REVIEW PAPER

Recent Developments in Inorganic Hg^{2+} Detection by Voltammetry

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Abstract

This review presents recent developments in electrochemical Hg^{2+} detection by voltammetry, summarizing and evaluating the use of different voltammetric techniques, working electrodes, and surface modifications. The remaining technical challenges are discussed and a future outlook offered.

Keywords: inorganic Hg^{2+}, voltammetry, mercury, electrode, surface modifier agents, limit of detection

Abbreviations

AdSV	- Adsorptive Stripping Voltammetry
AS	- Anodic Stripping
AuNPs	- Gold nanoparticles
BDD	- Boron Doped Diamond electrode
CILE	- Carbon Ionic Liquid Electrode
CPE	- Carbon Paste Electrode
CV	- Cyclic Voltammetry
DP	- Differential Pulse
GC	- Glassy Carbon
g-C_3N_4	- Graphitic Carbon Nitride
ITO	- Indium Tin Oxide
LS	- Linear Sweep
MWCNTs	- Multi-walled carbon nanotubes
PbNPs	- Lead nanoparticles
rGO	- Reduced-Graphene Oxide
SPCE	- Screen Printed Carbon Electrode
SPE	- Screen Printed Electrodes
SW	- Square Wave
SWCNTs	- Single-walled carbon nanotubes
TiO_2	- Titanium Dioxide

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1. Introduction

Mercury exists in elemental, inorganic and organic forms.[1–4] Each form of mercury has a different ecosystem circulation, accumulation, behavior, and toxicity level to the human body.[3] Exposure to inorganic Hg^{2+} by the consumption of contaminated drinking water and food products may result in mortality, reproductive failure and other health effects in humans.[3] The acceptable limit of inorganic Hg^{2+} in drinking water has been set by the World Health Organization (WHO) and the USA Environmental Protection Agency (EPA) as 30.0 nM[5] and 10.0 nM[6] respectively. UK regulations set a limit of 5.0 nM[7] for inorganic mercury. Taking this into account, the development of advanced methods and devices with a facile fabrication that are reproducible, sensitive, selective, and inexpensive are needed.

The detection of inorganic Hg^{2+} can be achieved with various analytical methods, which include visible spectrophotometry or colorimetric assay,[8] gas chromatography,[9] atomic fluorescence spectrometry,[10] atomic emission spectroscopy,[11] inductively coupled plasma[12] X-ray fluorescence spectrometry[13] cold vapor atomic fluorescence spectrometry[14] high performance liquid chromatography,[15] enzyme-linked immunosorbent (ELISA),[16] and electrochemiluminescent immunoassay.[17] Generally, these techniques are reliable and have good sensitivity. However, they may need extensive sample preparation or a speciation/separation step prior to analysis (which is complicated) and may face difficulties in the detection of trace or ultra-trace levels of Hg^{2+} owing to matrix interferences and insufficient sensitivity. In addition, they are all limited with respect to *in situ* analysis and may require professional training of the user.

To overcome these limitations, attention has turned to voltammetry due to its ability to achieve high sensitivity and, in niche applications, selectivity. Additionally, it is user-friendly, allows rapid analysis, is relatively inexpensive and highly suitable for *in situ* applications.[1,2,4] To date, voltammetry has become one of the most powerful techniques for the detection of inorganic Hg^{2+}. The most commonly used voltammetric techniques are chronopotentiometry,[18] cyclic voltammetry (CV),[19] linear sweep voltammetry (LSV),[20–25] anodic stripping voltammetry (ASV),[26,27] square wave voltammetry (SWV),[28–35] differential pulse voltammetry (DPV)[36–48], and others. In this review, *recent* developments of the most promising techniques and a future perspective of this field are presented.

This review focuses on recent advances in voltammetric techniques to detect ultra-trace levels of inorganic Hg^{2+} in aqueous solution, aiming to provide an overview and a critical evaluation. For other works detailing the detection of mercury, please see references[4,49,50,51,52,53]. This review is organized in sections based on the type of voltammetric technique, and the working electrode and surface modifier used. Finally, technical challenges are discussed and a future perspective offered.

2. Voltammetric techniques for the detection of inorganic Hg^{2+}

In this section, various voltammetric techniques for the detection of inorganic Hg^{2+} in aqueous media will be discussed, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), anodic stripping voltammetry (ASV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV). These techniques will be categorized into three main groups, which are adsorptive stripping voltammetry (AdSV), anodic stripping voltammetry (ASV), and non-adsorptive/stripping voltammetry. The attention will focus both on optimum analytical parameters and on the resulting limits of detection.

Adsorptive stripping voltammetry (AdSV) is a two-step process that is used extensively for the detection of inorganic Hg^{2+}. The first step is a pre-concentration (or accumulation) step, and is performed by allowing Hg^{2+} to adsorb onto the working electrode surface (or complex with an electrode surface modifying agent). The second step involves the use of voltammetry to remove or *strip* the adsorbed Hg^{2+}. The charge passed during the stripping step allows inference, via Faraday's 1^{st} law, of the amount of accumulated material and hence with suitable calibration the concentration in the solution from which it was accumulated.

The most popular continuous wave techniques are cyclic voltammetry[19] or linear sweep voltammetry[20–22] (CV or LSV). These techniques can be performed in conjunction with AdSV. One valuable achievement using CV-adsorptive (CV-AdSV) to detect inorganic Hg^{2+} was developed by Isa *et al.*, who used single-walled carbon nanotube (SWCNT) paste electrodes modified with a layered double Zn/Al hydroxide-3(4-methoxyphenyl)propionate nanocomposite (Zn/Al-LDH-MPP/SWCNT), obtaining a detection limit of 1.0 nM.[19] An excellent selectivity was shown with no significant influence on the resulting mercury oxidation peak in the presence of interference metal ions of 25-fold concentration in excess. In this experiment, the adsorptive stripping approach was applied by reacting the modified electrode with Hg^{2+} in the solution prior to the CV measurements. The following mechanisms underpinning the analysis were proposed:.

Zn/Al-LDH-MPP/SWCNT + Hg^{2+} (solution) → Zn/Al-LDH-MPP/SWCNT-Hg^{2+} ……..…..…… (1)

Zn/Al-LDH-MPP/SWCNT-Hg^{2+}(ads) + $2e^-$ → Zn/Al-LDH-MPP/SWCNT-Hg^0(ads) ……..……..…….. (2)

Zn/Al-LDH-MPP/SWCNT-Hg^0 (ads) → Zn/Al-LDH-MPP/SWCNT + Hg^{2+} + $2e^-$ ……..…… (3)

When using AdSV, the adsorption time affects the detection limit and sensitivity of the electrode. For example, the use of a lengthy accumulation time of 500 s[21] was shown to be an issue when applying this technique, though a very favorable detection limit of 0.12 nM has been achieved by LS-AdSV (Figure 1).

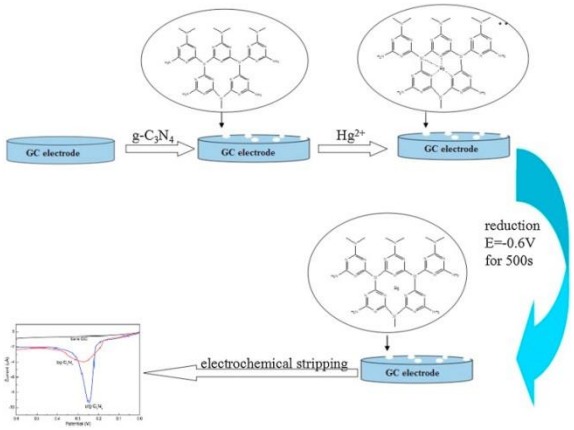

Figure 1. Schematic illustration of the electrochemical sensing Hg^{2+} using g-C_3N_4 nanosheet-modified GC electrode (adsorptive stripping), with accumulation time of 500 s.[21] Reprinted from Electrochimica Acta, Vol 186, Zhang, J.; Zhu, Z.; Di, J.; Long, Y.; Li, W.; Tu, Y., "A Sensitive Sensor for trace Hg^{2+} Determination Based on Ultrathin g-C_3N_4 Modified Glassy Carbon Electrode", 192-200, Copyright (2015), with permission from Elsevier.

As with CV-AdSV and LS-AdSV, square-wave voltammetry[54,55] can be performed in combination with adsorptive stripping (SW-AdSV).[28–32,35] Yan He and co-workers[28] used SW-AdSV to detect Hg^{2+} in the range of 1.0 aM to 100 nM with an impressive detection limit of 0.001 aM (where the detection limit is defined as the mean value of background signals plus three times standard deviation of background signals rather than a quantifiably observed signal) (Figure 2). The treatment time of 30 minutes between methyl blue (MB) and nano gold carriers functionalized with 29-mer guanine-rich DNA probe; and reaction time (not an accumulation time) of 30 minutes with Hg^{2+} may limit the use of the method. However, this approach showed excellent selectivity towards some metal ions in solution, including K^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, and Fe^{3+} and their mixtures.

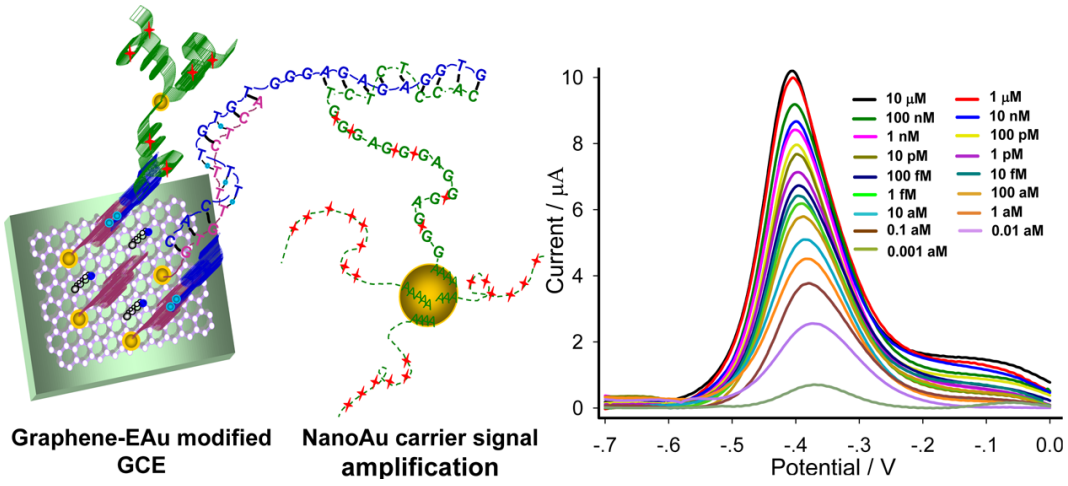

Figure 2. *Electro*-deposited graphene-Au modified glassy carbon electrode with amplified signal[28] Reprinted with permission from Zhang, Y.; Zeng, G. M.; Tang, L.; Chen, J.; Zhu, Y.; He, X. X.; He, Y. Electrochemical Sensor Based on Electrodeposited Graphene-Au Modified Electrode and Nanoau Carrier Amplified Signal Strategy for Attomolar Mercury Detection. *Anal. Chem.* **2015**, *87* (2), 989–996. Copyright 2015 American Chemical Society.

Another voltammetric technique is differential pulse voltammetric (DPV)[54,55], which enables a favorable signal to noise ratio that makes it an effective approach for the detection of Hg^{2+}. DPV can be performed in combination with adsorptive stripping (DP-AdSV).[36–42,47,48] DP-AdSV requires careful and systematic optimization of many analytical parameters, namely scan rate, sampling width, pulse period, and pulse amplitude, that influence the sensing performance. Armas *et al.*[38] used a Plackett-Burman design to minimize the number of experiments needed to optimize these parameters. A Plackett-Burman design is a two level fractional factorial screening design for studying N-1 variables using N experimental runs, where N is a multiple of 4.[38] Using this approach, information about the effect of each variable on the Hg^{2+} electrochemical response can be assessed and one can select the most critical parameters for subsequent optimization. As with other techniques, DP-AdSV still faces the problem of lengthy accumulation time (for example 300 s,[38] 500 s,[37] and 600[39]). A shorter accumulation time (90 s or less) of Hg^{2+} may be applied in line with other optimized analytical parameters, but the resulting limit of detection may not fulfil the guidelines approved by EPA and others for drinking water quality.[48] One valuable achievement using DP-AdSV at a shorter accumulation time of 35 s was demonstrated using carbon ionic liquid paste electrode (CILE) impregnated with novel ion imprinted polymeric nanobeads based on dithizone, resulting in a detection limit of 0.1 nM.[40]

In summary, a comparison of various analytical performances using adsorptive stripping techniques (AdSV) published in the recent literature is shown in Table 1.

Table 1. Comparison of different voltammetric techniques using adsorptive stripping voltammetry.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
CV-AdSV	Carbon Paste	Zn/Al Hydroxide-3(4-methoxyphenyl) Propionate/ SWCNTs	N/A	0.1 μM-1.0 mM and 1.0 nM-0.1 μM	1 nM	Food Products	19
LS-AdSV	Carbon Paste	12-Crown-4-Ether/MWCNTs	30	25 mM-0.55 mM	1.25 nM	Blood, Urine, Tap Waters	20
LS-AdSV	GC	Ultrathin g-C_3N_4 Nanosheet	500	0.5-75 mM	0.12 nM	Tap Waters, Lake Waters, River Waters	21
LS-AdSV	GC	Nano TiO_2-MWCNTs	240	0.1-100 mM	25 nM	River Waters, Wastewaters	22
SW-AdSV	GC	Graphene-AuNPs/29-mer Guanine-rich DNA	1800	1.0 aM-100 nM	0.001 aM	Tap Waters, River Waters, Landfill, Leachate Samples	28
SW-AdSV	GC	1-(2, 4-dinitrophenyl)-dodecanoylthiourea	360	0-10 mM	3.2 nM	Drinking Waters, Tap Waters	29
SW-AdSV	Carbon Paste	Nano-Ion Imprinted Polymer	250	1 nM-8.0 mM	0.2 nM	River Waters, Wastewaters, Foodstuff	30

SW-AdSV	GC	Nafion/rGO-Ion Imprinted Polymers	50	0.35 mM-0.4 mM	0.1 nM	Tap Waters, River Waters, Wastewaters	31
SW-AdSV	GC	PbNPs/Thiol-functionalized Polysiloxane Film	120	0.001-1.0 mM	0.35 nM	River Waters	32
SW-AdSV	SPCE	Sodium Dodecyl Sulfate Doped-Polyaniline	30	6-35 nM	2.4 nM	Tap Waters	35
DP-AdSV	Au Disk	Thymine-containing DNA	-	10-500 nM	10 nM	Soil Samples, Tuna Fish	36
DP-AdSV	Carbon Paste	Reduced Graphene Oxide/Au NPs	500	5-840 nM	2.04 nM	Soil Samples	37
DP-AdSV	SPCE	Polystyrene Sulfonate-NiO-Carbon Nanopowder	300	0.25-10 mM, 10 mM-0.37 μM	0.11 nM	River Waters	38
DP-AdSV	Carbon Paper	Selenium Particles /AuNPs	600	0.07-17.5 nM	5 nM	Lake Waters	39
DP-AdSV	CILE	Nano-sized Ion Imprinted Polymers (Dithizone)	35	0.5-10 nM, 0.08-2.0 μM	0.1 nM	Wastewaters	40
DP-AdSV	GC	Polypyrrole-Pt Nanospherical	-	5-500 nM	0.27 nM	Ground Waters, Pipe Waters	41
DP-AdSV	Carbon Paste	g-C_3N_4/Chitosan	-	1-80 μM, 0.5-5 mM	10 nM	River Waters, Lake Waters	47
DP-AdSV	GC	Amino-calix[4]arene-Graphitic Composite	300	10-100 nM	2.49 nM	Tap Waters, Industrial Effluents, Lake Waters	48
DP-AdSV	GC	Poly(3,4-ethylenedioxythio-phene) Nanorods/GO	360	10.0 nM-3.0 mM	2.78 nM	Tap Waters	42

Anodic stripping voltammetry (ASV) is another well-known sensitive voltammetric method, and again has two steps for the detection of Hg^{2+}. The first step is also a pre-concentration process, but which now involves holding the electrode at a sufficiently negative potential for a set length of time, resulting in the electrochemical reduction of Hg^{2+} to Hg^0 at the electrode surface. In the second step, a voltammetric sweep of the potential from reductive to oxidative potentials is made, which oxidizes Hg^0 usually back to Hg^{2+}, producing a characteristic stripping peak. The magnitude of the resulting anodic peak current is proportional to the amount of the analyte *electro*-deposited onto the working electrode surface during the pre-concentration process. The choice of deposition potential and length of pre-concentration time can be optimized to achieve lower detection limits.

ASV has been used to detect inorganic Hg^{2+} in aqueous solutions.[26,27] In the presence of dissolved oxygen, ASV is still capable of detecting Hg^{2+} (detection limit of 0.5 nM) using a sub-micrometer particulate Cu film-modified glassy carbon electrode.[26] However, the deposition time of 300 s and equilibration period of 15 s prior to ASV measurement results in a relatively long analytical

processing time. Ratner and Mandler[23] overcome this problem using gold nanoparticle (Au NP)-modified indium-tin oxide (ITO) electrodes by applying shorter accumulation time of 30 s for mercury deposition before LS-ASV measurement with a detection limit of 1.0 μM. The authors suggested that mercury is preferentially stripped from the ITO electrode base, with the Au NPs serving as nucleation sites for the deposition of Hg (whereby they do not undergo amalgam formation).

In principle, by applying a longer deposition time, more metallic ions are reduced and thus increased stripping peak currents are observed. However, when the deposition time is extremely long, especially in the case of mercury being incorporated into, for example, an apatite structure,[45] the peak current limits at long deposition times as the surface becomes saturated. Meanwhile, the deposition potential also plays an important role in ASV. Optimizing the deposition potential, generally by shifting the potential to a more negative value, may increase the stripping peak current. However, applying very negative deposition potentials may result in the signal being convoluted with concurrent hydrogen evolution.[56] An optimum deposition potential may be obtained where the stripping peak currents were maximised and there were no peak distortions due to concurrent reactions.[56] An alternative approach to lowering the limit of detection in ASV, besides prolonging the pre-concentration step and modifying the potential sweep, is using pre-created nucleation centers (leaving a small metal nuclei in electrode surface for subsequent metal deposition).[57] The main advantage of this strategy lies in its simplicity as it involves a simple drop casting of a metal nanoparticle suspension followed by oxidation of the nanoparticles. However, there are disadvantages of using the drop casting method as will be discussed in the next section below.

Square-wave voltammetry (SWV)[54,55] in combination with anodic stripping voltammetry (SW-ASV)[33,34] has been used to detect inorganic Hg^{2+} because of its ability to be operated at high frequency. In either SW-ASV or SW-AdSV, many analytical parameters such as pre-concentration time, accumulation potential, frequency, modulation pulse amplitude, square wave step potential (step height of the staircase), equilibration time (time between deposition and stripping) and cleaning potential, need to be optimized to find a clearly visible stripping peak, optimal signal-to-noise ratio and the lowest background current. Some recent works in 2015 to date still suffer from lengthier pre-concentration times. Cinti *et al.*[33] used a screen-printed electrode (SPE)-modified with a carbon black-gold nanoparticle (CBNP-AuNP) nanocomposite to detect inorganic Hg^{2+}, resulting in a claimed detection limit of 15 pM. However, the accumulation time of 400 s before SW-ASV measurement is an ineffective analytical processing time. In addition, with respect to an excellent LoD of 80 pM, the detection value of 19 ± 3 pM for *real sample* analysis was achieved after using a preconcentration time of 3,000 s.[34]

Meanwhile, using differential pulse-anodic stripping voltammetry (DP-ASV),[43–46] a shorter accumulation time of 90 s was used by Lahrich *et al.*[45] employing lacunar apatite-modified carbon paste electrode. However, the resulting detection limit of 11.1 nM barely meets the 10 nM guidelines issued by EPA for inorganic mercury in drinking water. The supporting electrolyte may also significantly influence the magnitude of the resulting stripping peak height.[44,46] In particular, the stripping peak current was significantly higher in a solution containing chloride.

DP-ASV can be performed in conjunction with another analytical technique to achieve

improved stripping peak signals with a shorter accumulation time of 120 s, such as the liquid-liquid extraction of Hg^{2+} with ionic liquids.[43]

In summary, a comparison of the analytical performances of different voltammetric techniques in conjunction with anodic stripping voltammetry (ASV) published in the recent literature is shown in Table 2.

Table 2. Comparison of different voltammetric techniques using anodic stripping voltammetry.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
LS-ASV	ITO	Au NPs	30	0-100 μM	1.0 μM	-	23
ASV	GC	sub-Micrometer Particulate Cu Film	300	50-500 mM	0.5 nM	-	26
ASV	GC	Reduced Graphene Oxide/Au NPs Nanocomposite	600	1-150 nM	0.6 nM	Tap Waters	56
SW-ASV	SPCE	Carbon Black-Au NPs	400	0-0.3 nM, 0.3-0.5 nM	15 pM	River Waters, Soil Samples	33
SW-ASV + Chloride Desorption Step	GC Rotating Disk	Au NPs	300	0.4-6.0 nM	80 pM	Natural Groundwater	34
DP-ASV + Extraction	Au	-	120	0-25 mM	0.25 nM	Tap Waters, Pond Waters, Wastewaters	43
DP-ASV	ITO	Au NPs	300	0.5-5 mM	0.15 nM	Tap Waters, Lake Waters, Milk, Soil Samples	44
DP-ASV	Carbon Paste	$KCdPb_3(PO_4)_3$ Lacunar Apatite	90	0.2-100 mM	11.1 nM	Sea Waters, Fish Samples	45
DP-ASV	Au	Au-TiO_2 NPs/Chitosan	240	5.0-400.0 nM	1.0 nM	Tap Waters	46

As discussed above (see Table 1 and Table 2), most voltammetric techniques rely upon adsorptive stripping (AdSV) or anodic stripping voltammetry (ASV) to accumulate Hg^{2+} onto the electrode modifier agent. However, some publications have shown that inorganic Hg^{2+} is detectable without the use of an adsorptive or anodic stripping step (Table 3). LSV in combination with chronoamperometry has been used to detect inorganic Hg^{2+} in aqueous solutions[24,25] Bhanjana *et al*. used LSV with a zinc oxide quantum dots-modified gold electrode with a detection limit of 25 pM.[24] LSV was applied also for the direct sensing of Hg^{2+} on a nanogold platform, but this resulted in a higher detection limit of 19 nM.[25]

Table 3. Comparison of different voltammetric techniques using non-adsorptive/ anodic stripping voltammetry.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.

LSV + Chronoamperometry	Au Disk	Zinc Oxide Quantum Dots/ Nafion		25 pM-250 nM	25 pM	River Waters, Underground Waters, Drinking Waters	24
LSV + Chronoamperometry	GC	Au NPs/Nafion (binder)	-	0-2.5 mM	19 nM	River Waters, Underground Waters, Distilled Waters	25

Overall it can be seen that different types of voltammetry have been shown to ably detect inorganic Hg^{2+} at either trace or ultra-trace levels. Various analytical parameters need to be optimized in parallel with selection of the working electrode and pre-treatment process, considering time and cost, reproducibility, and detection limit to fulfill the guidelines approved by specific governing authorities, and allow voltammetry to continue to outperform other analytical methods.

Recently, progress has been made in applying effective pre-treatment processes to the working electrode and optimizing analytical parameters of the voltammetry. In the next section, the selection of the working electrode and its pre-treatment, including selection of chemical modifiers and the remaining challenges in this topic will be discussed.

3. Working Electrodes

In this section, bare working electrodes and those with different surface modifiers will be discussed, including their advantages and disadvantages, and include model studies that embrace real samples.

Bare metallic electrodes such as gold,[43,58,59]silver,[60] and platinum[61] are often used to detect Hg^{2+} since they have a high affinity with mercury. Ordeig *et al*.[58] used bare gold ultra-microelectrode arrays, with single microelectrodes wired in parallel, each one acting diffusionally independently, achieving a detection limit of 16 nM. The large number of microelectrodes making up the array allows for high sensitivities and a low detection limit using short deposition times of 30 s and small overpotentials. Although individual electrodes may undergo irreversible deactivation, this approach still has excellent reproducibility because overall only a small number microelectrodes lose electrochemical activity, which does not have a significant effect on the overall stripping signal. Giacomino *et al.*[59] used a bare gold macroelectrode, and applying a deposition time of 120 s in SWASV, achieved a detection limit of 0.1 nM. Similarly in early work, Pinilla *et al.*[61] used a bare platinum (disk) macroelectrode to adsorb mercury via open circuit accumulation, followed by constant potential reduction and an anodic stripping voltammetric scan in a separate cell to detect inorganic Hg^{2+}. This allowed a detection limit of 12 nM, and under optimum experimental conditions no adsorption of other heavy metal ions was observed. However, the use of three separate cells (for removing platinum oxides from electrode surface, for the mercury accumulation step, and for constant potential-stripping analysis step) is inefficient.

The most common problem in the use of gold and silver bare metal electrodes is amalgam

formation that causes structural changes to the electrode surface and thus leads to decreasing sensing performance. In the case of platinum electrodes, the mercury strongly adsorbs to the surface of electrode.[61] Therefore, long cleaning treatments to achieve or to maintain a satisfying reproducibility are required. Moreover, these electrodes may suffer from interference effects caused by surface-active compounds and many metal ions which are present in the analyte solution. In addition, memory effects on these electrodes, whether they return to mercury-free states after voltammetric sweeping or not, also contribute to decreasing sensing performance. Another issue regarding a disadvantage of these electrodes is their cost compared to other electrode materials.

Some bare non-metallic electrodes such as glassy carbon (GC)[62] and boron-doped diamond (BDD)[63–65] were also shown to capably detect *ultra-trace* levels of Hg^{2+} in aqueous solution. These type of electrode materials have been widely used due to their low cost and low chemical reactivity. However, the sensitivity and selectivity of these materials are generally low and preconcentration times needed are not acceptable, leading to unsatisfactory limit of detection or limit of quantification. A comparison of voltammetric performances using different bare electrodes published in the literature is shown in Table 4.

Table 4. Comparison of voltammetric performance using different bare electrodes.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
DP-ASV + Extraction	Au	-	120	0-25 mM	0.25 nM	Tap Waters, Pond Waters, Wastewaters	43
SW-ASV	Rotating Ag (RSE)	-	300	0.1-800 mM	46.1 nM	Milk and Breast Milk	60
LS-ASV	Pt Disk	-	480	40-500 nM	12 nM	Natural and Distilled Waters	61
LS-ASV	Au Ultra-microelectrodes	-	30	10 nM-1 mM	16 nM	River Waters	58
SW-ASV	Au Macroelectrode	-	120	1 nM-5.0 mM	0.1 nM	Canned Tuna Fish	59
Chronopotentiometry Stripping	GC Vessel	-	600	25-150 pM, 25-100 nM	0.5 pM	Tap, Rain, Well, Lake, and Spring Waters	62
ASV + Sequential Injection	BDD	-	150	0.5-150 nM, 25-300 nM	0.2 nM	Seawater, Salmon, Squid, *etc*.	63
DP-ASV	BDD	-	60	2.5 pM-0.25 nM	0.35 pM	Power Plant Samples	65
DP-ASV	BDD	-	30	10-50 pM	10 pM	-	64

Other types of non-metallic working electrode materials, such as carbon paste electrodes (CPE),[19,20,30,37,45,66] carbon paper electrodes,[39] carbon ionic liquid paste electrodes (CILE),[40] indium tin oxide (ITO) glass electrodes,[44] and screen-printed electrodes (SPE),[33,38,67] have shown promise in

practical voltammetry applications. The latter have been customized with various surface modifier agents, including gold,[33,67] and silver,[68] and can be prepared with a variety of low cost substrates (plastic, paper, or ceramic).

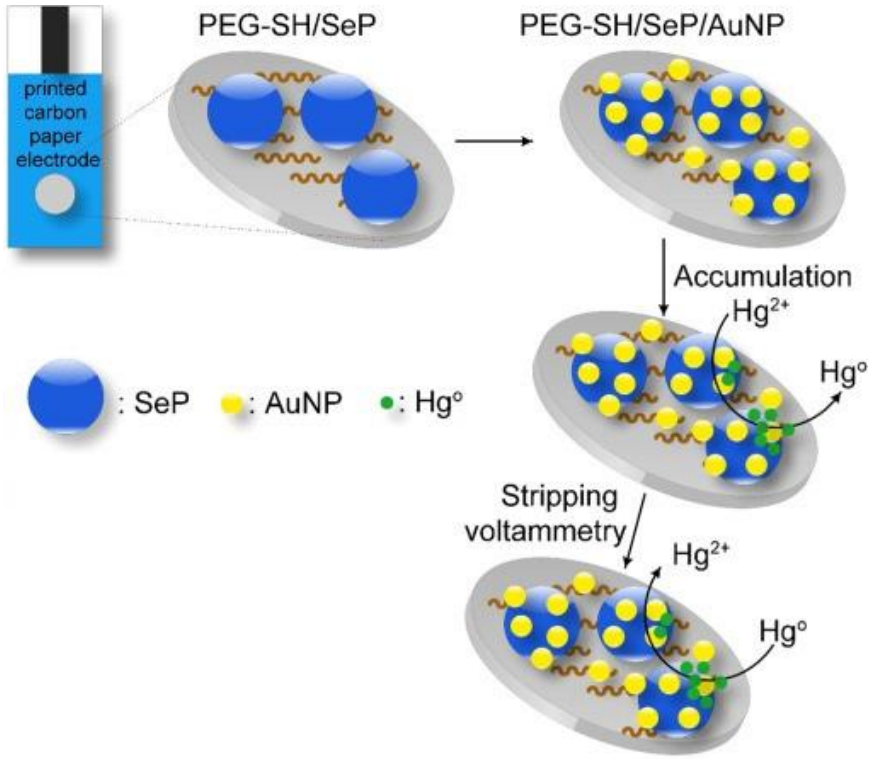

Figure 3. Schematic illustration of the fabrication process of the modified disposable carbon paper electrode.[39] Reprinted from Biosensors and Bioelectronics, Vol 85, Bui, M. P. N.; Brockgreitens, J.; Ahmed, S.; Abbas, A., "Dual Detection of Nitrate and Mercury in Water Using Disposable Electrochemical Sensors", 280-286, Copyright (2016), with permission from Elsevier.

Figure 3 shows the schematic illustration of the modification process of disposable carbon paper electrodes, which were functionalized with selenium particles (SePs) and gold nanoparticles (AuNPs). The AuNPs served as nucleation sites for Hg^{2+}, whilst the SePs further reinforced the mercury ion nucleation due to their high binding affinity to mercury.

A comparison of the performance of different non-metallic electrodes published in the literature is shown in Table 5.

Table 5. Comparison of voltammetric performance using different non-metallic electrodes.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
CV-AdSV	Carbon Paste	Zn/Al Hydroxide-3(4-methoxyphenyl) Propionate/ SWCNTs	N/A	0.1 μM-1.0 mM and 1.0 nM-0.1 μM	1 nM	Food Products	19
LS-AdSV	Carbon Paste	12-Crown-4-Ether/MWCNTs	30	25 mM-0.55 mM	1.25 nM	Blood, Urine, Tap Waters	20
SW-AdSV	Carbon Paste	Nano-Ion Imprinted	250	1 nM-8.0	0.2 nM	River Waters,	30

		Polymer (Mercapto ethylamino Monomer)		mM		Wastewaters, Foodstuff Samples	
DP-ASV	Carbon Paste	$KCdPb_3(PO_4)_3$ Lacunar Apatite	90	0.2-100 mM	11.1 nM	Sea Waters, Fish Samples	45
DP-ASV	Carbon Paste	Au NPs-Bismuth	200	10-50 nM	1.4 nM	Groundwater, Soil Samples	37
DP-AdSV	Carbon Paste	Dithizone-functionalized siliceous mesocellular foam	40	0.01-0.5 nM, 0.5-10 nM	3.0 pM	Water Samples	66
DP-AdSV	Carbon Paper	Selenium Particles /Au NPs	600	0.07-17.5 nM	5 nM	Lake Waters	39
DP-AdSV	CILE	Nano-sized Ion Imprinted Polymers (Dithizone)	35	0.5-10 nM, 0.08-2.0 µM	0.1 nM	Wastewaters	40
DP-ASV	ITO	Au NPs	300	0.5-5 mM	0.15 nM	Tap Waters, Lake Waters, Milk, Soil Samples	44
SW-ASV	SPCE	Carbon Black-Au NPs	400	0-0.3 nM, 0.3-0.5 nM	15 pM	River Waters, Soil Samples	33
DP-AdSV	SPCE	Polystyrene Sulfonate-NiO-Carbon Nanopowder	300	0.25-10 mM, 10 mM-0.37 mM	0.11 nM	River Waters	38
SW-ASV	SPE	Au NPs	360	5-500 nM	5.0 nM	Groundwater	67

As discussed above, voltammetric analysis of inorganic mercury can be successfully performed using various bare electrodes, which are simpler and easy to use. However, bare electrodes have some disadvantages, mainly because of low sensitivity and selectivity, and require long preconcentration times. If Hg^{2+} is bound using a modified electrode (as in AdsSV), then as soon as the electrode is immersed in the solution binding accumulation will start. If Hg^{2+} is reduced (as in ASV), accumulation only starts when a reducing potential is applied. Therefore, control of the accumulation time is easier for ASV and hence this method is likely more reproducible. In both cases the maximum signal is likely to be obtained when the pre-concentration time is diffusion controlled and hence independent of the surface. Under these conditions, the optimal sensitivity is likely to be similar for all electrodes if the diffusion field is the same. Modification will change the potentials needed and provide selectivity.

As previously discussed, the use of metallic bare electrodes is challenging because of the structural changes of their surface caused by formation of amalgam (in the case of silver and gold) or surface adsorption (in the case of platinum) and possible lack of long-term reliability. Moreover, with increases in the complexity of real samples, the linear working range may be affected due to the presence of various ions that interfere during analysis. To overcome these challenges, electrode modification or pre-treatment is needed.

4. Surface Modifier Agents

To overcome the problems encountered when using bare electrodes and to provide greater selectivity, surface modification – the creation of chemically modified electrodes (CMEs) – can be an alternative. In this section, some surface modifier agents such as nanoparticles, polymers, functionalized-DNA probes, surfactants, other organic compounds, and composite materials, and their advantages and disadvantages will be discussed.

4.1. Nanoparticles

In recent years, increasing interest has been focused on the use of metallic nanoparticles to achieve a better sensing performance of Hg^{2+}. Nanoparticles have specific properties such as high active surface area, sometimes good catalytic ability and high adsorption capacities, excellent mass transport, leading in analytical terms to low detection limits and better signal-to-noise ratios.[24,37] Nanoparticles such as gold (Au NPs),[23,34,37,44,67,69] platinum (Pt NPs),[41] and zinc oxide (ZnO NPs)[24] immobilized onto electrode surfaces have become promising alternatives for the voltammetric analysis of inorganic Hg^{2+}. Modification of the electrode surface using a suitable nanomaterial renders a high surface area for adsorption. Ratner and Mandler[23] found that Au NPs modified surfaces yielded higher sensitivity, sharper and more reproducible stripping peaks of Hg^{2+} as compared with bare electrodes.

In the context of electrodes (CMEs) chemically modified with nanoparticles, aggregation/agglomeration effects can often present a serious problem, which can often lead to incomplete stripping analysis.[70–74] In this context, electrode surfaces modified by electrophoresis or *electro*-deposition have shown better homogeneity and a smaller aggregate/agglomerate particle size.[74] Drop casting, which involves depositing a nanoparticle suspension onto the electrode and evaporating the solvent to leave a layer of nanoparticles on the electrode surface prior to stripping analysis, may result in extensive nanoparticle aggregation/agglomeration and frequently results in incomplete stripping,[74] which should be taken into account when considering the stripping voltammetry. A comparison of different nanoparticles as surface modifier agents published in the literature is shown in Table 6.

Table 6. Comparison of voltammetric performance using different nanoparticles.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
LS-ASV	ITO	Au NPs	30	0-100 μM	1.0 μM	-	23
SW-ASV + Chloride Desorption Step	GC Rotating Disk	Au NPs	300	0.4-6.0 nM	80 pM	Natural Groundwater	34
DP-ASV	ITO	Au NPs	300	0.5-5 mM	0.15 nM	Tap Waters, Lake Waters, Milk, Soil Samples	44
DP-ASV	Carbon Paste	Au NPs-Bismuth	200	10-50 nM	1.4 nM	Groundwater,	37

						Soil Samples	
SW-ASV	SPE	Au NPs	360	5-500 nM	5.0 nM	Groundwater	67
SW-ASV + Sequential Injection	SPE	Au NPs	110	5-100 nM	1 nM	Water Samples, Sea Waters	69
DP-AdSV	GC	Polypyrrole-Pt Nanospherical	-	5-500 nM	0.27 nM	Ground Waters, Pipe Waters	41
LSV + Chronoamperometry	Au Disk	Zinc Oxide Quantum Dots/ Nafion		25 pM-250 nM	25 pM	River Waters, Underground Waters, Drinking Waters	24

4.2. Polymers

Polymers can be used to modify electrodes to allow selective detection of Hg^{2+} through adsorption or specific binding. Three different categories will be discussed below – molecular imprinted polymers, conducting polymers, and DNA-based probes.

4.2.1 Molecular Imprinted Polymers

Molecular imprinted polymers (MIP) (with specific molecular recognition sites) or ion-imprinted polymers (IIP) (with specific inorganic ion selective sites)[30,31,40] have shown highly selective synthetic receptors (recognition sites) designed for inorganic Hg^{2+}. The ion imprinting technology can be performed generally in bulk polymerization or via *in situ* surface imprinting polymerization.[31] The first method may suffer from incomplete polymerization and template removal, slow mass transfer of binding and release of the analyte from the sites, and high cross-linking density (thus may lead to poor electron transfer and poor site accessibility for Hg^{2+}).[31] Ghanei-Motlagh *et al.*[31] used SW-ASV in conjunction with an ion-imprinted polymer/reduced graphene oxide modified GC to detect Hg^{2+} with a linear range of 0.07 to 80 μg L^{-1}.

4.2.2 Conducting Polymers

Conducting polymers, such as polyaniline,[35] polypyrrole,[41] and chitosan,[47] have shown good electrical conductivity, good adhesion and can adsorb Hg^{2+}. Their high adsorption ability enables the accumulation of Hg^{2+} at the electrode surface through complex formation between the analytical target (Hg^{2+}) and suitable ligand (either polymerizable or non-polymerizable). Bahrami *et al*.[40] used a non-polymerizable ligand, dithizone, in a carbon ionic liquid paste electrode (CILE) with a short accumulation time of 35 s, resulting in a LoD of 0.1 nM. Conductive films based on polyaniline have been used as surface modifier agents[35] via *electro*-synthesis on the surface of screen-printed carbon electrodes in the presence of sodium dodecyl sulfate (SDS) as the dopant. SDS, an anionic surfactant, acts as a counter-ion and thus the modified polyaniline becomes a cationic-sensitive polymer able to bind Hg^{2+}. However, controlling the pH may become a challenge for the protonation of the polymer since it may affect the adsorption capacity of Hg^{2+} and the overall sensitivity. The decrease in the Hg^{2+}

stripping peak current at certain pHs may be due to the competition between Hg^{2+} and other ions in binding to the donating atoms of the cavities of polymer at the surface of the electrode.[30,31] In addition, the main limitation of the polymer-modified interface is generally slow diffusion across the films and the possible swelling or denaturation of the polymer during prolonged accumulation time.

4.2.3 DNA-based Probes

The use of redox-tagged oligonucleotides constitutes a potential platform for the detection of Hg^{2+}.[29,36] An advantage of this approach is ability to tune the distance of redox labels from the electrode surface via analyte-induced conformational switches, strand dissociation or surface hybridization of certain oligonucleotide probes that carry the electroactive reporters. DNA has been found to be an effective and specific modification agent for the detection of Hg^{2+}. Thymine-thymine pairs in DNA sequences can selectively bind Hg^{2+} to form a T-Hg^{2+}-T complex.[29,37] This design relies on a very specific DNA probe coverage, and it is very sensitive to distance between neighbors. Zhang *et al*.[28] have used Au NPs functionalized with a 29-mer guanine-rich DNA probe, resulting in the lowest LoD reported in the literature of 0.001 aM (the mean value of background signals plus three times standard deviation of background signals) and dynamic linear range of 1.0 aM to 100 nM.

A comparison of different polymers and functionalized-DNA probes as surface modifier agents published in the recent literature is shown in Table 7.

Table 7. Comparison of voltammetric performance using polymers and functionalized-DNA probes.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
SW-AdSV	GC	Graphene-AuNPs/29-mer Guanine-rich DNA	1800	1.0 aM-100 nM	0.001 aM	Tap Waters, River Waters, Landfill, Leachate Samples	28
DP-AdSV	Au Disk	Thymine-containing DNA	-	10-500 nM	10 nM	Soil Samples, Tuna Fish	36
SW-AdSV	Carbon Paste	Nano-Ion Imprinted Polymer (Mercapto ethylamino Monomer)	250	1 nM-8.0 mM	0.2 nM	River Waters, Wastewaters, Foodstuff Samples	30
SW-AdSV	GC	Nafion/rGO-Ion Imprinted Polymers	50	0.35 mM-0.4 mM	0.1 nM	Tap Waters, River Waters, Wastewaters	31
SW-AdSV	SPCE	Sodium Dodecyl Sulfate Doped-Polyaniline	30	6-35 nM	2.4 nM	Tap Waters	35
DP-AdSV	CILE	Nano-sized Ion Imprinted Polymers (Dithizone)	35	0.5-10 nM, 0.08-2.0 µM	0.1 nM	Wastewaters	40
DP-AdSV	GC	Polypyrrole-Pt Nanospherical	-	5-500 nM	0.27 nM	Ground Waters, Pipe Waters	41

DP-AdSV	Carbon Paste	g-C_3N_4/Chitosan	-	1-80 µM, 0.5-5 mM	10 nM	River Waters, Lake Waters	47

4.3. Surfactant and Organic Compounds

Surfactants or organic compounds can make good surface modifiers due to their good electrode anchoring ability and ability to enable efficient *electro*-catalysis.[75] Many surfactants are capable of specific interaction with Hg^{2+} due to the presence of a large number of donor groups in their chemical structures. Thus, Zahid *et al*.[29] have used a thiourea-based surfactant, 1-(2,4-dinitrophenyl)-dodecanoylthiourea (DAN), to detect Hg^{2+} in aqueous solution using SWV with an accumulation time of 360 s, resulting in a LoD of 3 nM. Organic compounds with a mercapto (or -thiol) group are well-known for their capacity to form a stable bond with Hg^{2+}. Longer chains lead to more ordered structures, but self-assembled mono-layers (SAMs) of the less ordered shorter alkyl chain compounds are more useful candidates for voltammetric applications. Sahoo *et al*.[76] have used SAMs of 2-mercapto benzothiazole (MBTH) to modify a bare gold macroelectrode and have successfully achieved a LoD of 1.2 nM. Meanwhile, other organic compounds such as indigo carmine (IC), as reported by N'Dri *et al*.,[77] show a good LoD of 7.5 nM using DPV through a complex formation of IC with Hg^{2+}. However, numerous experimental parameters affecting the Hg^{2+}-IC complex formation (including temperature) need to be optimized and it requires a 10 min reaction time. Arulraj *et al*.[78] have used reduced *p*-nitrobenzoic acid film-modified glassy carbon electrodes to detect inorganic Hg^{2+} using DPASV, resulting in a LoD of 0.24 nM. This organic film showed a strong interaction between Hg^{2+} and the lone pair of electrons on the nitrogen atoms of *p*-nitrobenzoic acid, although it still requires an accumulation time of 110 s. The performances of different surfactant and organic compounds as surface modifier agents is summarised in Table 8.

Table 8. Comparison of voltammetric performance using different surfactant and organic compounds.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
SW-AdSV	GC	1-(2, 4-dinitrophenyl)-dodecanoylthiourea	360	0-10 mM	3.2 nM	Drinking Waters, Tap Waters	29
DP-ASV	Au Disk	2-mercapto benzothiazole	300	5-50 nM	2 nM	Medicinal Samples	76
DP-AdSV	Carbon Paste	Indigo Carmine (Food Dye)	-	25-200 nM	7.5 nM	Tap Waters, Well Waters	77
DP-AdSV	GC	p-Nitrobenzoic Acid	110	5-500 nM, 2.5-15.5 mM	240 pM	Tap Waters	78

4.4. Composite Materials

Modification of an electrode with composite materials containing different types of organic or inorganic compounds, which act as redox mediators to facilitate charge transfer between the electrode and the redox species, is a possibly promising avenue for Hg^{2+} detection. Various composite materials such as palladium oxide-doped natural phosphate,[79,80] reduced graphene oxide-Au NPs,[37,56] bismuth-

gold (Bi-Au NPs),[81] 12-crown-4 ether/multi-walled carbon nanotubes,[20] graphitic carbon nitride (C_3N_4),[21,47] zinc/aluminum hydroxide-3(4-methoxyphenyl)propionate/single-walled carbon nanotubes,[19] TiO_2 nanoparticles/multi-walled carbon nanotubes,[22] poly(3,4-ethylenedioxythiophene) nanorods/graphene oxide (PEDOT/GO),[42] carbon black NPs/Au NPs,[34] and composites of selenium particles (SePs)-Au NPs,[40] have been shown to successfully detect inorganic Hg^{2+} in aqueous solution. These composite materials are generally prepared by electrochemical deposition,[80] *in situ* polymerization,[42] or a thermal polycondensation process.[21] Note that changing the rate of electron transfer leads to the need for lower potentials which can improve selectivity. In experimental protocols potentials are selected to fully drive the electron transfer so as to achieve diffusion controlled conditions. Hence a change in selectivity is unlikely unless the material absorptively pre-concentrates the target. In the latter case, it becomes important to control the length of time the electrode is exposed to the target analyte before the electrochemical analysis starts.

J. Zhang *et al*.[21] have used an ultrathin graphitic carbon nitride (utg-C_3N_4) modified-glassy carbon electrode which showed a strong affinity between Hg^{2+} and utg-C_3N_4 through its -NH and -NH_2 groups, resulting in a LoD (3σ) of 0.1 nM. However, one of the main challenges using such a composite material is adjusting the pH conditions[37,66] and the presence of other metal ions or organic compounds which can inhibit the adsorption process of Hg^{2+} onto the electrode surface. For example, when using dithizone as an organic ligand,[66] the use of pHs higher and lower than 4.0 leads to increased hydrolysis of Hg^{2+} and protonation of the heteroatoms of dithizone respectively, thus decreasing the stripping signals. Lahrich *et al*.[45] have used lacunar apatite [$Na_{1-x}K_xCdPb_3(PO_4)_3$] as a modifier in a carbon paste electrode. The use of this platform has shown high selectivity of Hg^{2+} in the presence of many different heavy metal ions, relatively short preconcentration times of 60 s though resulting unfavorable detection limit of 11.1 nM. To the best of our knowledge, the optimal Hg^{2+} detection, that is the lowest LoD achieved with a reasonable waiting time, using composite material is shown by Bojdi *et al*.[66] in which they used a dithizone-functionalized siliceous mesostructured cellular foam-modified carbon paste electrode, with a resulting LoD of 3.0 pM (at S/N = 3) and a short accumulation time of 40 s. The use of different composite materials as surface modifier agents is presented in Table 9.

Table 9. Comparison of voltammetric performance using different composite materials.

Voltammetry	Electrode	Modifier	Accumulation Time (s)	Linearity	LoD	Real Samples	Ref.
DP-AdSV	Carbon Paste	Pd Particles- Natural Phosphate	120	0.5-70 mM	49.9 nM	Tap Waters, Wastewaters	80
DP-ASV	Carbon Paste	Palladium Oxide-Natural Phosphate	180	0.25-100 mM	19.3 nM	Tap Waters	79
ASV	GC	Reduced Graphene Oxide/Au NPs Nanocomposite	600	1-150 nM	0.6 nM	Tap Waters	56
DP-AdSV	Carbon Paste	Reduced Graphene Oxide/Au NPs	500	5-840 nM	2.04 nM	Soil Samples	37
DP-ASV	Carbon Paste	Au NPs-Bismuth	200	10-50 nM	1.4 nM	Groundwater, Soil Samples	81

LS-AdSV	Carbon Paste	12-Crown-4-Ether/MWCNTs	30	25 mM-0.55 mM	1.25 nM	Blood, Urine, Tap Waters	20
LS-AdSV	GC	Ultrathin g-C_3N_4 Nanosheet	500	0.5-75 mM	0.12 nM	Tap Waters, Lake Waters, River Waters	21
DP-AdSV	Carbon Paste	g-C_3N_4/Chitosan	-	1-80 μM, 0.5-5 mM	10 nM	River Waters, Lake Waters	47
CV-AdSV	Carbon Paste	Zn/Al Hydroxide-3(4-methoxyphenyl) Propionate/ SWCNTs	N/A	0.1 μM-1.0 mM and 1.0 nM-0.1 μM	1 nM	Food Products	19
LS-AdSV	GC	Nano TiO_2-MWCNTs	240	0.1-100 mM	25 nM	River Waters, Wastewaters	22
DP-AdSV	GC	Poly(3,4-ethylenedioxythio-phene) Nanorods/Graphene Oxide	360	10.0 nM-3.0 mM	2.78 nM	Tap Waters	42
SW-ASV	SPCE	Carbon Black-Au NPs	400	0-0.3 nM, 0.3-0.5 nM	15 pM	River Waters, Soil Samples	33
DP-AdSV	Carbon Paper	Selenium Particles /Au NPs	600	0.07-17.5 nM	5 nM	Lake Waters	39
DP-ASV	Carbon Paste	$KCdPb_3(PO_4)_3$ Lacunar Apatite	90	0.2-100 mM	11.1 nM	Sea Waters, Fish Samples	45
DP-AdSV	Carbon Paste	Dithizone-functionalized siliceous mesocellular foam	40	0.01-0.5 nM, 0.5-10 nM	3.0 pM	Water Samples	66

The differences in the achieved LoDs and in linear ranges for modified electrodes depend on the compounds used as modifiers and the accumulation time. However, in general, the excellent results from the works discussed above are tempered by a complex modification process or synthesis of modifiers. Finally, since the overall approach should be as simple as possible, because the more modification or pre-treatment process an approach comprises, the more difficult it is to perform *in situ* and the greater the risk of contamination in real samples.

5. Some Technical Challenges

In the voltammetric analysis of Hg^{2+}, numerous interferences both organic and inorganic species may be present in real samples.[1,2,4] The presence of organic species (e.g., surfactants, proteins and humic acid), which can be found in many natural samples, can adsorb on the electrode and foul it partly or even totally – leading to passivation of the electrode.[1] If the sample contains elemental mercury in addition to Hg^{2+}, it can react with any chloride present to form insoluble calomel (Hg_2Cl_2). Calomel formation can also be a drawback because it can precipitate onto the electrode surface, thus reducing the active electrochemical area and decreasing the electrode substrate's sensing performance. Calomel formation could be avoided by total Cl^- elimination from the analyte solution, using a non-chloride containing reference electrode and supporting electrolyte, working

below a concentration of 2 mM chloride or above a concentration of 3.5 M,[82] using a combination of voltammetry and extraction[43] or a chloride desorption step[34] prior to the measurement. The latter procedure can both remove unwanted components (chloride) and concentrate the analyte from the bulk sample into a small volume, which may increase the sensitivity of detection. Z. Li *et al.*[43] have used N-octylpyridinium ionic liquids as extracting agent to extract Hg^{2+}, while interfering ions were reduced by two orders of magnitude, prior to voltammetric analysis by ASV, resulting in a LoD of 0.25 nM.

Aggregation/agglomeration[83] of particles upon electrode surface modification (during electro-deposition or drop casting process), is disadvantageous for most voltammetric applications. This is because the irreversible aggregation of nanoparticles affects many physical and chemical properties[71,73,74] thus effecting sensing performance by decreasing the fraction of nanoparticles that are electroactive (partial oxidation or incomplete stripping).

The pre-concentration time in voltammetry can be tuned, depending on the Hg^{2+} concentration in solution. Very low Hg^{2+} concentrations (trace to ultra-trace levels) may require very long pre-concentration times to build up enough Hg^{2+} on the electrode surface to be accurately measured. In this context, the LoD is lowered because the relative repeatability of the blank measurement is improved, and the LoD is defined as the mean value of background signals plus three times standard deviation of background signals rather than a quantifiably observed signal. For example, Laffont *et al*.[34] detected ultra-trace levels of Hg^{2+} (19 ± 3 pM) in natural groundwater samples by using a Au NPs modified-GC electrode with 3000 s preconcentration time. In conclusion, a long preconcentration time can be employed to detect trace or ultra-trace levels of Hg^{2+}, but it has the disadvantage of limiting the number of samples that can be analyzed. Thus, an important improvement in voltammetric analysis is decreasing the accumulation time without compromising the sensitivity, selectivity and linear range of the response.

6. Conclusions and Future Perspectives

Inorganic mercury has become a serious threat to human and environment health due to its high toxicity. Currently, measurements of mercury – especially inorganic Hg^{2+} – are still performed using conventional analytical techniques. However, these latter techniques need trained personnel to perform the analysis, are relatively expensive and are not applicable for *in situ* applications. It is for these reasons and the fact that voltammetry can be used with high sensitivity, low cost, simple instrumentation, easy implementation, and portability that makes it superior to other analytical techniques.

As of now, voltammetry is the most promising technique for the *in situ* detection of trace or ultra-trace levels of inorganic Hg^{2+}. As discussed above, there have emerged many promising approaches of specific voltammetric techniques, electrode materials, surface modifier agents and an alternative to overcome some technical challenges, including long preconcentration times and creating straightforward and practical electrode modification protocols. To the best of our knowledge, the lowest LoD of 0.001 aM reported in the literature was claimed by Zhang *et al*.,[28] with a linear range of 1.0 aM to 100 nM. Note that 0.001 aM corresponds to just 600 molecules per litre of solvent! This

would require special solution handling and great patience in waiting for the species to arrive at an electrode since the average ion separation is *ca.* 1 cm. Assuming a diffusion coefficient of 10^{-5} cm^2 s^{-1}, it would take a molecule *ca.* 250,000 seconds to diffuse to the electrode.

Although particular aspects remain open for improvement (e.g. accumulation time, simpler modification process, portability and *in situ* application), the detection of trace and ultra-trace levels of inorganic Hg^{2+} using voltammetry is a promising technique. Recent advances in this field have brought us closer to replacing conventional methods with an excellent voltammetric technique, providing a simplified sensing platform (chemical sensor) for *in situ* monitoring of inorganic mercury. Future work needs to honestly and directly tackle issues of selectivity and heterogeneity. In addition to this, it is only by engaging with environmental samples that the full potential of voltammetry can be realised.

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