$) and a linear range over two orders of
379 magnitude. Due to the high porosity of the electrode structure, the electrode has a larger area impacting
380 positively on the mercury preconcentration.

381 Other electrodes employed for the determination of mercury are the graphite tube electrodes
382 modified with 2-mercaptobenzothiazole[76] or 2-mercaptobenzoxazole.[77] This electrode was
383 employed in a flow system (as continuous flow and flow injection analysis) for the continuous analysis
384 of Hg^{2+} ions. The regeneration was performed by the application of a positive potential during 60s in a
385 washing buffer to eliminate mercury from the electrode. Although this system worked for the
386 determination of Hg^{2+} , the LOD is not enough for routine analysis and the time of preconcentration is
387 high (600 s).

388 Disposable thick film graphite electrodes modified with Au(III)/pyrrolidinedithiocarbamate
389 (PDC) were used for mercury analysis. The PDC works as a complexing agent for mercury ions, and
390 the Au(III) could be able to form a gold film in-situ after the electrochemical reduction step, bringing
391 the best features of each system to achieve a high sensitivity and a low LOD (0.005 $\mu\text{g/L}$).[78] As
392 mentioned, Hg(II) in presence of chloride ions form anionic complexes that are able to bind to the
393 protonated amino groups of chitosan. This feature has been used with screen-printed carbon electrodes
394 modified with chitosan for the preconcentration of Hg (II) and its electrochemical measurement.[79]
395 Also, SPCEs modified with a chelating resin containing dithiocarbamate groups have been reported for
396 the determination of Hg^{2+} . [80]

397 Differences in the LODs and in the linear range for the electrodes modified with complexing
398 agents (Table 2) depend mainly on the compound used as a modifier and the accumulation time.
399 Articles have been published where GCEs, SPCEs and other electrodes present both low and high
400 LODs. The publication of a comparative study between these electrodes using the same modifier and
401 similar conditions would be interesting.

402 **3.3. DNA modified electrodes**

403 One of the materials employed in chemically modified electrodes for the selective
404 determination of Hg^{2+} ions is DNA. The ability of DNA strands to have different structures depending
405 on their composition is an advantage that can be used for the selective detection of several analytes.
406 Hg^{2+} binds selectively to DNA strands containing several thymines in the structure by means of
407 binding to T-T mismatches, stabilizing the hybridization of the double strand. Strands that bind
408 selectively to mercury are called mercury specific oligonucleotides (MSO). Authors claim that other
409 cationic metals such as Ag^+ , Cu^{2+} , Ni^{2+} , Fe^{2+} , etc. do not show a stabilizing effect of T-T mismatches,
410 and therefore the selectivity for Hg^{2+} ions is high.[81]

411 A mechanism employed in some of the published works for the determination of mercury using
412 poly-thymine oligonucleotides is the preconcentration of Hg^{2+} on the double strand and their
413 subsequent reduction and stripping. Wu et al. modified a gold electrode with an oligonucleotide with
414 several thymines. After 15 minutes at open circuit, the Hg^{2+} is preconcentrated in the surface of this
415 electrode due to the T-Hg-T interaction with the oligonucleotide and is measured electrochemically by
416 ASV.[82] A gold disk electrode was modified with a DNA strand that is bound by hybridization to
417 another strand attached to a gold nanoparticle. This nanoparticle has several strands that can selectively
418 bind Hg^{2+} due to the structure with several thymines. With this system, the sensitivity is very high
419 because each strand that modifies the electrode can preconcentrate several Hg^{2+} ions. After this
420 preconcentration, an electrochemical measurement is performed consisting in reducing Hg^{2+} by square-
421 wave voltammetry using a cathodic sweep.[83] The LODs for these methods were 0.012 $\mu\text{g/L}$ and 0.1
422 $\mu\text{g/L}$, respectively, but the accumulation time was long (15 min and 60 min). In the other hand,
423 although no information about the regeneration of the electrodes was given, it probably needs to be
424 mechanically polished and freshly modified with DNA strands.

425 Another mechanism widely used to detect Hg^{2+} employing DNA strands is the alteration of the
426 distance from the electrode of a redox label due to a conformational change, dissociation or
427 hybridization of DNA strands. For example, gold disk electrodes were modified with self-assembled
428 monolayers and a MSO initially hybridized with a ferrocene-labeled DNA strand. If the solution
429 contains Hg^{2+} ions, it can bind to the MSO and the ferrocene-labeled strand moves away the electrode.
430 Therefore, the analytical signal, which corresponds to the electrochemical measurement of ferrocene,
431 decreases with the concentration of Hg^{2+} in the sample (signal-off detection). Good performance was
432 achieved with this methodology, reaching a LOD of 0.012 $\mu\text{g/L}$, and a linear range of over three orders
433 of magnitude. Furthermore, the regeneration of the electrode could be achieved washing with ascorbic
434 acid solution for 1 h and a posterior hybridization with the ferrocene-labeled strand.[84] Zhuang et al.

435 used a similar system, but with strands able to form hairpin structures. When Hg^{2+} ions are not present
436 in solution, the strand is forming a structure that leaves the ferrocene out of the electrode surface,
437 inhibiting the electron transfer. On the contrary, when there are Hg^{2+} ions in solution, the MSO binds to
438 the ion and the strand structure positions the ferrocene close to the electrode, enhancing the electron
439 transfer. Therefore, the signal increases with the concentration of Hg^{2+} in solution (signal-on detection).
440 The regeneration of the electrode was achieved after immersion for 10 min in a Tris-HCl pH 7.4
441 solution containing 1 M NaCl and 1 M I^- . [85] A chip with gold on silver electrodes was modified with
442 a MSO initially hybridized with a DNA strand. A redox mediator, hexaminruthenium (III) chloride
443 (RuHex), which can bind to the double strand, is employed. When there are Hg^{2+} cations in solution,
444 the MSO binds this metallic ion and the double strand is not formed, therefore, the amount of RuHex is
445 lower than when there are not Hg^{2+} ions in solution, and the analytical signal decreases (signal-off). [86]

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

449 Other innovative systems employing DNA strands have been used for the determination of
450 Hg^{2+} . For example, a system where after binding Hg^{2+} ions, DNA strands modified with ferrocene and
451 glucose oxidase are placed very close and work as a electric relay with the gold electrode achieving the
452 possibility of sensitive electrochemical measurement of Hg^{2+} , with a LOD of 0.02 $\mu\text{g/L}$ and a linear
453 range of four orders of magnitude. [90] The electrocatalytic activity of the hemin group towards the
454 reduction of H_2O_2 has been exploited in a DNA system for the specific and sensitive determination of
455 Hg^{2+} . The hemin group is bound to the DNA probe after the reaction of Hg^{2+} with a polythymine
456 capture probe. [91] Park et al. used a hairpin-DNA adsorbed on the surface of a ITO-coated glass
457 modified with reduced graphene. After the reaction of the DNA strand with Hg^{2+} ions, the change of
458 the electrode surface is measured by electrochemical impedance spectroscopy (EIS). [92]

459 Although most of the LODs obtained with DNA-modified electrodes are below 0.5 $\mu\text{g/L}$ and
460 have satisfactory sensitivity for use in routine analysis, other aspects as the long analysis time,
461 especially when performing a hybridization reaction, is a very significant disadvantage with respect to
462 other kinds of modified electrodes. Moreover, these electrodes are only applicable to Hg^{2+} because it is
463 the specie that binds to the DNA strands.

464 **3.4. IIPs modified electrodes**

465 Molecularly imprinted polymers (MIP) are synthetic receptors capable to bind specifically to a
466 given analyte. These materials have a high capacity for preconcentration, high selectivity and often
467 show high stability. MIP technology can also be used for the preparation of polymers containing ions
468 selective sites. In this specific case, the right term used is ion-imprinted polymers (IIP). The method of
469 fabrication is generally performed using a monomer in the presence of the ion of interest and the
470 polymerization is carried out, either chemically by use of an initiator or electrochemically applying an
471 electrical potential at an electrode. After the polymerization, the ion is removed from the polymer
472 through a washing solution leaving cavities (imprinted sites) on the polymer structure with similar
473 shape and size to the employed ion.

474 Carbon paste electrodes were modified with a IIP for Hg^{2+} . This IIP was synthesized in
475 presence of Hg^{2+} from 4-vinylpyridine, a cross-linker (ethylene glycol dimethacrylate) and an initiator
476 (2,2-azobisisobutyronitrile). After the polymerization and washing steps, the carbon paste was modified
477 with the IIP to fabricate the electrode. Hg^{2+} is preconcentrated on the electrode at open circuit (15
478 minutes). Enhanced sensitivity is observed using the IIP electrode compared to use an electrode with a
479 no specific IIP or without using polymer (only CPE). The method was employed to analyze Hg^{2+} in
480 water samples, and a LOD of 0.1 $\mu\text{g/L}$ was calculated.[93]

481 Another example is the modification of GCE with a nanohybrid of AuNPs/SWCNTs and a
482 specific IIP for Hg^{2+} ions, poly(2-mercaptobenzothiazole). The nanohybrid material provides a high
483 number of surface sites to enhance the total effective imprinted sites. After preconcentration at open
484 circuit for 12 minutes, Hg^{2+} is measured electrochemically by DPASV. A sensitive and selective
485 method for Hg^{2+} was developed and a LOD of 0.016 $\mu\text{g/L}$ was achieved. [94] Also, recently, the
486 modification of GCE with multi-walled carbon nanotubes (MWCNTs) and a IIP for Hg^{2+} has been
487 reported, with a higher limit of detection (1 $\mu\text{g/L}$) but a shorter accumulation time (5 min).[95]

488 Electrodes modified with IIPs present very promising characteristics such as an high selectivity
489 and good sensitivity, though with the disadvantage that to obtain low LODs it is necessary a large
490 accumulation time, usually superior to 10 min. With the improvement of materials and the development
491 of new imprinted polymers, it will be easier to get an electrode with better performance and shorter
492 time of analysis.

493 **3.5. Others**

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

496 The preconcentration of Hg (II) by means of the interaction of the metallic ion and the
497 hydroxide groups of silica particles have also been reported. Carbon paste electrodes were modified
498 with silica particles and applied to the determination of mercury in water. Nevertheless, a low
499 sensitivity compared with other methods is obtained with this electrode.[96]

500 Tchinda et. al. employed thiol-functionalized porous clay heterostructures (PCHs) from
501 mesoporous organosilica. This material was deposited as a thin film on GCE and after accumulation at
502 open circuit, Hg (II) was electrochemically determined by DPASV. The wide open porous structure

503 provides an improvement in the ability of preconcentration resulting in high sensitivity (LOD of 0.1
504 $\mu\text{g/L}$). These structures form robust thin films without the need of using polymers.[97]

505 Clay and mica minerals have also been used for preconcentration of mercury ions in chloride
506 media due to the ability to exchange anions, for example the modification of CPEs with
507 vermiculite[98], montmorillonite[99] or biotite.[100] The modification of this kind of minerals with
508 complexing groups have also been reported.[101,102] However, the analytical performance of the
509 electrodes modified with these minerals is not good enough for routine analysis because is not possible
510 to detect levels of Hg^{2+} in water below the values set in the legislation (see Table 2).

511 Metallic ions can inactivate some enzymes, characteristic exploited by Rodriguez et al.
512 employing a SPCE modified with urease. Hg^{2+} ions hinder the enzymatic reaction, which is measured
513 by an amperometric assay.[103] The modification of a platinum electrode with a enzyme clay gel with
514 several enzymes (glucose oxidase, invertase and mutarotase) was employed by the indirect
515 determination of several mercury species (inorganic mercury, methyl and phenylmercury). Interference
516 by silver was important because it also inhibits the enzymatic reaction.[104] In spite of being
517 innovative methodologies, a limit of detection fairly high (8.5 and 2 $\mu\text{g/L}$, respectively) was obtained
518 for both cases. Besides, the necessary time of incubation for the enzymatic reaction is very long.

519 Water hyacinth is a plant able to uptake heavy metal ions, characteristic that have been used for
520 the determination of Hg (II) after the modification of CPEs with fibers of this plant.[105]

521 Although CMEs may have some potential in the selective electrochemical analysis of mercury,
522 there are important issues to its application in routine analysis, considering the low sensitivity that most
523 of these electrodes have, and the high preconcentration time necessary to achieve the detection of trace
524 amounts of mercury. In the case of DNA as electrode modifier, it is necessary to perform the reaction

525 of hybridization between DNA strands, reaction that takes a high time and needs to be done in specific
526 and careful conditions.

527 **4. Nanostructured electrodes**

528 An important trend in recent years is Nanotechnology. Nanomaterials have excellent and novel
529 properties different from macroscopic materials due to two main reasons: they behave according to the
530 laws of quantum chemistry instead of the laws of classical physics, and have a high surface area being
531 sensitive to surface processes.

532 Therefore, due to the novel characteristics of nanomaterials, they are being widely used in
533 electrochemical analysis. Some of the nanomaterials properties have a significant effect in
534 electrochemical analysis such as: the high surface area of these materials that increases the electrode
535 area, the ability to catalyze the electron transfer, the high adsorption power of some of these
536 nanomaterials and the ability to modify its surface with compounds of interest such as biomolecules.

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

539 **4.1. Metal nanoparticles**

540 Metal nanoparticles are clusters formed by between 100 and 1000 atoms with nanometric
541 dimensions and its physical and electronic properties generally depend on their size. In the field of
542 electroanalysis, the use of metal nanoparticles was popularized in the recent years due to the
543 advantages offered over the use of unmodified electrodes. Some of these advantages are: improved
544 electron transfer between the electrode and the electroactive substances, catalysis of some
545 electrochemical reactions decreasing the overpotential required for the reaction to occur and therefore
546 the process behaves in a more reversible way.[106] The major drawback of metal nanoparticles is their

547 higher reactivity compared to macroscopic material[107]. This may be a disadvantage for a specific
548 application. Due to all the advantages offered, the use of metal nanoparticles is present in a large
549 number of applications of electrochemical analysis.[108]

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

553 A special case of metal nanoparticles is gold nanoparticles, as they have some advantages such
554 as an easy surface modification and high biocompatibility. Its surface chemistry allows to bind thiol
555 groups very effectively. Gold nanoparticles have been used as electrode material for the analysis of
556 several analytes of interest, including mercury. Electrode modification with gold nanoparticles can be
557 done by adsorption from colloidal gold solutions[110] or could be electrochemically deposited
558 controlling the size and dispersion.[111]

559 GCEs have been modified with gold nanoparticles for the determination of $\text{Hg}(\text{II})$ in different
560 samples such as drinking water, ocular gel and sediments using ASV. In comparison with gold and
561 gold film electrodes, lower LODs and better repeatability were obtained with GCE modified with
562 AuNPs.[112] The same authors used the mentioned tool for the analysis of other certified samples such
563 as ashes, sea lettuce, tuna fish and wastewater.[113] Using this same electrode, the analysis of
564 methylmercury and inorganic mercury was achieved with a methodology involving first the
565 determination of inorganic mercury and after an acid digestion in a microwave oven, the determination
566 of total mercury as inorganic mercury.[114] Other authors have also used GCEs employing different
567 electrochemical techniques to modify the electrode with AuNPs. Hezard et al. synthesized AuNPs on
568 the electrode by applying cyclic voltammetry to a solution containing HAuCl_4 and then, determined Hg
569 (II) by ASV. The best results were obtained with a high density coating of small size gold
570 nanoparticles.[115] The same authors performed a similar experiment but using more techniques for

571 the deposition of AuNPs: cyclic voltammetry, chronoamperometry and potentiostatic double-pulse.
572 Chronoamperometry was the technique obtaining the best results which corresponded to the smaller
573 nanoparticles generated with a high density of particles on the electrode surface.[116] Thus, it appears
574 that the density and size of gold nanoparticles have an important influence on the analytical signal of
575 Hg (II). As shown in the Table 3, the LODs for all these works were below 0.2 $\mu\text{g/L}$, however, there
576 are some distinction between them. This difference may be due to the several methodologies employed
577 for the generation of AuNPs, and the different characteristics of the AuNPs generated.

578 Analysis of Hg(II) using a GCE modified with PEDOT/AuNPs did not present an improvement
579 compared to the simpler GCE/AuNPs electrode. Although PEDOT has sulfur atoms that may interact
580 with metals such as mercury, this effect seems not to influence the determination of Hg (II).
581 Furthermore, an electrochemical treatment and the use of EDTA is necessary after the measurement to
582 remove the mercury deposited on the electrode.[117]

583 Commercial screen-printed carbon electrodes modified with gold nanoparticles have also been
584 used for the analysis of Hg (II) in rain, river and industrial water samples.[118] A higher sensitivity and
585 lower LODs (0.8 $\mu\text{g/L}$) than using commercial screen-printed gold electrodes were obtained.[35] Such
586 electrodes have been successfully employed to analyze mercury in indoor dust samples after an
587 ultrasonic extraction method.[119,120]

588 Another system employing gold nanoparticles for electrochemical analysis of mercury is gold
589 nanoelectrode ensembles (GNEE). This system consists in the modification of a gold electrode with a
590 three dimensional network of silicate and the addition of gold nanoseeds (5-6 nm) to this network. The
591 fabricated electrode achieved to measure 0.1 $\mu\text{g/L}$ of Hg(II) using ASV technique, and was able to
592 detect simultaneously Hg(II), As(III) and Cu(II).[121]

593 Gold nanoparticles seem to be an important electrode material for electrochemical analysis of

594 mercury. The UPD of mercury on gold is an adsorption process that depends largely on the electrode
595 area, therefore the use of AuNPs, which have a high surface area, improves the behavior of these
596 processes and significantly enhance the analytical response of mercury. Moreover, the deposition of
597 mercury on AuNPs is reversible at low concentrations, as shown in some of the reviewed works,
598 eliminating the memory effects and achieving a renewable electrode surface. Electrodes made with
599 gold nanoparticles for the determination of mercury have all the advantages of the macroscopic
600 material and also some of their issues, and therefore is one of the most promising materials for
601 electrochemical analysis of mercury. Although it is necessary to consider that the signals obtained for
602 Hg(II) in these electrodes tend to occur at a potential where there is a wide baseline in the i-E curve. No
603 clear explanation for this fact has been published to date. This fact is certainly a disadvantage for the
604 simplicity of the analysis because it is necessary to do a blank subtraction to obtain good visual signals
605 and easier to measure.

606 **4.2. Carbon nanomaterials**

607 Carbon nanomaterials have been extensively used in electrochemical analysis. These
608 nanomaterials have significant adsorption ability, and mercury can preconcentrate over the electrode
609 surface, achieving a higher sensitivity when compared with non-modified electrodes.

610 The carbon nanomaterial most widely used in the recent years is carbon nanotubes. Carbon
611 nanotubes are cylindrical structures with a diameter of a few nanometers. It can be considered as a
612 single sheet of graphite rolled on itself. There are different types of carbon nanotubes, the main two
613 are: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). The most important
614 properties that exhibit these nanomaterials are: high electrical conductivity, high mechanical strength
615 and high thermal conductivity. The interest held by carbon nanotubes in their application to
616 electrochemical analysis is mainly due to improvements in the performance of the modified electrode

617 such as: higher reversibility of processes for increasing the velocity of electron transfer[122], reduction
618 of overpotentials achieving a higher selectivity[123] and increased sensitivity due to the increased
619 electrode surface area. A negative effect of the modification of electrodes with carbon nanotubes could
620 be the increment of the capacitive current, since this current also increases with the electrode area, and
621 sometimes this effect can be negative to the analytical signal.[124]

622 Several kinds of electrodes have been modified with carbon nanotubes for the electrochemical
623 determination of mercury.

624 The study performed by Ly et al. showed a higher sensitivity for Hg(II) with a carbon nanotube
625 paste electrode than with other carbon electrodes such as carbon fiber, glassy carbon or carbon paste in
626 the same conditions.[125] The increased sensitivity is clearly due to the higher surface area presented
627 by this electrode compared to the other carbon electrodes.

628 CPEs have been modified with carbon nanotubes for the analysis of Hg(II). The addition of
629 chitosan crosslinked with glutaraldehyde (GA) to carbon paste improves the sensitivity of the analysis
630 of Hg (II), which could be due to some complexing power of the chitosan-GA system to the
631 Hg(II).[126] In another work, MWCNTs-CPE is also modified with a Schiff base. This compound can
632 form a complex with metal ions, and employing the modified electrode, the simultaneous determination
633 of Pb (II) and Hg (II) is performed in several samples as tuna fish, shrimps, tobacco and human teeth.
634 Only the use of carbon nanotubes improves the analytical signal, but the effect of the modification with
635 the Schiff base is much higher, achieving a LOD of 0.18 $\mu\text{g/L}$, lower than 0.48 $\mu\text{g/L}$ of the previous
636 example.[127]

637 Yi modified a GCE with MWCNTs to analyze Hg (II) in lake water samples. The use of
638 MWCNTs produced a significant improvement compared to bare GCE. Furthermore, the addition of KI
639 improves the stripping peak of Hg(II), as well as avoids the interference of Cu (II) due to CuI_2

640 precipitation.[128] The covalent functionalization of CNTs with Fast Violet B and subsequent
641 modification of a GCE allows the selective determination of Hg(II) because Fast Violet B binds
642 specifically to Hg (II).[129] Comparing the low levels of the linear range, the electrode modified with
643 Fast Violet B reach a value lower than three orders of magnitude than the electrode without
644 modification. The chemical interaction between the modifier and mercury, improves the
645 preconcentration effect and therefore, higher sensitivity is obtained.

646 Screen-printed electrodes made of carbon, bismuth and carbon nanotubes ink were used for the
647 determination of Hg(II) in tap water and human hair. The addition of Bi and CNTs to the carbon ink to
648 fabricate the screen-printed electrode, improves the sensitivity separately and especially together.[130]
649 Nguyen et al. modified a silicon chip with an array of Poly(1,8-diaminonaphthalene) (PDAN), a
650 conductive polymer, and carbon nanotubes. A selective adsorption of Hg²⁺ at open circuit is produced
651 and the electrochemical determination is carried out, but the sensitivity obtained is inferior than for
652 other electrodes.[131]

653 Other carbon nanostructured material that has been employed in the analysis of Hg (II) is
654 carbon black, material with a high number of surface defects. This material has high sensitivity to the
655 measurement of thiol groups, which form a stable complex with Hg (II). Paleschi et al. developed an
656 amperometric sensor employing screen-printed electrodes modified with carbon black for the indirect
657 analysis of Hg (II) in drinking water. The sensor responds to the oxidation of thiols and the analytical
658 signal is lower when Hg (II) is present in the sample.[132]

659 Heated screen-printed electrodes with carbon nanoparticles (SPCNPsE) were employed for
660 heavy metals determination in seawater. The use of heated electrodes increased the mobility of ions
661 achieving a faster deposition and a higher sensitivity. A LOD of 1 µg/L was obtained.[133]

662 The use of carbon nanomaterials in the electrochemical determination of mercury presents some

663 important improvements in comparison to the unmodified electrodes. The increased surface area of the
664 working electrode increases the sensitivity and the measurement of low amounts of mercury is
665 achieved. However, where carbon nanomaterials stand out is when accompanying the modification
666 with other selective compounds resulting in a higher power of preconcentration over the electrode and
667 a higher sensitivity. Although graphene has excellent properties for use in electrochemical analysis, the
668 modification of electrodes with only graphene or its derivatives has not been tested for mercury
669 determination. In the published works the modification of electrodes with graphene has always been
670 accompanied with species that can interact with mercury as gold nanoparticles or species containing
671 functional groups.

672 **4.3. Nanohybrid materials**

673 Although the use of single nanostructured materials could present advantages to the
674 macroscopic material, researchers are still looking for new ways to enhance these characteristics with
675 innovative technologies. One such technology is the use of hybrid nanostructured materials. These
676 hybrid systems can have properties that amplify those of the single nanostructured materials.

677 There are several methodologies for modifying electrodes with nanohybrid materials, similar to
678 the modification with single nanomaterials, which depend largely on the kind of working electrode and
679 the materials used. Several nanohybrid materials have been used in different applications of
680 electrochemical analysis, and also in the determination of mercury.

681 GCEs were modified with a nanohybrid of AuNPs/CNTs. The nanoparticles were chemically
682 synthesized on the CNTs by citrate reduction in a microwave oven. After synthesizing the nanohybrid,
683 the electrode was modified by placing a drop on its surface until dryness. Using this nanohybrid
684 material, the determination of Hg(II) with a high sensitivity is achieved (LOD of 0.06 $\mu\text{g/L}$).[134]

685 Gong et al. modified GCE with a nanohybrid consisting of gold and platinum nanoparticles and
686 3,3',5,5'-tetramethylbenzidine (TMB) nanofibers. The nanoparticles are homogeneously distributed in
687 the nanofibers forming a three-dimensional nanoporous network. Analysis of Hg (II) is carried out with
688 ASV obtaining great sensitivity and reaching a LOD of 8 ng/L.[135] The same authors also modified a
689 GCE with a nanohybrid consisting of graphene and gold nanoparticles. The composite nanohybrid
690 improves the electronic transfer and the sensing behavior, reaching LODs for Hg(II) of 6 ng/L (120s of
691 deposition time) and 0.6 ng/L (300s of deposition time). This fact is due to the combination of the
692 excellent properties of graphene (unique electrical conductivity and high surface area) with the
693 properties of AuNPs (high catalytic activity and good conductivity). Graphene/AuNPs nanohybrid
694 showed a higher sensitivity than a nanohybrid formed by CNTs/AuNPs.[136]

695 Graphene oxide and gold nanoparticles have also been used to modify glassy carbon electrodes,
696 with the help of an ionic liquid, employed for the determination of Hg (II) in drinking and
697 environmental water samples. The modification with the nanohybrid material brings to the electrode an
698 highly enhanced electron conductive nanostructured membrane and a large electroactive surface
699 area.[137]

700 Screen-printed carbon electrodes have also been modified with nanohybrid materials such as
701 graphene/AuNPs and MWCNTs/AuNPs. The screen-printed electrodes were modified with carbon
702 nanomaterials by means of physical adsorption, and then the AuNPs were generated applying a
703 constant current to a solution of HAuCl₄. The use of nanohybrid materials improved the sensitivity and
704 lower LODs than using only AuNPs were obtained (0.2 and 3.3 µg/L, respectively). The results showed
705 that the nanohybrid formed by MWCNTs/AuNPs was more adequate for analysis of Hg(II). Moreover,
706 the reutilization of the screen-printed electrodes modified with nanohybrids for several measurements
707 of Hg(II) in water samples was achieved.[20]

708 As seen on these works, nanohybrid materials are beginning to be used in the electrochemical
709 analysis of mercury but have showed characteristics very interesting for mercury determination at
710 levels necessary to identify a contamination, even at low levels. Moreover, the ease of modification
711 with these materials and the good stability shown are advantageous features. As seen in the Table 3, the
712 time of analysis required is low, and therefore for a low price and in a short time, the analysis of
713 mercury in water at sub-ppb levels can be performed. However, the developed electrodes have been
714 only used to determine Hg^{2+} in aqueous samples, the performance with other samples and different
715 mercury species should be studied.

716 **4.3 Other nanostructured materials**

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

724 Also, an alumina/gold composite working electrode modified with bunch-like bismuth
725 nanostructures was able to detect different heavy metal ions, including Hg^{2+} . [139]

726 **5. Conclusions and future perspectives**

727 The electrochemical analysis of mercury is of great interest and has been under investigation for
728 many years. Continuous development of new materials has been contributing to the advance of
729 mercury determination techniques. Considerable research has been done in the recent years with
730 advanced materials such as DNA, IIP and especially nanomaterial. Therefore, there is now a wide

731 range of tools available for the electrochemical analysis of mercury, ranging from the use of bare
732 electrodes of several materials to the modification of these electrodes with compounds that can improve
733 significantly the sensitivity.

734 Each kind of electrode published in the literature and reviewed here have some advantages and
735 disadvantages. For example, bare carbon electrodes present a low interaction with mercury, and thus
736 the effect of preconcentration is small. This effect is significant in the case of the gold electrodes, either
737 bare or film electrodes, due to the UPD process. As a result, low LODs are obtained with an acceptable
738 preconcentration time. The benefit of using gold film electrodes is that the cost of a thin layer of gold is
739 lower than a full gold electrode. Performance obtained with other bare electrodes published in the
740 literature depends on the used material, but generally, it is worse than with gold electrodes (higher
741 LODs). Similarly, electrodes modified with polymers and complexing agents present differing results
742 depending on the material used to modify and the accumulation time. Good results, in terms of
743 sensitivity and LODs, are obtained with DNA-modified electrodes due to the preconcentration ability
744 of mercury by DNA strands and the innovative methodologies developed. Negative points are the
745 difficulty of working with DNA and the high time required to perform the hybridization reaction.
746 Similar results are obtained with electrodes modified with IIP, being its most negative point the
747 accumulation time used for mercury preconcentration, comparatively higher than for other electrodes.
748 Excellent performance is obtained using electrodes nanostructured with AuNPs or CNTs, but the
749 results are improved with nanohybrid-modified electrodes. Very low LODs with low analysis time are
750 obtained with this material, placing nanohybrid electrodes as the most promising for electrochemical
751 analysis of mercury.

752 However, it is of notice that considering all the advantages of electrochemical instrumentation,
753 these technologies are still not in use for routine analysis. For punctual analysis of mercury, screen-
754 printed electrodes present certain advantages such as low cost, ease of use, low volume of sample
755 needed and the possibility of using portable instrumentation, which make this technology very

756 interesting for this application. Screen-printed electrodes had been reported for the analysis of mercury,
757 however the LODs are close to the levels permitted by law, hence the analysis could not be reliable.
758 The modification of these electrodes with different nanomaterials may allow a more sensitive detection
759 in order to fulfill all the requirements for routine analysis. The main advantage of the screen-printed
760 electrodes in the analysis of mercury is the fact that these electrodes are single-use, avoiding the
761 memory effects due to the deposition-stripping steps of mercury and tedious cleaning steps. A
762 completely different application is the continuous analysis of mercury, of which only a few examples
763 are published in the literature. For this application, the electrode employed needs a very high stability
764 and robustness to work under the same conditions after a number of continuous analysis. The biggest
765 issue that exists currently is the regeneration of the electrodes because mercury is strongly deposited on
766 the surface and when it is removed, it could cause a change in the electrode surface and the
767 measurement conditions could be deteriorated with the continuous analysis. Therefore, to solve this
768 application it is necessary to find an electrode which is stable, which does not deteriorate with the
769 continuous use and able to detect low concentrations of mercury.

770 It is also important to highlight the lack of published works where electrochemical analysis of
771 mercury is done for blood samples, whether whole blood, serum or plasma. Achieving an
772 electrochemical method for this application would be very important as it would be much easier to
773 carry out and probably in less time than the conventional methods currently implemented at hospitals.
774 The main problem is the difficult extraction of mercury from the blood as it binds strongly to proteins
775 that contain various functional groups with sulfur. Therefore, the achievement of a reliable and easy
776 extraction method of mercury to a simpler matrix than blood still remains a subject of continuous
777 effort.

778

779 Bearing in mind that there are still some issues to be solved regarding the electrochemical analysis of
780 mercury, the new advances in this field have brought us closer to a future replacement of conventional
781 methods by electrochemical methods. Anyway, currently we are closer to use electrochemical methods
782 for mercury detection in routine analysis than ten years ago, and without doubt it will be achieved very
783 soon.

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964 **Tables**

Table 1: Analytical characteristics of bare electrodes published in the literature

REF	Electrode	Analyte	Sample	Linear range	LOD	Information
<u>Carbon bare electrodes</u>						
[16]	Carbon fiber	Hg ²⁺	natural waters	1-20 µg/L	<i>nda</i> ^a	DPASV (3.5 min deposition) In presence of Au(III)
[17]	Carbon fiber	CH ₃ Hg ⁺	distilled water	15-600 mg/L	<i>nda</i>	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)
<u>Gold bare electrodes</u>						
[24]	Gold wire electrode	Hg ²⁺	natural waters	<i>nda</i>	0.3 µg/L	PSA (5 min deposition) 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	<i>nda</i>	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	<i>nda</i>	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	<i>nda</i>	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) DPASV (1 min deposition)
[36]	GCE/Gold film	Total Hg	table salt	1.0-3.0 µg/L	0.17 µg/L	Medium exchange after deposition

[37]	GCE/Gold film	Hg(II)	hemodialysis concentrates	0.5-2.5 $\mu\text{g/L}$	0.12 $\mu\text{g/L}$	DPASV (1 min deposition)
[38]	Gold film from CDs	Total Hg	urine	<i>nda</i>	<i>nda</i>	PSA (5 min deposition)
[39]	Gold film from CDs	Total Hg	fish	5-100 $\mu\text{g/L}$	0.30 $\mu\text{g/L}$	PSA (10 min deposition)
[40]	Gold film from CDs	Hg ²⁺ CH ₃ Hg ⁺	SRM groundwater	0.02-200 $\mu\text{g/L}$	0.008 $\mu\text{g/L}$	PSA CH ₃ Hg ⁺ determination after UV degradation
[41]	Gold film from CDs	Total Hg	fish and shrimps	<i>nda</i>	5 ng/g	PSA (5 min deposition)
[42]	SPCE/Gold film	Hg ²⁺	distilled water	2.5-100 $\mu\text{g/L}$	0.9 $\mu\text{g/L}$	SWASV (2 min deposition)
[43]	SPCE/Gold film	Total Hg	fish	1-1000 $\mu\text{g/L}$	0.9 $\mu\text{g/L}$	SWASV (2 min deposition)
[44]	SPCE/Gold film	Hg ²⁺	tap water	0.2 – 0.8 $\mu\text{g/L}$	0.08 $\mu\text{g/L}$	SWASV (2 min deposition) Preconcentration with magnetic particles
<u>Other bare electrodes</u>						
[46]	BDD	Hg ²⁺	distilled water	2-10 $\mu\text{g/L}$	<i>nda</i>	DPASV (2 min deposition)
[47]	Rotating BDD	Hg ²⁺	gas samples from a combustion system	0.005-50 $\mu\text{g/L}$	0.070 $\mu\text{g/L}$	DPASV (6 min deposition)
[48]	Iridium microdisks	Hg ²⁺	drinking water	1-9 $\mu\text{g/L}$	0.6 $\mu\text{g/L}$	SWASV (6 min deposition)
[49]	Gold-plated Iridium Nano-Band array ultramicroelectrode	Hg ²⁺	soil	10-180 $\mu\text{g/L}$	0.5 $\mu\text{g/L}$	SWASV (4 min deposition)
[50]	SPA _g E	Hg ²⁺	cosmetics	500 – 4500 $\mu\text{g/L}$	98 $\mu\text{g/L}$	Indirect determination of Hg ²⁺ by measuring the oxidation of I ⁻
[51]	CPE/Bi film	Hg ²⁺	distilled water	4-18 $\mu\text{g/L}$	0.50 $\mu\text{g/L}$	SWASV (2 min deposition)
[52]	Pt/Sb film	Hg ²⁺	water sample	2.5 – 80 $\mu\text{g/L}$	0.39 $\mu\text{g/L}$	SWASV (2 min deposition)

966 ^anda: no data available.

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

REF	Electrode	Analyte	Sample	Linear range	LOD	Information
<u>Polymer coating electrodes</u>						
[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	10-10000 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)
<u>Electrodes modified with complexing agents</u>						
[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	<i>nda</i>	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	<i>nda</i>	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 ₃ Hg ⁺	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)
<u>DNA modified electrodes</u>						
[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 SWASV (60 min open-circuit accumulation)
[83]	GDE/Polythymine MSO	Hg ²⁺	distilled water	0.1-20 µg/L	0.1 µg/L	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/Polythymine 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)
[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 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 DPV of Fc (signal off)
[88]	Gold/Polythymine MSO	Hg ²⁺	distilled water	<i>nda</i>	2 μg/L	RuHex is bound to DNA-AuNPs. Hg ²⁺ binds the electrode with AuNPs 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 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 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 Enzymatic reaction of H ₂ O ₂ with hemin group and amperometric detection
<u>Electrodes modified with IIP</u>						
[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-mercaptopbenzothiazole) 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	2-140000 μg/L	1 μg/L	DPASV (5 min open-circuit accumulation) (100 s deposition)

Other electrodes chemically modified

[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	<i>nda</i>	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)

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

REF	Electrode	Analyte	Sample	Linear range	LOD	Information
<u>Electrodes modified with nanoparticles</u>						
[109]	GCE/Fe(OH) ₃ NPs	Hg(II)	Tap and river waters	0.2-16000 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	<i>nda</i>	<i>nda</i>	SWASV (2 min deposition)
[114]	GCE/AuNPs	Hg ²⁺ CH ₃ Hg ⁺	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)
<u>Electrodes modified with carbon nanomaterials</u>						
[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-methoxybenzylideneamino)-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	<i>nda</i>	SWASV (15 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 SWASV (2 min deposition)
[133]	SPCNPsE	Hg ²⁺	Distilled water	1-10 μg/L	<i>nda</i>	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)
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