# Voltammetric determination of metal ions beyond mercury electrodes. A review.

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## Abstract

For a long time mercury electrodes have been the main choice for the analysis of metal ions and some metalloids. However, in the last years, safety and environmental considerations have restricted their use and encouraged the search for alternative materials more environmentally friendly and with more possibilities for *in-situ* and flow analysis. This research has been reinforced by the popularisation of nanomaterials, biomolecules and screen-printed electrodes, as well as for the new advances in sensor miniaturization and integration of the electrodes in multi-sensor platforms and electronic tongues. The present review critically summarizes and discusses the progress made since 2010 in the development and application of new electrodes for the analysis of metals and metalloids.

## Introduction

Metal and metalloid ions are prominent contaminants on the Earth surface. Their persistence in some ecosystems as waters and soils, consequence of their non-biodegradability, together with the fact that they can be biotransformed, bioaccumulated or biomagnificated, make them a subject of major concern. Although some of them (e.g., iron, selenium, copper, cobalt, manganese, zinc) are essential for human life in small levels, most of these metals are harmful when they are at high concentrations. They reach the environment from both natural (atmospheric inputs and aeolian processes) and anthropogenic (industrial processes, agriculture and mining industry) sources, being anthropogenic sources the most problematic ones. In general, natural sources set the background levels, although contamination by natural sources is a priority in several regions of the world. These facts make necessary the control of metal and metalloids contamination and the establishment of safety limits or maximum contaminant levels in some media and products [1-8]. Thus, the establishment of analytical methodologies to analyze or detect metal ions at low concentrations levels, not only in environmental samples (water, soils, biota) but also in food, drugs and biological samples, is nowadays an urgent challenge. Organizations as World Health Organization (WHO), USA Environmental Protection Agency (EPA) or Food Agricultural Organization (FAO) publish periodically guidelines to define the recommended limits for contaminants in different media. As an example, the maximum limits of some elements regulated or recommended by different organizations in drinking water and in food are summarized in Tables 1 and 2 respectively.

Among the different analytical methods described in the literature, atomic absorption and emission spectroscopies, cold vapor atomic fluorescence and inductively coupled plasma techniques (both optical and mass spectrometry modalities) are those commonly used for routine analysis of metal ions at low concentration levels. Literature devoted to the application of these techniques to the analysis of metal ions is very abundant and methodologies for the determination of these analytes in different samples have been described [9-13]. However, simple, rapid, inexpensive and *in-situ* analysis cannot be allowed with these techniques, at least working in the usual way. On other hand, voltammetric techniques are also very suitable for the determination of metal ions at small levels of concentration, in particular stripping techniques because of their favorable detection limits, sensitivity, capability to multielement determination and availability of simple and portable instrumentation. Related with these techniques, the development of sensing platforms has opened new possibilities in the development of analytical methodologies to perform measurements out of the lab, reducing sampling and monitoring costs. Chemical sensors represent a new class of analytical devices characterized by their small size, low price, and friendly use, and by the fact that can ideally provide information at real time. They can be incorporated to the usual instrumentation used in the lab or to specially designed instruments to carry out measurements on site. Sensors basically have two well-differentiated parts: i) a recognition element that can be more or less complex and interact directly with the analyte, and ii) an instrumental element that transduces the interaction with the analyte in a processable signal.

Voltammetry, in particular with mercury electrodes, has been considered a very powerful technique for the analysis of either inorganic or organic analytes, with low detection and quantification limits and with high reproducibility and repeatability [14]. Figure 1a (adapted from reference [14]) shows a schematic representation of the relative application ranges and the concentration limits of conventional voltammetric techniques relative to other analytical techniques. Classical mercury electrodes have been particularly interesting for the analysis of metal ions by voltammetry. These mercury based electrodes are the hanging mercury drop electrode (HMDE), the dropping mercury electrode (DME/SMDE) and the mercury film electrode (MFE). These classical mercury devices have the advantages of high sensitivity and reproducibility, high hydrogen overpotential, wide cathodic potential range, e possibility to form amalgams and facility to obtain pure surfaces.

Because of mercury toxicity, in the last decades, some European regulations devoted to the banning of exports and safe storage of metallic mercury have caused a policy against this material which has led to its almost total disappearance in some products or processes. In the case of voltammetry, the use of mercury is not forbidden and many researches still produce valuable works with mercury electrodes. However, such restrictive policy has discouraged the use of mercury drop and mercury film electrodes, as shown by the slow but continuous decrease of publications involving these devices, For instance, in the Web of Science, a fast research with the keywords “mercury” and “HMDE, SMDE or MFE” produced 43 matches in 2010 and 29 in 2016. However, this limitation, instead of reducing the use of voltammetry as an analytical technique, has encouraged researches to explore alternative electrode materials with features similar to those of mercury but with lower toxicity. The introduction of new electrode materials has open voltammetry to new challenges involving the development of new electrodic designs that allow moving measurements performed in a classical laboratory to *in-situ* analysis or process control. Hence, the aim of this work is to present a general overview of the evolution of electrode materials to build sensors used in voltammetric measurements since 2010 until now for the analysis of metal ions, paying especial attention to the recognition elements, the relevance of the device modifications, their configurations and their analytical applications.

From classical mercury electrodes used for the analysis of metal ions by voltammetric techniques, voltammetric devices have changed greatly over the years. In 2000, bismuth was proposed as electrodic material [15]. This metal, with features close to those of mercury and the additional advantage of being more environmental friendly, has become a valuable and attractive alternative to mercury based electrodes not only for the analysis of metal ions, but also for the analysis of organic compounds [16-19]. Subsequently, antimony has been considered as another relevant electrodic material, with toxicity higher than that of bismuth, but still lower than that of mercury. This electrodic material provides interesting features such as favorable hydrogen overpotential, with the plus of a wider operational potential window, the possibility of working in very acidic media (pH ≤ 2) and a relatively small signal related with its own oxidation [20-22]. Although in some cases solid electrodes based on these materials are considered, the use of bismuth and antimony electrodes usually implies the preparation of a film coated on a substrate via an appropriate coating method. The use of gold or carbon (carbon paste, glassy carbon, carbon ink, boron-doped diamond) electrodes as devices to analyze metal ions by voltammetry has been also considered in some classical applications.

These bare electrodes suffer very often from a lack of sensitivity or selectivity that needs to be improved. With the aim of increasing these parameters, an additional step based on the modification of the substrate can be included in its fabrication procedure. Thus, modifications involving nanoparticles or nanomaterials, which increase the effective surface and improve the electro-transfer kinetics, are considered. Other modifications involve conducting polymers, ionic liquids, (bio)molecules among others that are devoted to increase the device selectivity. Usually combinations of different materials and molecules are considered for electrode modifications conferring to the device a hybrid character [23, 24]. Figure 2 shows the most relevant aspects to be considered in the development of a voltammetric sensor.

Another important point that has to be taken into account in the development of voltammetric sensors for analytical purposes is the design of the devices to allow measurements on-site, with portable instruments,  etc. The use of screen-printed electrodes (SPE) or the implementation of sensing systems in more complex platforms (electrode arrays, electronic tongues, …) can be also considered in this point. Nowadays, SPEs represent a good approach for the preparation of voltammetric sensors, due basically to their simple, accessible, low cost and mass production character. The number of publications related to these devices is enormous as it can be seen in these reviews [19,25-29], indicating the strong potential of this electrodic design.

Related to voltammetric techniques, differential pulse voltammetry (DPV) or square wave voltammetry (SWV) are preferred if a preconcentration step is not required. However, the use of stripping techniques is mandatory when low levels of concentrations have to be determined, being anodic stripping voltammetry (ASV) the most common mode for metal analysis, although in some cases adsorptive stripping voltammetry (AdSV) is applied. In AdSV, the preconcentration step does not involve an electrodic process since the analyte is incorporated to the electrode by adsorption through a complexation process with a reagent that can be in the bulk solution or previously integrated in the same electrode surface (modified electrodes with recognition elements). In both cases, a differential pulse (DP) or a square wave (SW) scan is applied in the stripping step [30,31]. Figure 1b shows the most relevant voltammetric techniques that can be used with voltammetric sensors.

Several reviews appear in the literature totally or partially devoted to the analysis of metal ions [23,25-28,32-37], or to the analysis of particular metal ions as platinum group metal [38], inorganic arsenic [39] or mercury [40] using modified voltammetric electrodes. Nevertheless, we would like to complement these valuable works with a general, panoramic view of the different strategies that have been applied in the last years to substitute mercury electrodes by environmentally safer devices in the determination of heavy metals and metalloids. Such strategies mainly involve electrode modification, but also combination of electrodes in sensor arrays, and intend to not only approach the excellent electrochemical properties of mercury but also surpass some traditional limitations of this material for flow or on-site analysis.

The work includes references since 2010 until now and is structured in tables devoted to the main electrode modifiers. Mercury electrodes are the first to be discussed; later classical substrates as gold and carbon have been considered. Bismuth and antimony are discussed next as the main alternative to mercury substrate. In each case, different strategies of modification are considered, from the simplest to the most complex ones. Selective modification with (bio)molecules and biomaterials are subsequently introduced followed by methods based on arrays of electrodes and voltametric tongues. A critical evaluation is made on the actual improvements achieved in comparison to mercury as well as future perspectives.

## Mercury electrodes

Mercury electrodes have demonstrated to be an excellent tool for the analysis of metal ions. The review of Barek *et al.* [14] summarizes very clearly the most relevant properties of these devices, i.e. the easy way to obtain pure surfaces (new drops or thin films can be easily created), the generation of a pseudostationary state for linear sweep voltammetry at high scan rates, and the large potential range in the cathodic zone (from 0.4 V to -2.5 V depending on the supporting electrolyte). These facts, together with their high reproducibility and repeatability, are responsible for the good performance of the commercial electrodes. Moreover, the favorable signal-to-noise ratio makes these devices very appropriate for the analysis of both organic and inorganic compounds, and particularly for the analysis of metal ions due to their wide cathodic potential range in which the standard reduction potential of most metal ions is included. In contrast, the narrow anodic range hinders the application of mercury electrodes to organic substances that can be easily either reduced or oxidized.

However, as it has been explained in the introduction section, the policy against mercury has caused a significant decrease in the use of mercury based electrodes. Table 3 shows some published works from 2010 that involve the use of conventional mercury electrodes, together with some works that include a modification of the mercury electrode. The evaluation of these publications shows that HMDE is used in control analysis of Cd(II), Pb(II), Cu(II) and Zn(II) in samples related with real or potential contaminated areas which are presented as case studies

[41-53]. ASV has been the voltammetric technique considered and almost all works are more focused on the sample and the required treatment than on the method for the analysis of these metal ions. However, Rodrigues *et al*. [54] present an approach to improve the classical ASV methodology in which a very cathodic accumulation potential is applied allowing an increase of the voltammetric peak current of 5-10 folds. Authors point out that this effect is likely due to both mercury drop oscillation at such cathodic potentials and the added local convection at the drop surface caused by the evolution of hydrogen bubbles. Although HMDE is the most commonly used, MFE has also been proposed [53].

Cathodic stripping voltammetry (CSV) is a technique closely linked to mercury electrodes, since during the accumulation step a complex or an insoluble salt is formed between the analyte and the oxidized form of the electrode material. Although this voltammetric mode is mainly considered for the analysis of organic compounds, some inorganic anions can also be determined, among them some metalloids as selenium, antimony or arsenic. Using this technique Se(IV) is determined in milk and dairy products applying in the stripping step a DP scan [51].

The use of ASV implies the formation of an amalgam. This amalgam can be considered as a recognition element which interacts selectively with certain metal ions. Not all the metals or metalloids have the same solubility in mercury, or can be easily reoxidized, thus hindering their analysis. In these cases, AdSV appears as a good option to determine these compounds at low concentration levels. Although this methodology using mercury electrodes is already well established, works devoted to the improvement of the analysis of some elements still appear in the literature. Among them, those reported by Arancibia *et al.* [55-59] related with the analysis of Sb(III), As(III), V(V) and Co(II) (see Table 3). These authors consider the use of ligands containing sulfonic groups, pointing out that the effect of sulfonic groups causes lower adsorption of the free ligand on the HMDE, allowing a greater adsorption of the complexes and minimizing the competition of the ligand and the complex for the free sites on the electrode surface [55-57]. For the analysis of As(III) in river water [58], an AdSV indirect methodology based on the formation of complexes with ammonium pyrrolidine dithiocarbamate (APDTC) or ammoniumdiethyl dithiophosphate (ADDTP), prior to the formation of an intermetallic compound with copper, was proposed. The application of AdSV to the determination of metal ions as Co(II), Fe(III), Ni(II), Cu(II), Zr(IV) or V(V) in human serum [60], pore water [61] or natural waters [62] is also described. In these works, the classical methodology is improved with the aim to determine these analytes in particular samples. Caprara *et al.* [63] determine Fe(III) in seawater using 2,3-dihydroxynaphthalene as complexing agent and exploiting the catalytic effect of atmospheric oxygen. The particularity of this work comes from the cell design that allows the determination in 500 µL sample volume. Although very good and well stablished ASV methods devoted to the determination of Cd(II) and Cu(II) have been published, in [64] an AdSV method for their analysis is presented.

The irruption in the market of the screen-printed technology has also affected mercury based devices. On one hand, screen–printed electrodes (SPEs) constitute a more attractive alternative to mercury than solid electrodes, since their disposable character avoids tedious polishing, cleaning and activation procedures commonly associated to solid surfaces, which have to be reused. On other hand, SPEs can be applied as a new support for the deposition of mercury films, with the above-mentioned advantages as compared to conventional solid electrode supports. For instance, Zaouak *et al.* [65,66] report an electrochemically adapted automation module with a carbon SPE, modified *ex-situ* with a very low concentration of mercury salt, coupled to a UV-photolysis unit. This apparatus can inform about total concentration and potentially bioavailable fraction of Cd(II) and consequently about sample toxicity. However, SPEs modified with mercury show important drawbacks because of the heterogeneous deposition of Hg on the rough surface of SPE which limits their suitability [67]. If one has to use a mercury film anyway, a mirror-like polished glassy carbon electrode seems to be a much better option.

The ability of mercury to form amalgams with some electrodic materials like gold and silver has also been considered to design sensors for the analysis of metal ions, although the improvement is not reliable. Nowadays, the use of these materials is combined with a proper design to give an added value to the electrode [68-70]. Likewise, the use of mercury oxide as a precursor for the formation of a mercury film has also been considered for the determination of Cd(II) and Pb(II) in milk samples [71].

In the last years, some sensors modified with others materials than mercury, have been introduced to increase the sensitivity of such platforms. The group of Prof. Arancibia [72-74] modifies glassy carbon electrodes (GCE) by dropping Nafion on the electrode surface and coating an *ex-situ* Hg film. This electrode has been proposed for the analysis of Zn(II), Cd(II) and Pb(II) in waters by AdSV using different complexing ligands, although better results are achieved with a HMDE and direct SV measurement. The negative Nafion film prevents the appearance of a signal related with the free ligand between the Pb(II)- and Cd(II)- complexes signals allowing a good resolution of both peaks.

As it has been explained above, the use of nanomaterials or nanoparticles for the preparation of voltammetric sensor devices is very common due to the unique properties of these materials that cannot be achieved considering only the classical electrodic substrate. Despite of the limited use of mercury, mercury electrodes based on these nanomaterials are described. Thus, the *in-situ* deposition of mercury on the surface of a GCE modified with graphene [75] or the formation of mercury-droplets on the surface of a carbon SPE (SPCE) modified with multi-walled carbon nanotubes (MWCNTs) [76] are described. Also, a disposable gold nanoparticles (AuNPs) amalgam modified SPCE has been proposed for the monitoring of Cd(II) in water samples using a portable analytical system developed for on-site environmental detection [77]. The use of single-walled nanotubes (SWCNTs) coated on a GCE is also considered [78]; the synergistic effect of Hg and Bi, as well as the enlarged activated surface and good electrical conductivity of SWCNTs, contribute to the enhanced activity of the electrode.

In our opinion, traditional drop mercury electrodes, especially HMDE and SMDE, still can play an important role for some applications, like in the determination by ASV or AdSV of Cu(II), Pb(II), Cd(II), Zn(II) Co(II), Ni(II) and V(V) at ppb levels. This is because none of the attempts made has clearly surpassed the superior features of mercury drop, i.e. very wide cathodic potential range (allowing simultaneous determination of many ions) and continuous refreshing of the electrode surface (minimizing fouling and increasing reproducibility). As for mercury film electrodes (MFE), more suitable for *in-situ* or flow measurements than drop mercury electrodes, we believe that the improvements should essentially go in the direction of replacing mercury by alternative materials. The development of new supports does not significantly improve the characteristics of classical MFE or even those of mercury drops, and the electrodes may be more environmentally dangerous than SMDE or HMDE especially if concentrated Hg(II) solutions are used to form the film.

## Gold electrodes

Gold electrodes have been, in general, scarcely used for the analysis of metal ions because of their limited working potential range at negative potentials and worse detection limits in comparison with mercury electrodes. An additional disadvantage of gold electrodes with respect to mercury electrodes is their capacity to adsorb anions onto their surfaces. This problem can be solved applying a negative desorption potential between the deposition and the stripping step. However, the use of Au for the analysis of Hg(II) has demonstrated to be very appropriated due to its high mercury affinity that enhances the preconcentration effect. Table 4 shows some relevant examples, in which gold electrodes or carbon based electrodes modified with AuNPs are considered for the analysis of Hg(II). Locatelli *et al.* [45-50] describe the analysis of Hg(II) in different biological and environmental samples by SWASV in a classical gold electrode. In these works the subsequent determination of Cu(II), Pb(II), Cd(II) and Zn(II) with a HMDE is also presented (Table 3). The analysis of Hg(II) and As(III) in milk and water samples is carried out using a gold rotating disc electrode (AuRDE) [52]. The use of gold screen-printed electrodes (SPAuE), both commercial [79] or prepared in a PET support [80], is also considered for the analysis of Hg(II) in natural and contaminated samples.

The use of AuNPs instead of the classical gold electrode improves the sensitivity in the analysis of Hg(II) [81-86]] (Table 4). A rigorous comparison of SPCE modified with nanomaterials or with hybrid nanomaterials shows the advantages that can provide the combination of different nanomaterials in one device [86]. The deposition of gold on GCE modified with graphene (graphene-based gold nanocomposite electrode) has also been reported for Hg(II) determination [87].

In the voltammetric analysis of inorganic arsenic, gold electrodes have demonstrated to be the most suitable ones. In the last years, some works devoted to the analysis of As(III) have been published in which nanomaterials play a key role [88-90]. While in the case of mercury electrodes CSV is the most convenient voltammetric approach for the analysis of As(III), in the case of gold electrodes measurements are basically carried out by ASV since the oxidation of Au is more difficult than that of Hg.

Gold based electrodes have also been used for the analysis of Zn(II), Cd(II), Pb(II) or Cu(II) and Cr(VI) [91-96], in which the incorporation of gold microwires [91], SPAuE [92] or nanomaterials on the device [93-96] are considered. But, in any case, really cathodic reduction potentials are not allowed (see Table 4). Alves *et al.* [91] justified the use of gold microwires electrodes not only to allow the simultaneous analysis of Cu(II), Pb(II), Zn(II) and Hg(II) but also to avoid the formation of Zn-Cu intermetallic compounds that can affect voltammetric signals of these metal ions in mercury electrodes. Rueda–Holgado *et al.* [92] propose the use of a SPAuE for the analysis of Cu(II) and Pb(II) in atmospheric solid deposits, being the main interest of the work the coupling of an atmospheric elemental fractionation sampler to a semiautomatic measurement system. Determination of Cr(VI), based on its direct reduction to Cr(III) in highly acidic media, has been performed with a gold film carbon composite electrode [97], but the surface of the working electrode needs to be modified with a new electroplated gold film before each experiment. The use of AuNPs has also been proposed for the modification of some electrodes for the analysis of Pb(II) and Cd(II) [93], or Pb(II) and Cu(II) [94,96]. In the first work [93], AuNPs were electroless plating on a SPCE modified with graphene; while in reference [94] AuNPs were dispersed on a carbon foam structure and the whole was bound to a gold surface using chitosan as binder. Carbon foams are a new form of carbon material that has been used extensively as electrode material for supercapacitors because of its large porosity, good electrical conductivity, and high specific surface area [98,99]. The electrochemical deposition of AuNPs on SWCNTs allows [96] the fabrication of a flexible device when SWCNTs are created onto a flexible PET support. AuNPs enhanced the stripping peak current of metal ions in acidic media without peak splitting compared to the performance of bare SWCNT electrodes. The possibility to create a porous gold electrode modified with graphene nanodots has also been described for the analysis of Pb(II) and Cu(II) [95], allowing the analysis without a preconcentration step.

In summary, gold electrodes have been classically used in the determination of Hg(II) and, in lesser extent, As(III). These applications are still in use with the implementation of AuNPs or the inclusion of other nanomaterials on the gold electrode surface, allowing also the determination of other metals with acceptable detection limits.

## Carbon based electrodes

The use of conventional carbon electrodes for the analysis of metal ions has been relatively scarce. In this section, we have included those electrodes essentially based on carbon (in its different forms) materials. Modifications with other materials are included in the following sections depending on the nature of the substrate or the main modifier. The only reference found using a GCE has been one related to the analysis of Pb(II) and Cd(II) in poultry and bird game meat [100], in which authors determine these analytes after acidic digestion of the sample and establish the figures of merit of the methodology with meat reference materials. However, in recent years the incorporation of structures based on carbonaceous materials like carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene or conductive diamond has become a good option to improve chemical, physical, and electronic properties of the bare material. A review devoted to the use of graphene based materials for the determination of hazardous ions has been recently published [37]. In Table 5 works devoted to these electrodes published since 2010 are presented. Stefanova *et al.* [101] consider a GCE and a paraffin impregnated graphite electrode both modified with MWCNT for the analysis of Pb(II). However, the application of DCV measurements allows very poor detection limits. The use of the stripping mode, together with the incorporation of Nafion in the device design improves the detection limits of the method [102]. Carbon electrodes modified with graphene have also been considered [103,104]. In the first case, a graphene ultrathin film electrode is used for the analysis of Pb(II) with a good performance [103]. A relevant increase in the sensitivity is allowed modifying covalently the surface of a GCE with graphene oxide for the analysis of Pb(II) and Cd(II) [104].

Boron-doped diamond (BDD) appears as an attractive electrodic material in voltammetric analysis due to its particular properties such as a wide potential window in aqueous media, low background current, low capacity of adsorption, high stability against corrosion, long-term response stability and low dissolved oxygen sensitivity [105,106]. In Table 5, works related with the use of BDD based electrodes are presented, in which the analysis of Pb(II) in tap water

[107], Cd(II), Pb(II), Cu(II) and Hg(II) in waste water [108] and Zn(II) in environmental rubber industry samples [109] are described. Special attention is paid to the analysis of Sb(III) reported in [110], which considers edge plane pyrolytic graphite and SPE electrodes, both modified with BDD. Although Sb(III) is an element of significant environmental concern, there are not many works devoted to its analysis. The use of boron doped nanocrystalline diamond is presented in [111,112] for the analysis of Pb(II), Cu(II) and Hg(II), where the reduction of diamond grain size improves the sensitivity and the selectivity together with its catalytic activity.

Wei *et al.* [113] propose the functionalization of MWCNTs with $NH_3$-plasma using the modification to enhance the sensitivity for the detection of metal ions taking profit of the acid–base interaction between electron-rich amino ligands and electron-deficient metal ions.

Nowadays the use of pure carbon based electrodes is limited, but they are valued substrates for modification as it can be seen in Table 5 and following. In contrast, BDD is a promising material with a wide working potential range, but it has important drawbacks as the difficulty of being modified.

## Bismuth electrodes

With the publication in 2000 of a work devoted to the use of a bismuth-coated carbon electrode for the analysis of metals by Wang *et al.* [15], the great revolution promoting the practical displacement of mercury as electrodic material starts. Since 2000 until now, a great deal of works devoted to the use of bismuth electrodes have been published. At this point, we want to highlight some reviews, which clearly show the evolution and possibilities of this material as voltammetric electrode. In 2005, Wang and Economou [16,17], almost simultaneously, wrote the first reviews devoted to this subject, emphasizing its advantageous analytical properties and remarking that bismuth based electrodes are especially convenient for stripping analysis due to their capability to form alloys with other metals. Later in 2010, Svancara *et al.* [18] published a commemorative review devoted to the first decade of bismuth devices. In 2013 Serrano *et al.* [19] dedicated another review to bismuth screen-printed electrodes, in which the design and the fabrication of these economical disposable devices are emphasized. Therefore, in the present work, only the latest investigations not included in previous reviews will be considered.

As it happens with other materials, we can consider not only the bismuth bare or the bismuth film electrodes, but also those devices in which although bismuth is the main active material, nanomaterials play a key role. At this point, it is important to remark the relevance of the kind of bismuth coating to the substrate, being the most general and well established approaches the *ex-situ* plating, the *in-situ* plating and the "bulk" methods. In the *ex-situ* plating method, bismuth is deposited on the electrodic surface by electroplating in a Bi(III) solution, and later the modified electrode is immersed in the measurement solution. In the case of the *in-situ* plating method, Bi(III) is added directly to the measurement solution and bismuth is deposited on the electrode surface during the analysis. The "bulk" method implies the presence of a precursor in the surface of the device that has been incorporated during the manufacturing of the bismuth electrode, and has to be reduced to metallic bismuth prior to the sample analysis. The most common precursors are bismuth oxide, bismuth citrate or bismuth aluminate.

Table 6 shows the most relevant works devoted to the analysis of metal ions published since 2010, which are not included in reviews cited above. Although bare bismuth electrodes have not been considered very often, Armstrong *et al.* [114] present a bare bismuth electrode (BiE) made in-house by melting bismuth needles into a hand-blown glass casing for the individual and simultaneous analysis of Pb(II), Cd(II) and Zn(II). De la Gala *et al.* [115,116] propose the use of an electrode, also made in-house, fabricated from a bismuth rod for the analysis of the same metal ions in environmental and biological samples. Methodologies involving the formation of bismuth film via both *in-situ* and *ex-situ* or "bulk" are the most relevant approaches. The use of different designs is also considered, as well as the incorporation of nanomaterials or other modifiers. Kawde [117] analyzed Pb(II), Cd(II) and Zn(II) modifying different carbon surfaces as glassy carbon (GC), carbon paste (CP) or graphite pencil (GP). *Ex-situ* approach is preferred in AdSV analysis, as Segura *et al.* [118] and Rojas-Romo *et al.* [119] propose for the analysis of Ni(II) and Sb(III) using 1-nitroso-2-napthol and quercetin-5-sulfonic acid as chelating agents, respectively. In the first case, a carbon disc electrode was considered while in the second a SPCE was used.

A special design of an electrodic device that allows the analysis of Pb(II) using only 15 µL of sample is described in [120]. A paper double-sided conductive adhesive nanostructured carbon tape was considered to electroplate the bismuth film. The incorporation of filter paper on the electrode surface, together with the incorporation of an Ag/AgCl and a Pt wires, allows quantifying migrated Pb(II) from toys by SWASV.

The use of a precursor is also considered in the fabrication of Bi-electrodes. Sopha *et al.* [121] describe a sensor that includes, mixed with CP, ammonium tetrafluorobismuthate that acts as precursor of metallic Bi. On other hand, the ionic character of this precursor provides to the electrode an additional benefit that is consequence of the favorable properties of ionic liquids when they are included in an electrochemical platform.

Different approaches have also been considered to lower the detection limits of bismuth electrodes for the analysis of metal ions. Thus, Chen *et al.* [122] prepare a porous carbon SPE combining a printing procedure of a graphite based layer doped with $CaCO_3$ powders and the subsequent dissolution of these powders. The Bi-film is formed via *in-situ*, electrodepositing Bi(III) together with the target analytes. In [123] a GCE is modified by successive electrodeposition of exfoliated graphene oxide (GO) and an *in situ* plating bismuth film. Other approach is the use of mixed metal films as it is presented in [124] or [125], where an *in-situ* Bi-Sb film and an *in-situ* Sn-Bi film are considered respectively, both using a GCE. In both cases detection limits lower than 1 µg $L^{-1}$ are achieved. Bi-Sb electrode offers a good performance in acidic media (pH≤2), which can be advantageous for trace metal ions analysis. The use of Bi-nanoparticles (BiNPs) directly embedded on the electrode surface has also been proposed by Yang *et al.* [126] and Lee *et al.* [127], who design a BiNPs/GCE and a BiNPs/AgPE for the analysis of Pb(II), Cd(II) and Zn(II) respectively. In the first case, Nafion is used to fix BiNPs on the GC surface. In the second one, the substitution of CP by silver paste as conducting layer produces an increase of the sensitivity due to the lower electrical conductivity of silver. Hybrid-nanomaterials are also considered in [128,129]. In the case of a GCE modified with BiNPs-enriched nanoporous carbon on graphene sheets (BiNPs-NPC-GS/GCE) [128], the differentiation of Tl(I) from Pb(II) and Cd(II) can be achieved. This modification is performed by pyrolysis of zeolitic imidazolate nanocrystals deposited on graphene oxide and subsequent *in-situ* deposition of BiNPs by chemical reduction of Bi(III) ions by $NaBH_4$. In the second case [129], BiNPs are uniformly anchored onto the surface of individual graphene nanosheets, which prevent restacking of graphene, resulting in good dispersion in solvents. It is interesting to remark that with this device the signal of Cu(II) appears before the oxidation signal of bismuth. The use of an electrochemically reduced graphene oxide (ERGO) film to modify a SPE [130] or a pencil-graphite electrode [131] has been considered for the preparation of an *in-situ* Bi-film electrode. In both cases, a conditioning step must be applied to the electrode after each measurement.

The use of other compounds, different from nanomaterials, can also be considered to improve the performance of the sensor. An example of a complementary compound used in the fabrication of sensors is Nafion. Although the basic role of Nafion in sensors for the analysis of metal ions is to act as an antifouling coating membrane to decrease the interference of the surface-active compounds, sometimes it is used as stabilizer to improve the mechanical stability of the bismuth film electrodes [132] or to enhance metal ion preconcentration due to its cation-exchange properties [133,134]. Thus, in Table 6 some electrodes, which include Nafion in their composition, are described. Xiao *et al.* [135] propose for the analysis of Pb(II) and Cd(II) an *in-situ* Bi-sensor based on a well-ordered porous carbon structure doped with nitrogen which is mixed with Nafion before the deposition on the surface of a GCE. In this work, this modifier allows the entrance and the accumulation of the metal analytes and prevents the adsorption of interfering surface active substances on the electrodic surface. Other bismuth based electrodes, in which Nafion plays a key role, are also reported in the literature to analyze Pb(II), Cd(II) and Zn(II). Dey *et al.* [136] describe a device in which an *ex-situ* Bi film is formed on a CP substrate modified with CNTs; in this electrode a film of Nafion is disposed on the bismuth film as a physical protector of the sensor. Huang *et al.* [137] consider a hybrid nanocomposite to enhance the preconcentration efficiency of metal ions and accelerate the electron transfer rate at the electrodic interface that consists of one-dimensional MWCNTs and two-dimensional graphene oxide sheets. Rehacek *et al.* [138,139] consider a pyrolyzed photoresist film (PPF) as substrate for the formation of a Nafion coated Bi-film in which Nafion acts as a barrier for biomolecules. These PPFs are highly electrically conductive materials with a microstructure similar to that of GC. The main benefit of PPFs is their very high smoothness and the possibility to pattern the film before pyrolysis by photolithography. This PPF material has also been considered in [140,141] to build *in-situ* or *ex-situ* Bi-modified pyrolyzed photoresist carbon electrodes for the determination of Ni(II) and Cr(VI) by AdSV using as complexing ligands DMG and pyrocatechol violet, respectively.

Moreover, the use of graphene functionalized with negatively charged poly(sodium 4-styrene sulfonate) (PSS) improves the sensitivity and linearity of the analysis of Pb(II) and Cd(II) creating more adsorbing sites [142].

In general terms, we consider that Bi films are at the moment the best alternative to mercury electrodes for metal determination by both ASV and AdSV modes. The provided detection limits are slightly higher (in the order of a few µg $L^{-1}$) and particularly in the *ex-situ* Bi-film approach the anodic working region is more limited than in HMDE devices, but many of the classical applications of mercury electrodes can be carried out with Bi films reasonably well. Moreover, the inclusion of nanomaterials as electrode modifiers improves their detection limits making Bi based electrodes better.

## Antimony electrodes

A parallelism between antimony and bismuth based electrodes can be established, not only in their preparation but also in their applications, although the acceptance of this material has not reached the levels of bismuth. As bismuth electrodes, antimony electrodes constituted an environmental friendly alternative to mercury based electrodes. On the other hand, antimony offers some particular and interesting properties as it has been pointed out in the introduction. Apart from a favorable negative overvoltage for hydrogen evolution and a wide potential window, antimony electrodes can work in very acidic media (pH < 2). In 2007, the first work devoted to antimony as electrodic material was published [20]. Recently, a review with an important number of applications devoted to the analysis of metal ions has been published [22]. On the other hand, in 2015, a critical paper in which different metal modified electrodes were compared for the analysis of Pb(II) and Cd(II) was published [143]. Bismuth, antimony, tin, and combinations thereof, were considered as modifiers of GCE, BDD electrodes and SPCE.

In the present review, only the latest works not included in the above-mentioned reviews will be considered (see Table 7). Thus, Sosa *et al.* [144] demonstrate the goodness of an *in-situ* antimony modified SPCE for the simultaneous analysis of Cd(II), Pb(II) and Cu(II) since no competition between Cu(II) and Sb(III) for the electrodic surface is noticed. Chen *et al.* [145] describe an antimony film modified sodium montmorillonite doped CPE for the analysis of Cd(II), in which Sb is coated *in-situ*. Sodium montmorillonite (NaMM) is a layered aluminosilicate clay mineral that exhibits excellent intercalation properties that facilitates adsorption and cation exchange. Commercial SPEs modified with different carbon nanomaterials (graphene, CNTs and CNFs) have been tested as electrode platforms for the *in-situ* Sb film formation [146], being the CNF modified SPCE the most convenient for the analysis of Pb(II) and Cd(II). In [147] an *ex-situ* SbSPCE is proposed for the analysis of Ni(II) by AdSV using dimethylglyoxime as chelating agent. Comparison with an *ex-situ* BiSPCE and a $\mathrm{Bi_{sputtered}}$SPCE is also performed.

Sb-film electrodes are also considered for the analysis of rare earth metals [148] or metals of the platinum group [149,150] applying AdSV. In reference [148] the analysis is performed using alizarine as complexing agent and an *in-situ* antimony GCE, while in [149] an electrode formed by reduced graphene oxide impregnated with Sb-nanoparticle was considered. In reference [150] Pd(II) is analyzed using an *ex-situ* antimony film coated in a SPCE with dimethilglyoxime as complexing agent.

Just to conclude, Sb films, although less popular than Bi films, constitute a valuable and complementary alternative to them for measurements in acidic media or under oxidative potential (eg. Determination of Cu(II)-ions). As in the case of Bi films, the choice of the substrate and the incorporation of nanomaterials can improve the analytical features of Sb film electrodes.

## Other materials

Apart from the substrates considered above, other metals, metal oxides, and silica materials have also been considered as inorganic electrodic elements for the analysis of metal ions. In Table 8 some examples of devices based on these materials are presented. Although the use of copper electrodes for the analysis of metal ions is not very common because it is easily oxidized, Jovanovski *et al.* [151] consider a copper film on a GCE for the analysis of Pb(II) and

Hg(II) due to the advantageous formation of copper alloys or intermetallic compounds. Based on the same principles, Pei *et al.* [152] developed a copper-based point of-care sensor for Zn(II) determination in blood serum. In [153] a Ce-impregnated zeolite is used as modifier of a CPE and proposed for the simultaneous analysis of Pb(II) and Cd(II). The use of films of metal nanoparticles has been considered in references [154-156], in which tin nanoparticles have been used to decorate, through an electrodeposition step, the reduced graphene oxide (RGO) deposited on a GC sheet electrode (GCSE) [154] for the analysis of Pb(II), Cd(II) and Cu(II). Ni-nanoparticles were also deposited on a GCE modified with a carbon nanoporous material [155] for the analysis of Hg(II) in fish samples; this device takes advantage of the high area and roughness of the carbon material which is favourable for dispersion of nanoparticles. Xu *et al.* [156] consider a Sn-Pb hybrid metal electrode, in which the synergic effect between Sn-Pb particles and the mesoporous carbon (MPC) used as modifiers of a GCE improves the analysis of Cd(II) in river water samples.

Metal oxides, either nanostructured or not, have been also used in the analysis of metal ions due to their morphology, catalytic properties and low toxicity. As well, the use of iron oxides has been considered in [157,158] for the analysis of metal ions. In [157] a reduced graphene oxide (RGO)-$Fe_3O_4$ nanocomposite with high adsorption capacity was examined for the analysis of Pb(II), although the influence of Cd(II) and Hg(II) was also studied. In [158] the influence of different $\alpha$-$Fe_2O_3$ nanostructures on the electrochemical performance towards Pb(II) detection has been studied, demonstrating that nanorods are more sensitive than nanoplates or nanocubes. In the same line, Gao *et al.* [159], exploiting the adsorbent properties of $\gamma$-AlOOH, that is used as a solid-phase extraction sorbent for metal ions, modify the electrode surface of a GCE with aluminium oxide for the determination of Cd(II) and Pb(II) in drinking water. The use of highly adsorptive MgO with hierarchical micro/nanostructure of nanoflowers is considered in the electrode developed by Wei *et al.* [160] for the analysis of Pb(II) and Cd(II) in water. NiO-nanosheets with uniformly distributed mesoporosity modifying a

GCE allows the analysis of Hg(II) [161]; these nickel structures confer to the electrode a high conductivity, a larger surface, and a more efficient electron transfer. Other single oxides studied have been CoO [162] for the analysis of Cu(II), and $MnO_2$ [163] for Cd(II) and Pb(II) analysis. In the case of $MnO_2$, it was combined with different carbonaceous materials and the results found showed that the lowest LODs were achieved with the $MnO_2$/natural graphite composite. This is consequence of the highest catalytic activity for Pb(II) and Cd(II) in comparison with the other studied carbon materials. Lunsford *et al.* propose a CPE modified with a mixture of zirconium dioxide and titanium dioxide for the analysis of In(II) in the presence of Pb(II) [164], and the analysis of Cd(II) and Pb(II) [165] taking profit of the adsorptive capacity of both materials. Layered double hydroxides (LDHs) represent an important class of host–guest materials that can be useful for the analysis of some metal ions, as it has been demonstrated in [166], where the enhanced analytical signal for Cd(II) with respect other metals (Pb(II), Hg(II), Cu(II) and Zn(II)) facilitates its analysis. This electrodic material also presents a hierarchical flower-like structure.

Silicon carbide (SiC) is a semiconductor that could be considered as an alternative electrode material for ASV applications [167]. Similar to diamond, it shows a high degree of chemical and mechanical stability and, from an electrochemical point of view, SiC has a wide potential window, relatively low background current and good electrochemical activity in both aqueous and non-aqueous solutions. It is particularly interesting for the analysis of Ag(I) which cannot be determined in a mercury electrode due to its narrow anodic potential window. Nano-hollows spheres of $MgSiO_3$ were considered in [168] as a new material for the individual and simultaneous analysis of Cd(II), Pb(II), Cu(II), and Hg(II) demonstrating its convenience for the analysis of these metal ions in drinking water.

## Electrodes modified with molecules

The incorporation of organic molecules to the sensing system has essentially been proposed to increase selectivity. These molecules, either synthetic or natural, act as receptors and have the ability to recognise specifically metal ions. This specific recognition may be due to chemical affinity, cavity entrapment or both factors. In this section and in Table 9, we expose some relevant examples of electrodes modified with this kind of molecules. These molecules can be incorporated to different electrode substrates that have been already modified with nanomaterials or/and metal films.

Teng *et al.* [169] consider EDTA as modifier of a GCE previously inmobilized in graphene-like carbon nitride nanosheets for the analysis of Pb(II). Zhou *et al.* [170] describe a sensor for Hg(II) analysis, based on a graphene oxide (GO)-AuNPs hybrid indium tin oxide (ITO) electrode modified with 5-methyl-2-thiouracil (MTU). The goodness of this device could be attributed to the enhanced electron conductivity of the nanostructured membrane and the large electroactive surface area of the GO-AuNPs hybrid material, together with the expected selectivity due to the specific interaction between MTU and Hg(II). Small molecules have also been introduced in a sensor developed by Gupta *et al.* [171] for the analysis of Cd(II) and Cu(II), in which a graphene oxide terminated aminophenyl modified GC surface was considered. Afkhami *et al.* [172,173] select different Schiff bases as electrode modifiers, which form complexes with the target ions. In [172] they modified a CPE with N,N'-bis(3-(2-thenylidenimino)propyl)piperazine coated on silica NPs for the analysis of Cd(II), Cu(II) and Hg(II) in different complex matrices. In [173] the Schiff base 3-(4-methoxybenzylideneamino)-2-thioxothiazolodin-4-one and a CPE modified with MWCNTs as base electrode are proposed for the analysis of Pb(II) and Hg(II) also in complex matrices, while in [174] 2-hydroxybezaldehyde benzoylhydrazone is used as modifier of a CPE. The use of CPE modified with hexagonal mesoporous silica functionalized with acetyl-acetone by covalent coupling was considered by Popa *et al.* [175]. The high sensitivity achieved is a consequence of its high surface area, the numerous active sites, and the strong adsorption ability of the organically functionalized mesoporous silica.

Ionophores are macrocyclic molecules with well-defined cavities, which have the capability to extract selectively certain ions from an aqueous solution. These substances, which have commonly been used in polymeric membrane ion selective electrodes as ion carriers, can also be used in voltammetric sensors due to their selectivity toward a specific metal ion as Jiang *et al.* described [176]. They consider the N,N,N,N-tetrabutyl-3,6-dioxaoctanedi(thioamide), as specific cadmium ionophore, and an *in-situ* Bi film to improve the performance of the electrode.

Ionic liquids are a further possible modification. They are used not only as pasting binders of the CP substrate but also as extractive agent of the analytes. However, electrode modification with ionic liquids is combined with the addition of other molecules to increase not only sensitivity but also selectivity. Bagheri *et al.* [177] create a composite electrode using graphene, 1-n-octylpyridinum hexafluorophosphate as ionic liquid, that provides enlarged active surface area and strong adsorptive capability, and [2,4-$Cl_2C_6H_3C(O)CHPPh_3$] as a new synthetic phosphorus ylide that has a specific complexing ability. In [178] the ionic liquid is combined with an imprinted polymer that has been specially designed to recognise Hg(II) ions. In this work, a CPE is modified with an ionic liquid, the 1-octyl-3-methylimidazolium hexafluorophosphate, and impregnated with the imprinted polymer (ethyleneglycol dimethacrylate and dithizone) that has Hg(II) selective sites. Ion imprinted polymers have also been considered in [179,180]. Thus, Ghanei-Motlagh *et al.* [179] propose a new strategy to prepare the ion imprinted polymer, and the sensor obtained is applied to the analysis of Hg(II). In [180] a nanosized silver imprinted polymer was developed for the analysis of Ag(I). In the sensor developed by Es'Haghi *et al.* [181] for the analysis of Cd(II) and Pb(II), a porous polypropylene hollow fibre membrane was impregnated with a homogeneous mixture of nanomagnetic particles and an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate), locating a graphite rod inside the fibre lumen. In this sensor all the modifiers allow in only one-step the simultaneous purification, pre-concentration and trapping of Pb(II) and Cd(II) from water sample. In [182] the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, together with a mesoporous molecular sieve (P123-SH), which contribute with a large surface area and an uniform pore size distribution, build a sensor for Cd(II) analysis.

The use of crown ethers as receptors in voltammetric sensors is considered due to their conformational flexibility, the presence of multiple binding sites and the high selectivity to certain metal ions. These molecules have defined cavities for metal ion complexation enhancing their sensitivity and selectivity. Ghanei-Motlagh *et al.* [183] choose the aza-crown ether kryptofix 21 because interacts selectively with Cu(II) ions. The preparation of the kryptofix 21-capped AuNPs used to modify the CPE involves a step in which AuNPs are functionalized through the formation of a SAM with 11-mercaptoundecanoic acid. In [184] a CPE modified with 12-crown-4-ether and MWCNTs prepared by hand-mixing all the components was proposed for the analysis of Hg(II) ions in biological and environmental samples, while in [185] a CPE was modified with dicyclohexyl-18-crown-6-ether for the analysis of Tl(I). Simionca *et al.* [186] create a siloxane-crown ether polyamide copolymer based electrode for the analysis of Pb(II). They consider a SPCE modified by drop coating with a solution of the siloxane-crown ether polyamide copolymer dissolved in DMF.

Conducting polymers containing N or S atoms in their structure can strongly coordinate metal ions, and the analysis of these elements with CPs-based electrodes has received considerable attention in the last years. Yuan *et al.* [187] present the modification of three dimensional activated graphene nanosheets with a sulfonate-terminated polymer formed by chemical polymerization from m-aminobenzene sulfonic acid and aniline to prepare a sensor for the simultaneous analysis of Cd(II) and Pb(II). Tao *et al.* [188] consider, also for the analysis of Cd(II) and Pb(II), the polymer thiolated poly(m-phenylenediamine) created on the surface of a

GCE via electrochemical polymerization of *m*-phenylenediamine and mercaptosuccinic acid. Ruecha *et al.* [189] prepare a graphene-polyaniline nanocomposite for the modification of a SPCE for the analysis of Zn(II), Cd(II) and Pb(II). Polyaniline is also considered by Wang *et al.* [190] in the fabrication of a sensor to determine Cd(II) and Pb(II) by modifying a GCE via multipulse potentiostatic electropolymerization. In these works [187-190] the formation of an *in situ* bismuth film is considered as an additional modification. In [191] the polymeric modification performed implies first the formation of a graphene layer on the top of a GCE and the subsequent electropolymerization of m-aminobenzene sulfonic acid that enhances ion-exchange capacity and prevents the adsorption, in real samples, of macromolecules on the surface of the electrode. In this sensor the polymeric modification is complemented with the formation of an *in-situ* tin film. Liu *et al.* [192] fabricate an expanded-graphite paper based SPE, also for the analysis of Pb(II) and Cd(II), in which a self-doped sulfonated polyaniline is electropolymerized. Subsequently Sb-film is electrodeposited onto the conducting polymer surface. Expanded graphite maintains the good properties of graphite and overcome some others as hardness or fragility. Another example of antimony modified electrode based on conducting polymers is described in [193], in which poly(3,4-ethylenedioxythiophene)-sodium dodecyl sulfate is polymerized on the GC surface by electro-cycling scans. The modification proposed in [194] considers nanoparticles of a 4,4'-bipyridine-silver coordination polymer prepared by chemical modification, which are immobilized on the GCE surface via an organic electrodeposited layer that contains phenylmethyl-4,4'-bipyridinium and coordinated silver ions. In this work, Hg(II), Cu(II), Pb(II) were determined in fish and plant samples. In [195] a highly ordered multilayer graphene-based nanostructure containing polyallylamine hydrochloride generated by a layer by layer self-assembly method improved the analysis of Cu(II). In [196] the -CN groups of the conducting polymer coordinates Cd(II) and Pb(II) ions and improve the preconcentration at the electrode surface. Tyszczuk-Rotko *et al.* [197] propose a thiol-functionalized polysiloxane modified GCE for the analysis of Bi(III). These authors complement the accumulation capacity of the polymer with the *in-situ* incorporation of porous lead NPs in the reduction step.

Despite the large variety of molecules and immobilization strategies, the main goal of all these electrodes is, on one hand, to increase the selectivity towards metals ions that are not easily determined by Bi and Sb films and, on other hand, to increase sensitivity. Although detection limits have been improved (especially when nanomaterials are involved), scarce progresses have been made with regard to the metal ions determined, since most of the works are devoted to the determination of the “typical metal ions” Cd(II), Pb(II), Cu(II) and Hg(II). The main advantatges of this approach is that lie on cheap reagents, robust modification procedures and durable materials. The main drawback is that they usual require a cleaning or conditioning step after each measurement. We expect that, once tested the “classical” metals, these electrodes can be used for a large number of analytes and can provide a wide variety of metal sensors suitable not only for individual measurements but also to be integrated in voltammetric electronic tongues.

### Electrodes modified with biomolecules and biomaterials

In this section, a group of sensors in which the element that provides sensitivity and selectivity to the device is a biomolecule or a biomaterial are presented. These elements are combined with other modifiers that usually allow the attachment with the substrate and/or improve the sensitivity.

Table 10 shows examples of sensors based on the immobilization of small peptides or biothiol compounds [189-193]. D-Penicillamine [198] and glutathione [199] have been considered by Pérez-Ràfols *et al.* to modify a GCE and a commercial carbon nanofibers screen-printed electrode (SPCNFE) via an electrografting procedure. This strategy allows the formation of stable complexing monolayers: the recognition molecule is immobilized on aryl diazonium salt monolayers anchored onto the electrode surface. This strategy can overcome the major limitations of thiol self-assembled monolayers, mainly the limited reproducibility and the weakness of the binding to the electrode surface. The modified electrodes were applied for the simultaneous analysis of Cd(II) and Pb(II) in wastewaters. In [200] the immobilization of the Gly-Gly-His peptide is also performed by electrografting and it is applied to the analysis of Cu(II); in this work the preconcentration step is performed at open circuit and the media is changed for the measurement step. In [201], where an accumulation at open circuit is also included, different thiolate amino acids are proposed for the modification of a CPE; in this case, the paste electrode is prepared including also AuNPs and an ionic liquid. Viguier *et al.* [202] consider self-assembled peptide nanofiber for the modification of a gold electrode and an accumulation step at open circuit. In those cases, a regeneration of the electrode is recommended after each measurement. Modification with metallothioneins (MT), proteins containing a great number of cysteine units in their structure, is considered in [203,204]. In these works Ag(I) is determined analyzing the decrease of MT oxidation signal consequence of its complexation with Ag(I) [203], or analyzing the increase of the signal related with the oxidation of an Ag-MT complex [204]. In any case, the accumulation step is carried out at open circuit and a medium exchange is required before the measurement step. Also related with Ag(I), Liu *et al.* [205] consider the modification of a GCE with CNTs and guanine for Ag(I) determination following the observation that only Ag(I) shows a strong inhibitory effect on the electrocatalytic oxidation of guanine among a number of studied metal ions. Thymine is considered as biomodifier for the analysis of Hg(II) ions in [206,207]. In both cases, the thymine modification is performed via self-assembled layers, and the accumulation and measurement steps are essentially similar.

The use of biopolymers like chitosan is also considered in [208,209], since biopolymers are able to form films, and have high water permeability, good adhesion, biocompatibility, nontoxicity, high mechanical strength and are susceptible to chemical modifications. In the case of chitosan, the presence of reactive amino and hydroxyl functional groups, that lead to a large hydrophilic surface, is especially relevant for the analysis of metal ions; thus their analysis is considered in these works as it is shown in Table 10.

Modification with biomaterials is also considered in the development of sensors for metal ion determination. These devices are named biosensors. The term biosensor includes a group of sensors in which the mechanism that provides selectivity and sensitivity to the device is based in a biochemical one. Although biosensors are associated with the analysis of organic compounds or analytes of biological interest, they are also applied to the analysis of trace metal ions. In Table 10 examples of these devices published in the last years are presented. The modifications performed in these devices and the measurement procedures are in general relatively simple, similar to the ones already presented in previous Tables; however, mainly in enzymatic devices, the complexity of the fabrication, preservation and measurement procedure make them limitedly useful for routine analysis, at least in the present stage of the research. Moyo *et al.* [210-212] consider maize tassel as modifier due to its high sorption capacity of metal ions at low concentration levels. In the first work [210], a maize tassel CPE is studied for the analysis of Cu(II), where the accumulation step is carried out at open circuit and in the potential scan step the reduction of Cu(II) ions takes place. While in [211,212] horseradish peroxidase is also added as modifier and the resulting electrode is transformed in an inhibitor biosensor (the reduction process of hydrogen peroxide is inhibited by the presence of metal ions).

In [213] a microbial biosensor is presented for the analysis of Pb(II). In the analytical procedure a medium exchange between the accumulation (at open circuit) and the potential scan step is performed. The use of *Phormidium* algae is proposed in [214] also for the analysis of Pb(II), being the analytical procedure similar to that presented in the previous work of the same authors [213]. In this case, cell wall components of the algae, such as alginate and fucoidan, act as suitable sorbents for metal detection. Prasad and Fatma [215] modify a carbon pencil electrode for the analysis of Cu(II) with an algae (*Aulosira sp.*) through an one ion monomer imprinted polymer. The same alga is used in [216] to create a "complex template" imprinted polymer also for the analysis of Cu(II). Authors consider algae as a cheap substitute of MWCNTs.

Structures related with nucleic acids have also been considered in the literature. Diculescu *et al.* [217] have recently written an interesting work devoted to DNA as biomaterial for the construction of sensors. In this work, a section related with DNA-sensors for metal ions is presented. In Table 10 some examples related with this biomaterial are described. In [218] the analysis of Ag(I) ions is performed using a DNA sensor in which the dye ethyl green has also been incorporated along the modification process. In the presence of Ag(I), the reduction peak of the dye accumulated on the electrode decreases as a consequence of the hybridization of the probe with target DNA by forming C–Ag(I)–C base pairs. Li *et al.* [219] prepare a biosensor in which an aptamer is immobilized in a $SiO_2$-Pt@meso-$SiO_2$ core–shell nanoparticles modified graphene fluorine doped tin oxide electrode. The device is proposed for the analysis of Zn(II) in human blood and disrupted human cells. In [220] tetrahedron-structured DNA in combination with a functionalized oligonucleotide is proposed to develop a ''turn-on'' biosensor for Hg(II) ions. In [221,222] DNA-enzyme based electrodes are investigated. These works provide extremely low detection limits and very wide linearity ranges (in logarithmic scale), which should be confirmed in further works by the application to real samples, since the reported performance appears to be too optimistic (especially in reference 221).

Thus, as compared to the modifications of the previous section, the use of relatively simple and cheap biomolecules with especial affinity for metals present similar advantages and not many drawbacks. In addition, they can also be used as individual sensors or in combination with other sensors giving rise to a sensor array. Concerning to the use of biomaterials, as it is already discussed, the advantages are not so clear.

## Electrode arrays

Until here, we have considered sensing systems in which a single working electrode is used. However, the possibility to group electrodes in an array has been considered by some authors for the analysis of metal ions. In this point, it would be interesting to point out what is considered as electrode array or sensor array. Electrode or sensor arrays were introduced with two different purposes: i) identical electrodes working in parallel to enhance the analytical response; ii) different electrodes working simultaneously giving rise to independent and cross-reponses.

In this section and in Table 11 examples related with arrays formed with identical electrodes giving an unique response are presented. Table 11 shows how an array of 96 SPAuE has been considered for the analysis of Pb(II) providing a large number of replicates of the same measurement [223]. Authors point out that measurements of the different electrodes should be processed together with a pattern-recognition chemometric tool as PCA, PLS or ANN. Kanyong *et al.* [224] present an array of 8 SPCE modified with AuNPs for the analysis of Cu(II) and Pb(II) in tap water. The work is devoted basically to the fabrication and performance of the device. However, the implementation of microelectrode arrays (MEAs) is nowadays a subject of great interest. MEAs take profit of the particular advantages of the individual microelectrodes consequence of their small size: the diffusion of the analyte to the electrode surface turns from linear to radial, resulting in enhanced mass transport. On other hand, microelectrodes also present decreased ohmic drop, enhanced signal-to-noise ratios and lower capacitive currents. In these devices, individual microelectrodes operate in parallel achieving a significant improvement in the current magnitude [225-227]. Wan *et al.* [228] design an array of gold microelectrodes that include on the same wafer a light addressable potentiometric sensor for pH measurement which is applied for the a analysis of Zn(II), Pb(II) and Cu(II).

Kokkinos *et al.* [229-231] develop a Bi-MEA for the analysis of Pb(II) and Cd(II) by ASV or Co(II) and Ni(II) by AdSV. The use of ensembles of nanoelectrodes randomly distributed is considered by Mardegan *et al.* [232,233] who develop bismuth modified ensembles of gold nanoelectrodes and ensembles of gold nanowires electrodes for the analysis of Pb(II) and As(III), respectively.

## Voltammetric tongues

Classical research lines in the field of chemical sensors have focused on the development of more selective and sensitive devices that could determine simultaneously several species. These electrodes can be used for metal determination as a single-electrode sensor allowing the simultaneous determination of several metal ions when non-overlapped peaks are obtained. However, the analysis of real samples implies very often measurements of complex mixtures of metals with intricate voltammetric responses including overlapped peaks, signal shifts or with interactions between metals that cannot be resolved using a single- electrode sensor. The use of several electrodes grouped in sensor arrays is an efficient strategy to address this problem: these systems show a profitable cross-response performance, although presenting a low selectivity. The resulting platform formed by a group of different electrodes constitute a multisensor array also named (bio)electronic tongue that provides a multivariate response [234-237]. The use of an electronic tongue approach involves a change in the experimental design that requires not only of a multichannel potentiostat but also involves a large number of samples for calibration and validation. A key point of electronic tongues is the analysis of data that requires the use of chemometrics. Designs of electronic tongues based on voltammetric measurements since 2010 until now are summarized in Table 12. It should be pointed out that the development and application of electronic tongues to the determination of trace metals has been scarce until now, in contrast with numerous applications in the field of food analysis, which is more focused on the overall characterization of samples than on the quantification of specific analytes.

References [238-242] are devoted to the development of voltammetric tongues considering groups of electrodes prepared in a similar way to those described in previous Tables. Thus, in [238] three graphite-epoxy composite electrodes with different peptides immobilized onto the surface through a diazonium salt by electrochemical grafting have been considered. In references [239,240] crown ethers are considered as modifiers and deposited via electrografting through diazonium salts. In [241] the electronic tongue comprises SPCNFEs modified with both antimony via *ex-situ* and a crown ether, whereas in [242] the four electrodes of the array are a SPCE, an *ex-situ* antimony SPCNFE and two peptide modified SPCNFEs. For data treatment artificial neural network (ANNs) [238-240] and partial least squares (PLS) [241,242] were considered.

In references [243-245] microelectrode arrays are combined with other devices like multiple light-addressable potentiometric sensor (MLAPS) [243], impedimetric sensor of platinum interdigitated array of electrodes [244], and single light addressable potentiometric sensor [245]. Finally, in [246] a nanoband electrode array (NEA) together with a light addressable potentiometric sensor are considered. These devices could be understood as hybrid sensors more than as electronic tongues.

Just to summarize, voltammetric electronic tongues are a promising strategy to deal with complex mixtures of metal and metalloid ions. However, their consolidation as a routine analysis tool depends on the developments in the fields of electrode modification, multichannel data acquisition and chemometric methods for data treatment.

## Conclusions

For a long time since the invention of polarography heavy metals and some metalloids had been electrochemically analysed mostly with mercury electrodes and only a minority of authors proposed modifications of solid or carbon paste electrodes as an alternative to the mercury hegemony.

However, when in the new century safety and environmental considerations advised against mercury, an intensive research started to find substitutes for such a valuable but toxic material. The research focus was not obvious and multiple options were tested, encouraged by the increasing popularity and commercial availability of nanomaterials, biomolecules and screen-printed electrodes. The possibility of miniaturization and integration of different electrodes in multi-sensor platforms, with independent sensing or with cross-response of the sensors, and the development of powerful chemometric tools for the multivariate data treatment have also contributed to increase the number of publications on the mercury-free electrochemical analysis of heavy metals and metalloids.

Although, in the context of green chemistry, mercury replacement is the main driving force, the above-mentioned research also pursues the confirmation of voltammetry as a simple, reliable and economic alternative to ICP methods for the screening of multiple samples and for the *in-situ* monitoring of heavy metal contamination. Indeed, a fast comparison between Tables 1-2 and Tables 3-12 shows that practically all the works considered in the review have been devoted to the determination of elements of major concern for health and environmental protection agencies. Among them, lead and cadmium are ubiquitous but, in general, reviewed publications do not show a huge improvement in the analysis of these metals as compared to conventional drop or mercury films electrodes, except for the fact that mercury is not used. Anyway, we should be moderately critical about this point, since many proposed methods are really innovative and need a validation with some ‘model’ analytes such as lead and cadmium (electrochemically reacting at intermediate potentials and exhaustively studied with different electrodes) before they can be applied to more problematic elements like chromium, molybdenum or manganese (hardly cited or absent in the review) (Table 1). Another group of analytes not included in Tables 1-2 but deserving more attention in ‘mercury-free’ voltammetric literature is that of platinum-group elements (PGE), which are of increasing concern in pharmaceutic industry and environmental protection due to their intensive use as catalysers.

At this point, we want to stress the difficulties of comparing methods based exclusively on detection limits, since this figure of merit is estimated by the authors using different approaches. Unfortunately, in many cases, the signal-to-noise ratio approach is used, which frequently underestimates the LOD value as this approach does not take into account the baseline effects, which can be really important at so low concentrations. Additionally, when a deposition step is involved, it is not trivial to compare methods with very different accumulation times. Finally, matrix effects are differently considered in the reviewed works and it is hard to compare calibration plots made with synthetic solutions or real samples. Therefore, we consider that the goodness of the proposed devices should be judged in terms of applicability to real samples.

Nowadays we are living a time of maximum creativity and diversity of proposals which, as pointed out before, are mostly in the early stage of ‘proof of concept’ (just tested with standards in synthetic solutions) or in the slightly more advanced step of validation with real but ‘friendly-matrix’ samples (e.g. river or estuarine waters, either spiked or not). In our opinion, we are still far from the cheap, reliable and robust solutions that could result in commercial equipment. Nevertheless, so many promising methodologies have been proposed and investigated by now that we are invited to believe that in the next years some of these could succeed in the following challenges:

- *Multielement determination*. The works cited in the review simultaneously determine a maximum of 4 elements (typically 2-3 elements). In order to compete with ICP methods, a larger number of metals and metalloids should be determined in a single measurement. This could be achieved, for instance, by integrating in a single device many electrodes sensitive to several metals or modifying electrodes with wide-spectrum reagents able to preconcentrate simultaneously many analytes. In both cases, the accumulation and probable overlapping of signals from multiple species would surely require the development of customized chemometric methodologies for the data treatment.

- *Analysis of complex matrices*. A really robust screening or monitoring system should work properly in the presence of complex matrices containing organic and inorganic ligands, macromolecules, colloid and suspended particles... Unfortunately, voltammetry is very sensitive to matrix effects. The most dramatic case is when organic matter or particles get massively attached to electrodes and block the current, leaving the measuring device useless. Under less extreme conditions, matrix effects can allow measurements but seriously affect the relationship between currents and concentrations, producing a large error when comparing with the signals obtained with standards in simpler media. These problems could be overcome by finding suitable protection membranes (*e.g.*, improved versions of Nafion) and/or developing chemometric methodologies analogous to the well-known univariate approaches of standard addition or inner standard calibration.

- *Cheap, simple and portable solution for screening, in-situ measurements and flow systems monitoring*. This condition is quite restrictive for devices that are too expensive (*e.g.* involving expensive materials or reagents) or too fragile (e.g. involving biological materials that can be preserved just for a short time under controlled conditions). It can be achieved by designing durable electrodes resistant to fouling and producing small signal drifts or implementing systems based on cheap, reproducible and disposable electrodes to be changed after one or a few measurements. We also remark that the data treatment should be not excessively difficult or time-consuming and, ideally, it should be implemented in the measuring instrument.

Undoubtedly, the first research lines fulfilling such enormous but still realistic challenges would be ready to commercially produce cheap and portable electrochemical instruments as a complement to the accurate yet expensive and non-portable atomic spectrometers for the screening, monitoring and *in-situ* analysis of heavy metals and metalloids in environmental, industrial and biological samples.

## References

[1] S.E. Manahan, Environmental chemistry, 7th ed., CRC Press LLC, Boca Raton, 2000.

[2] G.F. Nordberg, B.A. Fowler, M. Nordberg, L.T. Friberg, Handbook on the toxicology of metals, 3rd ed., Elsevier Inc., London, 2007.

[3] B.J. Nebel, R.T. Wrigth, Environmental science: the way the world works, 4th ed., Prentice-Hall International, New Jersey, 1993.

[4] J.E. Fergunsson, The heavy elements: chemistry, environmental impact and health effects, 1st ed., Pergamon Press, Oxford, 1990.

[7] M. Lippmann, Environmental toxicants: human exposures and their health effects, 3rd ed., John Wiley & Sons Inc., New Jersey, 2000.

[8] G.W. VanLoon, S.J. Duffy, Environmental chemistry: a global perspective, 1st ed., Oxford University Press, Oxford, 2000.

[9] E.H. Evans, J.A. Day, C.D. Palmer, W.J. Price, C.M.M. Smith, J.F. Tyson, Atomic spectrometry update. Advances in atomic emission, absorption and fluorescence spectrometry, and related techniques. J. Anal. At. Spectrom. 20 (2005) 562-590.

[10] P. Pohl, Determination of metal content in honey by atomic absorption and emission spectrometries. Trac-Trends Anal. Chem. 28 (2009) 117-128.

[11] R.K. Soodan, Y.B. Pakade, A. Nagpal, J.K. Katnoria, Analytical techniques for estimation of heavy metals in soil ecosystems: a tabulated review. Talanta 125 (2014) 405 - 410.

[12] N.H. Bings, A. Bogaerts, J.A.C. Broekaert, Atomic spectroscopy. Anal. Chem. 85 (2013) 670-704.

[13] J.E. Marcovecchio, S.E. Botte, C.E. Domini, R.H. Frejie, Heavy metals, major metals, trace elements. In Handbook of Water Analysis (3rd ed.) (2014) 385-434.

[14] J. Barek, A.G. Fogg, A. Mick, J. Zima, Polarography and voltammetry at mercury electrodes. Crit. Rev. Anal. Chem. 31 (2001) 291-309.

[15] J. Wang, J. Lu, S.B. Hocevar, P.A.M. Farias, B. Ogorevc, Bismuth-coated carbon electrodes for anodic stripping voltammetry. Anal. Chem. 72 (2000) 3218-3222.

[16] J. Wang, Stripping analysis at bismuth electrodes: A review. Electroanalysis 17 (2005) 1341-1346.

[17] A. Economou, Bismuth-film electrodes: recent developments and potentialities for electroanalysis. Trac-Trends Anal. Chem. 24 (2005) 334-340.

[18] I. Svancara, C. Prior, S.B. Hocevar, J. Wang, A decade of bismuth electrodes in modern electroanalysis. Electroanalysis 22 (2010) 1405-1420.

[19] N. Serrano, A. Alberich, J.M. Díaz-Cruz, C. Ariño, M. Esteban. Coating methods, modifiers and applications of bismuth screen-printed electrodes. Trac-Trends Anal. Chem. 46 (2013) 15-28.

[20] S.B. Hocevar, I. Svancara, B. Ogorevc, K. Vytras, Antimony film electrode for electrochemical stripping analysis. Anal. Chem. 79 (2007) 8639–8643.

[21] V. Jovanovski, S.B. Hocevar, B. Ogorevc, Ex situ prepared antimony film electrode for electrochemical stripping measurement of heavy metal ions. Electroanalysis 21 (2009) 2321–2324.

[22] N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, Antimony- based electrodes for analytical determinations. Trac-Trends Anal. Chem. 77 (2016) 203–213.

[23] G. Aragay, J. Pons, A. Merkoçi, Recent trends in macro-, micro-, and nanomaterial-based tools and strategies for heavy-metal detection. Chem. Rev. 111 (2011) 3433–3458.

[24] L. Rassaei, M. Amiri, C.M. Cirtiu, M. Sillapää, F. Marken, M. Sillanpää, Nanoparticles in electrochemical sensors for environmental monitoring. Trac-Trends Anal. Chem. 30 (2011) 1704-1714.

[25] K.C. Honeychurch, J.P. Hart, Screen- printed electrochemical sensors for monitoring metal pollutants. Trac-Trends Anal. Chem. 22 (2003) 456-469.

[26] M. Li, V Li, V Li, Y.-T. Long, Recent developments and Applications of screen printed electrodes in environmental assays. A review. Anal. Chim. Acta 734 (2012) 31-44.

[27] Z. Talaet, A. Khoshroo, M. Mazloum-Ardakani, Screen-printed elèctrodes for biosensing: A review (2008-2013). Microchim. Acta 181 (2014) 865-891.

[28] G. Hughes, K. Westmacott, K.C. Honeychurch, A. Crew, R.M. Pemberton, J.P. Hart, Recent advances in the fabrication and application of screen-printed electrochemical (bio)sensors based on carbon materials for biomedical, agri-food and environmental analyses. Biosens. Bioelectron. 6 (2016) 50-89.

[29] J. Barton, M.B. González García, D. Hernández Santos, P. Fanjul-Bolado, A. Ribotti, M. McCaul, D. Diamond, P. Magni, Screen-printed electrodes for environmental monitoring of heavy metal ions: a review. Microchim. Acta 183 (2016) 503–517.

[30] J. Wang, Analytical electrochemistry. 3rd ed., John Wiley & Sons Inc., New Jersey, 2006.

[31] J. Wang, Stripping analysis: Principles, instrumentation and applications. VCH, Deerfield Beach, 1985.

[32] G. Aragay, A. Merkoçi, Nanomaterials application in electrochemical detection of heavy metals. Electrochim. Acta 84 (2012) 49-61.

[33] G. March, T.D. Nguyen, B. Piro, Modified electrodes used electrochemical detection of metal ions in environmental analysis. Biosensors 5 (2015) 241-275.

[34] L. Cui, J. Wu, H. Ju, Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials. Biosens. Bioelectron. 63 (2015) 276-286.

[35] X. Zhang, K. Qu, D. Li, Advance in the Stripping Voltammetry Using Alloy Electrodes for the Determination of Heavy Metal Ions. Int. J. Electrochem. Sci., 10 (2015) 8497 – 8512.

[36] S. K. Pandey, P. Singh, J. Singh, S. Sachan, S. Srivastava, S. K. Singh, Nanocarbon-based electrochemical detection of heavy metals. Electroanalysis 28 (2016) 2472-2488.

[37] J. Molina, F. Cases, L.M. Moretto, Graphene-based materials for the electrochemical determination of hazardous ions. Anal. Chim. Acta 946 (2016) 9-39.

[38] B. Silwana, C. van der Horst, E. Iwuoha, Screen-printed carbon electrodes modified with a bismuth film for stripping voltammetric analysis of platinum group metals in environmental samples. Electrochim. Acta 128 (2014) 119-127.

[39] Z.-G. Liu, X.-J. Huang, Voltammetric determination of inorganic arsenic. Trac-Trends Anal. Chem. 60 (2014) 25-35.

[40] C. Gao, X.-J. Huang, Voltammetric determination of mercury(II). Trac-Trends Anal. Chem. 51 (2013) 1-12.

[41] S.A. Mahesar, S.T.H. Sherazi, A. Niaz, M.I. Bhanger, S. Uddin, A. Rauf, Simultaneous assessment of zinc, cadmium, lead and copper in poultry feeds by differential pulse anodic stripping voltammetry. Food Chem. Toxicol. 48 (2010) 2357-2360.

[42] L. Al Attar, M. Al-Oudat, K. Shamali, B. Abdul Ghany, S. Kanakri, Case study: Heavy metals and fluoride contents in the materials of Syrian phosphate industry and in the vicinity of phosphogypsum piles. Environ. Technol. 33 (2) (2012) 143-152.

[43] S. Sobhanardakani, L. Tayebi, A. Farmany, M. Cheraghi, Analysis of trace elements (Cu, Cd, and Zn) in the muscle, gill, and liver tissues of some fish species using anodic stripping voltammetry. Environ. Monit. Assess. 184 (11) (2012) 6607-6611.

[44] P. Vukosav, M. Mlakar, N. Cukrov, Ž. Kwokal, I. Pižeta, N. Pavlus, I. Špoljarić, M. Vurnek, A. Brozinčević, D. Omanović, Heavy metal contents in water, sediment and fish in a karst aquatic ecosystem of the Plitvice Lakes National Park (Croatia). Environ. Sci. Pollut. Res. 21 (5) (2014) 3826-3839.

[45] D. Melucci, M. Locatelli, C. Locatelli, Trace level voltammetric determination of heavy metals and total mercury in tea matrices (*Camellia sinensis*). Food Chem. Toxicol. 62 (2013) 901-907.

[46] C. Locatelli, Proposal of a new analytical procedure for the voltammetric determination of total Hg(II) and toxic metals in algae: Potential aquatic environmental biomonitors. Curr. Anal. Chem. 6 (2010) 288-298.

[47] C. Locatelli, Mutual interference problems in the simultaneous voltammetric determination of trace total mercury(II) in presence of copper(II) at gold electrode. Applications to environmental matrices. Anal. Methods, 2 (2010) 1784-1791.

[48] C. Locatelli, D. Melucci, Sequential voltammetric determination of mercury(II) and toxic metals in environmental bio-monitors: Application to mussels and clams. Int. J. Environ. Anal. Chem.90 (2010) 49-63.

[49] C. Locatelli, D. Melucci, Voltammetric determination of ultra-trace total mercury and toxic metals in meals. Food Chem., 130 (2012) 460-466.

[50] C. Locatelli, D. Melucci, Voltammetric method for ultra-trace determination of total mercury and toxic metals in vegetables. Comparison with spectroscopy. Cent. Eur. J. Chem. 11 (2015) 790-800.

[51] Y. Shahbazi, F Ahmadi, F. Fakhari, Voltammetric determination of Pb, Cd, Zn, Cu and Se in milk and dairy products collected from Iran: An emphasis on permissible limits and risk assessment of exposure to heavy metals. Food Chem. 192 (2016) 1060-1067.

[52] I. Khan, U.J. Pandit, S. Wankar, S.N. Limaye, Centrifugation assisted digestion for simultaneous voltammetric determination of ultra trace metal ions in water and milk samples. Environ. Nanotec. Mon. Man. 7 (2017) 64-72.

[53] A. Annibaldi, S. Illuminati, C. Truzzi, G. Scarponi, SWASV speciation of Cd, Pb and Cu for the determination of seawater contamination in the area of the Nicole shipwreck (Ancona coast, Central Adriatic Sea). Mar. Pollut. Bull. 62 (2011) 2813-2821.

[54] J.A. Rodrigues, C.M. Rodrigues, P.J. Almeida, I.M. Valente, L.M. Gonçalves, R.G. Compton, A.A. Barros, Increased sensitivity of anodic stripping voltammetry at the hanging mercury drop electrode by ultracathodic deposition. Anal. Chim. Acta, 701 (2011) 152-156.

[55] C. Rojas, V. Arancibia, M. Gomez, E. Nagles, High sensitivity adsorptive stripping voltammetric method for antimony(III) determination in the presence of quercetin-5′ -sulfonic acid. Substituent effect on sensitivity. Sens. Actuators B-Chem 185 (2013) 560-567.

[56] C. Rojas-Romo, V. Arancibia, A Comparative Study of 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonic Acid for Antimony(III) Determination by AdSV: Substituent Effect on Sensitivity II. Electroanalysis 27 (2015) 1262-1267.

[58] C. Nuñez, V. Arancibia, M. Gomez, Determination of arsenic in the presence of copper by adsorptive stripping voltammetry using pyrrolidine dithiocarbamate or diethyl dithiophosphate as chelating-adsorbent agents. Effect of CPB on the sensitivity of the method. Microchem. J. 126 (2016) 70-75.

[59] C. Rojas, V. Arancibia, M. Gomez, E. Nagles, Adsorptive stripping voltammetric determination of cobalt in the presence of nickel and zinc using pyrogallol red as chelating agent. Int. J. Electrochem. Sci. 7 (2012) 979-990.

[60] M.N. Rashed, M.M. Ahmed, A.F. Al-Hossainy, S.M. Abd, Trends in speciation analysis of some heavy metals in serum of patients with chronic hepatitis C and chronic hepatitis B using differential pulse adsorptive stripping voltammetric measurement and atomic absorption spectrophotometry. J. Trace Elem. Med. Biol. 24 (2010) 138-145.

[61] J. Santos-Echeandía, Direct simultaneous determination of Co, Cu, Fe, Ni and V in pore waters by means of adsorptive cathodic stripping voltammetry with mixed ligands. Talanta, 85 (2011) 506-512.

[62] A.B. Schneider, P.C. Nascimento, D. Bohrer, L.M. de Carvalho, A. Guarda, C. Krause, B.A. Wiethan, A. Koschinsky, Determination of zirconium and vanadium in natural waters by adsorptive stripping voltammetry in the presence of cupferron, oxalic acid and 1,3-diphenylguanidine. Electroanalysis 27 (2015) 1864 – 1870.

[63] S. Caprara, L.M. Laglera, D. Monticelli, Ultrasensitive and fast voltammetric determination of iron in seawater by atmospheric oxygen catalysis in 500 $\mu$ L samples. Anal. Chem. 87 (2015) 6357−6363

[64] S. Abbasi, A. Bahiraei Food Chemistry 129 (2011) 1274‑1280. Abbasai, A highly sensitive method for simultaneous determination of ultra trace levels of copper and cadmium in food and water samples with luminol as a chelating agent by adsorptive stripping voltammetry. Food Chem. 129 (2011) 1274–1280.

[65] O. Zaouak, L. Authier C. Cugnet, A. Castetbon, M. Potin-Gautier, Electroanalytical device for cadmium speciation in waters.Part 1: development and characterization of a reliable screenprinted sensor. Electroanalysis 22 (2010) 1151–1158.

[66] O. Zaouak, L. Authier, C. Cugnet, E. Normandin, D. Champier, M. Rivaletto, M. Poitn-Gautier, Electroanalytical device for cadmium speciation in waters. Part 2: automated system development and cadmium semicontinuous monitoring. Electroanalysis 22 (2010) 1159–1165.

[67] C. Pérez-Ràfols, N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, Mercury Films on Commercial Carbon Screen-Printed Devices for the Analysis of Heavy Metal Ions: A Critical Evaluation. Electroanalysis 27 (2015)1345-1349.

[68] Q. Fan, G. Du, J. Tu, Simultaneous determination of Cd(II), Pb(II), Cu(II) and Bi(III) by square wave anodic stripping voltammetry and multivariate calibration. Tianjin Daxue Xuebao (Ziran Kexue yu Gongcheng Jishu Ban)/Journal of Tianjin University Science and Technology, 46 (2013) 145-149.

[69] H.-X. Zhao, W. Cai, D. Ha, H. Wan, P. Wang, The study on novel microelectrode array chips for the detection of heavy metals in water pollution. J. Innov. Opt. Health Sci. 5 (2012) 1150002.

[70] W. Opoka, B. Baś, W. Reczyński, M Płonka, D. Drozdowicz, Z Śliwowski, T. Brzozowski, Applicability of the silver amalgam electrode in voltammetric determination of zinc and copper in gastric juice and gastric mucosa of rats. Acta Pol. Pharm. 68 (2011) 481-492.

[71] J.F.Ping, J. Wu, Y.B. Ying, M.H. Wang, G. Liu, M. Zhang, Development of a novel carbon composite electrode for trace determination of heavy metals in milk. Trans. ASABE, 54 (2011) 1829-1835.

[72] E. Herrero, V. Arancibia, C. Rojas-Romo, Simultaneous determination of $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ by adsorptive stripping voltammetry using Clioquinol as a chelating-adsorbent agent. J. Electroanal. Chem. 729 (2014) 9-14.

[73] E. Nagles, V. Arancibia, C. Rojas, R. Segura, Nafion-mercury coated film electrode for the adsorptive stripping voltammetric determination of lead and cadmium in the presence of pyrogallol red. Talanta, 99 (2012) 119-124.

[74] E. Nagles, V. Arancibia, R. Rios, Determination of lead and cadmium in the presence of quercetin-5'-sulfonic acid by adsorptive stripping voltammetry with a hanging mercury drop electrode and a nafion-coated mercury film electrode. Int. J. Electrochem. Sci.7 (2012) 4545-4558.

[75] P.G., Iwuoha, E.I. Few-layer binder free graphene modified mercury film electrode for trace metal analysis by square wave anodic stripping voltammetry. Int. J. Electrochem. Sci. 8 (2013) 11125-11141.

[76] W. Song, L. Zhang, L. Shi, D.-W. Li, Y. Li, Y.-T. Long, Simultaneous determination of cadmium(II), lead(II) and copper(II) by using a screen-printed electrode modified with mercury nano-droplets. Microchim. Acta 169 (2010) 321–326.

[77] L. Zhang, D.-W. Li, W. Song, L. Shi, Y. Li, Y.-T. Long, High sensitive on-site cadmium sensor based on AuNPs amalgam modified screen-printed carbon electrodes. IEEE Sens. J. 10 (2010) 1583-1588.

[78] R. Ouyang, Z. Zhu, C.E. Tatum, J.Q. Chambers, Z.-L. Xue, Simultaneous stripping detection of Zn(II), Cd(II) and Pb(II) using a bimetallic Hg-Bi/single-walled carbon nanotubes composite electrode. J. Electroanal. Chem. 656 (2011) 78-84.

[79] E. Bernalte, C. Marin Sanchez, E. Pinilla Gil, Determination of mercury in ambient water samples by anodic stripping voltammetry on screen-printed gold electrodes. Anal. Chim. Acta 689 (2011) 60–64.

[80] X. Niu, C. Chen, Y. Teng, H. Zhao, M. Lan, Novel screen-printed gold nano film electrode for trace mercury(II) determination using anodic stripping voltammetry. Anal. Lett. 45 (2012) 764–773.

[81] M.A. Kamyabi, A. Aghaei, Electromembrane extraction and anodic stripping voltammetric determination of mercury(II) using a glassy carbon electrode modified with gold nanoparticles. Microchim. Acta 183 (2016) 2411-2419.

[82] M. Behzad, M. Asgari, M. Shamsipur, M.G. Maragheha, Impedimetric and stripping voltammetric detection of sub-nanomolar amounts of mercury at a gold nanoparticle modified glassy carbon electrode. J. Electrochem. Soc. 160 (2013) B31-B36.

[83] E. Fernández, L. Vidal, A. Costa-García, A. Canals, Mercury determination in urine samples by gold nanostructured screen-printed carbon electrodes after vortex-assisted ionic liquid dispersive liquid-liquid microextraction. Anal. Chim. Acta 915 (2016) 49-55.

[84] E. Bernalte, C. Marín Sánchez, E. Pinilla Gil, High-throughput mercury monitoring in indoor dust microsamples by bath ultrasonic extraction and anodic stripping voltammetry on gold nanoparticles-modified screen-printed electrodes. Electroanalysis 25 (2013) 289-294.

[85] E. Bernalte, C. Marín Sánchez, E. Pinilla Gil, Gold nanoparticles-modified screen-printed carbon electrodes for anodic stripping voltammetric determination of mercury in ambient water samples. Sens. Actuators B-Chem. 161 (2012) 669-674.

[86] D.M. Yerga, M.B. González García, A. Costa García, Use of nanohybrid materials as electrochemical transducers for mercury sensors. Sens. Actuators B-Chem 165 (2012)143–150.

[87] L. Ding, Y. Liu, J. Zhai, A.M. Bond, J. Zhang, Direct electrodeposition of graphene-gold nanocomposite films for ultrasensitive voltammetric determination of mercury(II). Electroanalysis 26 (2014) 121-128.

[88] A. Mardegan, P. Scopece, F. Lamberti, M. Meneghetti, L.M. Moretto, P. Ugo, Electroanalysis of trace inorganic arsenic with gold nanoelectrode ensembles. Electroanalysis 24 (2012) 798–806.

[89] J.C.M. Gamboa, L. Cornejo, J.A. Squella, Vibrating screen printed electrode of gold nanoparticle-modified carbon nanotubes for the determination of arsenic(III). J. Appl. Electrochem. 44 (2014) 1255–1260.

[90] S. Cinti, S. Politi, D. Moscone, G. Palleschi, F. Arduini, Stripping analysis of As(III) by means of screen-printed electrodes modified with gold nanoparticles and carbon black nanocomposite. Electroanalysis 26 (2014) 931-939.

[91] G.M.S. Alves, J.M.C.S. Magalhães, H.M.V.M. Soares, Voltammetric quantification of Zn and Cu, together with Hg and Pb, based on a gold microwire electrode, in a wider spectrum of surface waters. Electroanalysis 25 (2013) 493-502.

[92] F. Rueda-Holgado, L. Calvo-Blázquez, F. Cereceda-Balic, E. Pinilla-Gil, A semiautomatic system for soluble lead and copper monitoring in atmospheric deposition by coupling of passive elemental fractionation sampling and voltammetric measurement on screen-printed gold electrodes. Microchem. J. 124 (2016) 20-25.

[93] W. Feng, L. Hong-Wei, Y. Xin, C. Di-Zhao, Gs-Nafion-Au nanocomposite film modified SPCEs for simultaneous determination of trace $Pb^{2+}$ and $Cd^{2+}$ by DPSV. Int. J. Electrochem. Sci. 8 (2013) 7702-7712.

[94] W. Xiong, L. Zhou, S. Liu, Development of gold-doped carbon foams as a sensitive electrochemical sensor for simultaneous determination of Pb(II) and Cu (II). Chem. Eng. J. 284 (2016) 650-656.

[95] H. Zhu, Y. Xu, A. Liu, N. Kong, F. Shan, W. Yang, C.J. Barrow, J. Liu, Graphene nanodots-encaged porous gold electrode fabricated via ion beam sputtering deposition for electrochemical analysis of heavy metal ions. Sens. Actuators B-Chem. 206 (2015) 592-600.

[96] M.-P. Ngoc Bui, C.A. Li, K.N. Han, X.-H. Pham, G.H. Seong, Simultaneous detection of ultratrace lead and copper with gold nanoparticles patterned on carbon nanotube thin film. Analyst 137 (2012) 1888-1894.

[97] R.T. Kachoosangi, R.G. Compton, Voltammetric determination of chromium(VI) using a gold film modified carbon composite electrode. Sens. Actuators B-Chem. 178 (2013) 555–562.

[98] W. Xiong, M.X. Liu, L.H. Gan, Y.K. Lv, Z.J. Xu, Z.X. Hao, L.W. Chen, Preparation of nitrogen-doped macro-/mesoporous carbon foams as electrode material for supercapacitors, Colloid Surf. A-Physichem. Eng. 186 (2012) 34–39.

[99] M. Liu, L. Gan, F. Zhao, H. Xu, X. Fan, C. Tian, X. Wang, Z. Xu, Z. Hao, L. Chen, Carbon foams prepared by an oil-in-water emulsion method. Carbon 45 (2007) 2710–2712.

[100] M. Trevisani, M. Cecchini, L. Taffetani, L. Vercellotti, R. Rosmini, Quantification of lead and cadmium in poultry and bird game meat by square-wave anodic-stripping voltammetry. Food Addit. Contam. Part A-Chem. 28 (2011) 180-188.

[101] S. Štefánová, L. Pikna, Optimization of conditions for preparation of carbon origin solid electrodes modified with carbon nanotubes. Part. Sci. Technol. 29 (2011) 311-319.

[102] H. Xu, Q. Zheng, P. Yang, J. Liu, L. Jin, Sensitive voltammetric detection of trace heavy metals in real water using multi-wall carbon nanotubes/nafion composite film electrode. Chin. J. Chem. 29 (2011) 805-812.

[103] Z. Wang, E. Liu, Graphene ultrathin film electrode for detection of lead ions in acetate buffer solution. Talanta 103 (2013) 47-55.

[104] S. Yavuz, A. Erkal, I.A. Kariper, A.O. Solak, S. Jeon, I.E. Mülazımoğlu, Z. Üstündağ, Carbonaceous materials-12: a novel highly sensitive graphene oxide-based carbon electrode: preparation, characterization, and heavy metal analysis in food samples. Food Anal. Meth. 9 (2016) 322-331

[105] J.H.T. Luong, K.B. Male, J.D. Glennon, Boron-doped diamond electrode: synthesis, characterization, functionalization and analytical applications. Analyst 134 (2009) 1965–1979.

[106] C.A. Martinez-Huitle, M.A.Q. Alfaro, Recent environmental applications of diamond electrode: critical review, J. Environ. Eng. Manag. 18 (2008) 155-172.

[107] P. Chooto, P. Wararatananurak, C. Innuphat, Determination of trace levels of Pb(II) in tap water by anodic stripping voltammetry with boron-doped diamond electrode. Scienceasia, 36 (2010) 150-156.

[108] J.-H. Yoon, J.E. Yang, J.P. Kim, J.S. Bae, Y.-B. Shim, M.-S. Won, Simultaneous detection of Cd (II), Pb (II), Cu (II), and Hg (II) ions in dye waste water using a boron doped diamond electrode with DPASV. Bull. Korean Chem. Soc. 31 (2010)140–145.

[109] E. Culková, L. Švorc, P. Tomčík, J. Durdiak, M. Rievaj, D. Bustin, R. Brescher, J. Lokaj, Boron-doped diamond electrode as sensitive and selective green electroanalytical tool for heavy metals environmental monitoring: Zinc detection in rubber industry waste. Pol. J. Environ. Stud. 22 (2013) 1317-1323.

[110] M. Lu, K.E. Toghill, M.A. Phillips, R.G. Compton, Anodic stripping voltammetry of antimony at unmodified carbon electrodes. Int. J. Environ. Anal. Chem. 93 (2013) 213-227.

[111] E. Nurhayati, Y. Juang, M. Rajkumar, C. Huang, C.-C. Hu, Effects of dynamic polarization on boron-doped NCD properties and on its performance for electrochemical-analysis of Pb (II), Cu (II) and Hg (II) in aqueous solution via direct LSV. Sep. Purif. Technol. 156 (2015) 1047-1056.

[112] T.M. Arantes, A. Sardinha, M.R. Baldan, F.H. Cristovan, N.G. Ferreira, Lead detection using micro/nanocrystalline boron-doped diamond by square-wave anodic stripping voltammetry. Talanta 128 (2014) 132-140.

[113] Y. Wei, R. Yang, X. Chen, L. Wang, J.-H. Liu, X.-J. Huang, A cation trap for anodic stripping voltammetry: NH3-plasma treated carbon nanotubes for adsorption and detection of metal ions. Anal. Chim. Acta 755 (2012) 54-61.

[114] K.C. Armstrong, C.E. Tatum, R.N. Dansby-Sparks, J.Q. Chambers, Z.-L. Xue, Individual and simultaneous determination of lead, cadmium, and zinc by anodic stripping voltammetry at a bismuth bulk electrode. Talanta 82 (2010) 675-680.

[115] M. de la Gala Morales, M.R. Palomo Marín, L. Calvo Blázquez, E. Pinilla Gil, Performance of a bismuth bulk rotating disk electrode for heavy metal analysis: determination of lead in environmental samples. Electroanalysis 24 (2012) 1170 – 1177.

[116] M. de la Gala Morales, M.R. Palomo Marín, L. Calvo Blázquez, E. Pinilla Gil, Applicability of the bismuth rotating disk electrode for heavy metal monitoring in undisturbed environmental and biological samples: Determination of Zn(II) in rain water, tap water and urine. Anal. Methods 6 (2014) 8668-8674.

[117] A.-N. Kawde, Electroanalytical determination of heavy metals in drinking waters in the eastern province of Saudi Arabia. Desalin. Water Treat. 57 (2016) 15697-15705.

[118] R. Segura, M. Pradena, D. Pinto, F. Godoy, E. Nagles, V. Arancibia, Adsorptive stripping voltammetry of nickel with 1-nitroso-2-napthol using a bismuth film electrode. Talanta 85 (2011) 2316-2319.

[119] C. Rojas-Romo, N. Serrano, C. Ariño, V. Arancibia, J.M. Diaz-Cruz, M. Esteban, Determination of Sb(III) using an ex-situ bismuth screen-printed carbon electrode by adsorptive stripping voltammetry. Talanta 155 (2016) 21-27.

[120] Q.-M. Feng, Q. Zhang, C.-G. Shi, J.-J. Xu, N. Bao, H.-Y. Gu, Using nanostructured conductive carbon tape modified with bismuth as the disposable working electrode for stripping analysis in paper-based analytical devices. Talanta 115 (2013) 235-240.

[121] H. Sopha, L. Baldrianová, E. Tesařová, G. Grinciene, T. Weidlich, I. Švancara, S.B. Hoĉevar, A new type of bismuth electrode for electrochemical stripping analysis based on the ammonium tetrafluorobismuthate bulk-modified carbon paste. Electroanalysis 22 (2010) 1489-1493.

[122] C. Chen, X. Niu, Y. Chai, H. Zhao, M. Lan, Bismuth-based porous screen-printed carbon electrode with enhanced sensitivity for trace heavy metal detection by stripping voltammetry. Sens. Actuators B-Chem. 178 (2013) 339-342.

[123] S. Lee, S.-K. Park, E. Choi, Y. Piao, Voltammetric determination of trace heavy metals using an electrochemically deposited graphene/bismuth nanocomposite film-modified glassy carbon electrode. J. Electroanal. Chem. 766 (2016) 120-127.

[124] W.J. Yi, Y. Li, G. Ran, H.Q. Luo, N.B. Li, Determination of cadmium(II) by square wave anodic stripping voltammetry using bismuth-antimony film electrode. Sens. Actuators B-Chem. 166-167 (2012) 544-548.

[125] N.B. Li, W.W. Zhu, J.H. Luo, H.Q. Luo, A stannum-bismuth composite film electrode for simultaneous determination of zinc(II) and cadmium(II) using differential pulse anodic stripping voltammetry. Analyst 137 (2012) 614-617.

[126] D. Yang, L. Wang, Z. Chen, M. Megharaj, R. Naidu, Anodic stripping voltammetric determination of traces of Pb(II) and Cd(II) using a glassy carbon electrode modified with bismuth nanoparticles. Microchim. Acta 181 (2014) 1199-1206.

[127] G.-J. Lee, C.K. Kim, M.K. Lee, C.K. Rhee, Reliability evaluation of nano-Bi/silver paste sensor electrode for detecting trace metals. J. Nanosc. Nanotechnol. 12 (2012) 5673-5677.

[128] L. Cui, J. Wu, H. Ju, Synthesis of bismuth-nanoparticle-enriched nanoporous carbon on graphene for efficient electrochemical analysis of heavy-metal ions. Chem.-Eur. J. 21 (2015) 11525-11530.

[129] P.K. Sahoo, B. Panigrahy, S. Sahoo, A.K. Satpati, D. Li, D. Bahadur, In situ synthesis and properties of reduced graphene oxide/Bi nanocomposites: As an electroactive material for analysis of heavy metals. Biosens. Bioelectron. 43 (2013) 293-296.

[130] J. Ping, Y. Wang, J. Wu, Y. Ying, Development of an electrochemically reduced graphene oxide modified disposable bismuth film electrode and its application for stripping analysis of heavy metals in milk. Food Chem. 151 (2014) 65-71.

[131] K. Pokpas, S. Zbeda, N. Jahed, N. Mohamed, P.G. Baker, E.I. Iwuoha, Electrochemically reduced graphene oxide pencil-graphite in situ plated bismuth-film electrode for the determination of trace metals by anodic stripping voltammetry. Int. J. Electrochem. Sci. 9 (2014) 736-759.

[132] F. Torma, M. Kádár, K. Tóth, E. Tatár, Nafion®/2, 2_-bipyridyl-modified bismuthfilm electrode for anodic stripping voltammetry, Anal. Chim. Acta 619 (2008) 173.

[133] M. Shi, F.C. Anson, Dehydration of protonated Nation ® coatings induced by cation exchange and monitored by qua z crystal microgravimetry, J. Electroanal. Chem. 425 (1997) 117-123.

[134] I. Rubinstein, A.J. Bard, Polymer films on electrodes. 5. Electrochemistry and chemiluminescence at Nafion-coated electrodes. J. Am. Chem. Soc. 103 (1981) 5007-5013.

[135] L. Xiao, H. Xu, S. Zhou, T. Song, H Wang, S. Li, W. Gan, Q. Yuan, Simultaneous detection of Cd(II) and Pb(II) by differential pulse anodic stripping voltammetry at a nitrogen-doped microporous carbon/Nafion/bismuth-film electrode. Electrochim. Acta, 143 (2014). 143-151.

[136] M.K. Dey, A.K. Satpati, S. Sahoo, R. Kameswaran, A.V.R. Reddy, T. Mukherjee, Bi-Film on a carbon paste electrode modified with nafion film embedded with multiwall carbon nano tubes for the determination of heavy metals. Anal. Methods 3 (2011) 2540-2546.

[137] H. Huang, T. Chen, X. Liu, H. Ma, Ultrasensitive and simultaneous detection of heavy metal ions based on three-dimensional graphene-carbon nanotubes hybrid electrode materials. Anal. Chim. Acta 852 (2014) 45-54.

[138] V. Rehacek, I. Hotovy, M Vojs, Bismuth film voltammetric sensor on pyrolyzed photoresist/alumina support for determination of heavy metals. Electroanalysis 26 (2014) 898-903.

[139] V. Rehacek, I. Hotovy, M. Vojs, T. Kups, L. Spiess, Nafion-coated bismuth film electrodes on pyrolyzed photoresist/alumina supports for analysis of trace heavy metals. Electrochim. Acta 63 (2012) 192-196.

[140] L.M. Moretto, A. Mardegan, M. Cettolin, P. Scopece, Pyrolyzed photoresist carbon electrodes for trace electroanalysis of nickel(II). Chemosens. 3 (2015)157-168

[141] A. Mardegan, M. Cettolin, R. Kamath, V. Vascotto, A. M. Stortini, P. Ugo, P. Scopece, M. Madou, L.M. Moretto, Speciation of trace levels of chromium with bismuth modified pyrolyzed photoresist carbon electrodes. Electroanalysis 27 (2015) 128-134.

[142] C. Huangfu, L. Fu, Y. Li, X. Li, H. Du, J. Ye, Sensitive stripping determination of cadmium(II) and lead(II) on disposable graphene modified screen-printed electrode. Electroanalysis 25 (2013) 2238-2243.

[143] C. Foster, A.P. De Souza, J.P. Metters, M. Bertotti, C.E. Banks, Metallic modified (bismuth, antimony, tin and combinations thereof) film carbon electrodes. Analyst, 140 (2015) 7598-7612.

[144] V. Sosa, C. Barceló, N. Serrano, C. Ariño, J.M. Díaz-Cruz, M. Esteban, Antimony film screen-printed carbon electrode for stripping analysis of Cd(II), Pb(II), and Cu(II) in natural samples. Anal. Chim. Acta 855 (2015). 34-40.

[145] G. Chen, X. Hao, B.L. Li, H.Q. Luo, N.B. Li, Anodic stripping voltammetric measurement of trace cadmium at antimony film modified sodium montmorillonite doped carbon paste electrode. Sens. Actuators B-Chem. 237 (2016) 570-574.

[146] C. Pérez-Ràfols, N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, New approaches to antimony film screen-printed electrodes using carbon-based nanomaterials substrates. Anal. Chim. Acta, 916 (2016) 17-23.

[147] C. Barceló, N. Serrano, C. Ariño, J.M. Díaz-Cruz, M. Esteban, Ex-situ antimony screen-printed carbon electrode for voltammetric determination of Ni(II) - ions in wastewater. Electroanalysis 28 (2016) 640 - 644.

[148] M. Makombe, C. van der Horst, B. Silwana, E. Iwouha, V. Somerset, Antimony film sensor for sensitive rare earth metal analysis in environmental samples. J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. 51 (2016) 597-606.

[149] B. Silwana, C. van der Horst, E. Iwuoha, V. Somerset, Reduced graphene oxide impregnated antimony nanoparticle sensor for electroanalysis of platinum group metals. Electroanalysis 28 (2016) 1597-1607.

[150] C. Pérez-Ràfols, P. Trechera, N. Serrano, J. M. Díaz-Cruz, C. Ariño, M. Esteban. Determination of Pd(II) using an antimony film coated on a screen-printed electrode by adsorptive stripping voltammetry. Talanta 167 (2017) 1-7.

[151] V. Jovanovski, N.I. Hrastnik, S.B. Hočevar, Copper film electrode for anodic stripping voltammetric determination of trace mercury and lead. Electrochem. Commun. 57 (2015) 1-4.

[152] X. Pei, W. Kang,W. Yue, A. Bange, W.R. Heineman, I. Papautsky, Disposable copper based electrochemical sensor for anodic stripping voltammetry. Anal. Chem. 86 (2014) 4893–4900

[153] A. Kawde, A. Ismail, A.R. Al-Betar, O. Muraza, Novel Ce-incorporated zeolite modified-carbon paste electrode for simultaneous trace electroanalysis of lead and cadmium. Microp. Mesop. Mat. 243 (2017) 1-8.

[154] P.M. Lee, Z. Chen, L. Li, E. Liu, Reduced graphene oxide decorated with tin nanoparticles through electrodeposition for simultaneous determination of trace heavy metals. Electrochim. Acta 174 (2015) 207-214.

[155] P. Peerakumar, S.-M. Chen, R. Madhu, V. Veeramani, C.-T. Hung, S.-B. Liu, Nickel nanoparticle-decorated porous carbons for highly active catalytic reduction of organic dyes and sensitive detection of Hg(II) ions. ACS Appl. Mat. Interfaces 7 (2015) 24810-24821.

[156] L. Xu, R Ouyang, S. Zhou, H. Wen, X. Zhang, Y. Yang, N. Guo, W. Li, X. Hu, Z. Yang, L. Ouyang, Y. Miao, Sn-Pb hybrid nanoparticle decorated mesoporous carbon for sensitive stripping detection of Cd(II). J. Electrochem. Soc. 161 (2014) H730-H737.

[157] S. Xiong, B. Yang, D. Cai, G. Qiu, Z. Wu, Individual and simultaneous stripping voltammetric and mutual Interference analysis of $Cd^{2+}$, $Pb^{2+}$ and $Hg^{2+}$ with reduced graphene oxide-$Fe_3O_4$ nanocomposites. Electrochim. Acta 185 (2015) 52-61.

[158] W.-H. Xu, Q.-Q. Meng, C. Gao, J. Wang, Q.-X. Li, J.-H. Liu, X.-J. Huang, Investigation of the facet-dependent performance of $\alpha$-$Fe_2O_3$ nanocrystals for heavy metal determination by stripping voltammetry. Chem. Commun. 50 (2014) 5011-5013.

[159] C. Gao, X.-Y. Yu, R.-X. Xu, J.-H. Liu, X.-J. Huang, AlOOH-reduced graphene oxide nanocomposites: One-pot hydrothermal synthesis and their enhanced electrochemical activity for heavy metal ions. ACS Appl. Mat. Interfaces 4 (2012) 4672-4682.

[160] Y. Wei, R. Yang, X.-Y. Yu, L. Wang, J.-H. Liub, X.-J. Huang, Stripping voltammetry study of ultra-trace toxic metal ions on highly selectively adsorptive porous magnesium oxide nanoflowers. Analyst 137 (2012) 2183–2191

[161] Z. Wu, L. Jiang, Y. Zhu, C. Xu. Y. Ye, X. Wang, Synthesis of mesoporous NiO nanosheet and its application on mercury (II) sensor. J. Solid State Electrochem. 16 (2012) 3171–3177.

[162] T. Ndlovu, O.A. Arotiba, S. Sampath, R.W. Krause, B.B. Mamba, Electroanalysis of copper as a heavy metal pollutant in water using cobalt oxide modified exfoliated graphite elèctrode. Phys Chem. Earth 50-52 (2012) 127-131.

[163] M. Mališić, A. Janošević, B. Sljukic Paunkovic, I. Stojković, G. Ćirić-Marjanović, Exploration of $MnO_2$/carbon composites and their application to simultaneous electroanalytical determination of Pb(II) and Cd(II). Electrochim. Acta 74 (2012) 158-164.

[164] M. Sullivan, C. Spradlin, P.K.Q. Nguyen, S.K. Lunsford, A carbon paste composite electrode with mixture of zirconium dioxide and titanium dioxide to detect heavy metals studied by SEM and XPS. ECS Transactions 61 (2014) 25-36.

[165] P.K.Q. Nguyen, S.K. Lunsford, Electrochemical response of carbon paste electrode modified with mixture of titanium dioxide/zirconium dioxide in the detection of heavy metals: Lead and cadmium. Talanta 101 (2012) 110-121.

[166] R.-X. Xu, X.-Y. Yu, C. Gao, J.-H. Liu, R.G. Compton, X.-J. Huang, Enhancing selectivity in stripping voltammetry by different adsorption behaviors: The use of nanostructured Mg-Al layered double hydroxides to detect Cd(II). Analyst 138 (2013) 1812-1818.

[167] H. Zhuang, C. Wang, N. Huang, X. Jiang, Cubic SiC for trace heavy metal ion analysis. Electrochem. Commun. 41(2014) 5-7.

[168] R.-X. Xu, X.-Y. Yu, C. Gao, Y.-J. Jiang, D.-D. Han, J.-H. Liu, X.-J. Huang, Non-conductive nanomaterial enhanced electrochemical response in stripping voltammetry: The use of nanostructured magnesium silicate hollow spheres for heavy metal ions detection. Anal. Chim. Acta 790 (2013) 31-38.

[169] Z. Teng, H. Lv, L. Wang, L. Liu, C. Wang, G. Wang, Voltammetric sensor modified by EDTA-immobilized graphene-like carbon nitride nanosheets: Preparation. Characterization and selective determination of ultra-trace Pb (II) in water samples. Electrochim. Acta 212 (2016) 722-733.

[170] N. Zhou, H. Chen, J. Li, L. Chen, Highly sensitive and selective voltammetric detection of mercury(II) using an ITO electrode modified with 5-methyl-2-thiouracil, graphene oxide and gold nanoparticles. Microchim. Acta, 180 (2013) 493-499.

[171] V.K. Gupta, M.L. Yola, N. Atar, Z. Ustundagì, A.O. Solak, A novel sensitive Cu(II) and Cd(II) nanosensor platform: Graphene oxide terminated p-aminophenyl modified glassy carbon surface. Electrochim. Acta 112 (2013) 541-548.

[172] A. Afkhami, F. Soltani-Felehgari, T. Madrakian, H. Ghaedi, M. Rezaeivala, Fabrication and application of a new modified electrochemical sensor using nano-silica and a newly synthesized Schiff base for simultaneous determination of $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$ ions in water and some foodstuff samples. Anal. Chim. Acta 771 (2013) 21-30.

[173] A. Afkhami, H. Bagheri, H. Khoshsafar, M. Saber-Tehrani, M. Tabatabaee, A. Shirzadmehr, Simultaneous trace-levels determination of Hg(II) and Pb(II) ions in various samples using a modified carbon paste electrode based on multi-walled carbon nanotubes and a new synthesized Schiff base. Anal. Chim. Acta 746 (2012) 98-106.

[174] H. El-Mai, E. Espada-Bellido, M. Stitou, M. García-Vargas, M.D. Galindo-Riaño, Determination of ultra-trace amounts of silver in water by differential pulse anodic stripping voltammetry using a new modified carbon paste electrode. Talanta 151 (2016) 14-22.

[175] D.E. Popa, M. Mureseanu, I.G.H. Tanase, Organofunctionalized mesoporous silica carbon paste electrode for simultaneously determination of copper, lead and cadmium. Rev. Chim. 63 (2012) 507-512.

[176] L. Jiang, Y. Wang, J. Ding, T. Lou, W. Qin, An ionophore-Nafion modified bismuth electrode for the analysis of cadmium(II). Electrochem. Comm. 12 (2010) 202-205.

[177] H. Bagheri, A. Afkhami, H. Khoshsafar, M. Rezaei, S. Sabounchei, M. Sarlakifar, Simultaneous electrochemical sensing of thallium, lead and mercury using a novel ionic liquid/graphene modified electrode. Anal. Chim. Acta 870 (2015) 56-66.

[178] A. Bahrami, A. Besharati-Seidani, A. Abbaspour, M. Shamsipur, A highly selective voltammetric sensor for nanomolar detection of mercury ions using a carbon ionic liquid paste

electrode impregnated with novel ion imprinted polymeric nanobeads. Mat. Scien. Eng. C, 48 (2015) 205-212.

[179] M. Ghanei-Motlagh, M.A. Taher, A. Heydari, R. Ghanei-Motlagh, V.K. Gupta, A novel voltammetric sensor for sensitive detection of mercury(II) ions using glassy carbon electrode modified with graphene-based ion imprinted polymer. Mat. Sci. Eng. C, 63 (2016) 367-375.

[180] R. Zhiani, M. Ghanei-Motlag, I. Razavipanah, Selective voltammetric sensor for nanomolar detection of silver ions using carbon paste electrode modified with novel nanosized Ag(I)-imprinted polymer. J. Mol. Liq. 219 (2016) 554-560.

[181] Z. Es'Haghi, T. Heidari, E. Mazloomi, In situ pre-concentration and voltammetric determination of trace lead and cadmium by a novel ionic liquid mediated hollow fiber-graphite electrode and design of experiments via Taguchi method. Electrochim. Acta, 147 (2014) 279-287.

[182] J. Guo, Y. Luo, F. Ge, Y. Ding, J. Fei, Voltammetric determination of cadmium (II) based on a composite film of a thiol-functionalized mesoporous molecular sieve and an ionic líquid. Microchim. Acta, 172 (2011) 387-393.

[183] M. Ghanei-Motlagh, C. Karami, M.A. Taher, S.J. Hosseini-Nasab, Stripping voltammetric detection of copper ions using carbon paste electrode modified with aza-crown ether capped gold nanoparticles and reduced graphene oxide. RSC Adv. 6 (2016) 89167-89175.

[184] R.Y.A. Hassan, M.S. Kamel, H.N.A. Hassan, E. Khaled, Voltammetric determination of mercury in biological samples using crown ether/multiwalled carbon nanotube-based sensor. J. Electroanal. Chem. 759 (2015) 101-106.

[185] S. Cheraghi, M.A. Taher, H. Fazelirad, Voltammetric sensing of thallium at a carbon paste electrode modified with a crown ether. Microchim. Acta 180 (2013) 1157-1163.

[186] I.-M. Simionca, A. Arvinte, R. Ardeleanu, M. Pinteala, Siloxane-crown ether polyamide based electrode for electrochemical determination of lead(II) in aqueous solution. Electroanalysis 24 (2012) 1995-2004.

[187] X. Yuan, Y. Zhang, L. Yang, W. Deng, Y. Tan, M. Ma, Q. Xie, Three-dimensional activated graphene network-sulfonate-terminated polymer nanocomposite as a new electrode material for the sensitive determination of dopamine and heavy metal ions. Analyst 140 (2015) 1647-1654.

[188] Y. Tao, X. Gu, Y. Pan, L. Deng, Y. Wei, Y. Kong, W. Li, Overoxidation of conducting polymers combined with in situ plated bismuth film: An approach for simultaneous detection of cadmium and lead ions. J. Electrochem. Soc. 162 (2015) H194-H199.

[189] N. Ruecha, N. Rodthongkum, D.M. Cate, J. Volckens, O. Chailapakul, C.S. Henry, Sensitive electrochemical sensor using a graphene-polyaniline nanocomposite for simultaneous detection of Zn(II), Cd(II), and Pb(II). Anal. Chim. Acta 874 (2015) 40-48.

[190] Z.M. Wang, H.W. Guo, E. Liu, G.C. Yang, N.W. Khun, Bismuth/polyaniline/glassy carbon electrodes prepared with different protocols for stripping voltammetric determination of trace Cd and Pb in solutions having surfactants. Electroanalysis 22 (2010) 209-215.

[191] Z. Wang, H. Wang, Z. Zhang, X. Yang, G. Liu, Sensitive electrochemical determination of trace cadmium on a stannum film/poly(p-am inobenzene sulfonic acid)/electrochemically reduced graphene composite modified electrode. Electrochim. Acta 120 (2014) 140-146.

[192] R. Liu, H. Cao, Z. Nie, S. Si, X. Zhao, X. Zeng, A disposable expanded graphite paper electrode with self-doped sulfonated polyaniline/antimony for stripping voltammetric determination of trace Cd and Pb. Anal. Methods, 8 (2016) 1618-1625.

[193] E. Nagles, O. García-Beltrán, J Hurtado, Ex situ poly(3,4-ethylenedioxythiophene)-sodium dodecyl sulfate-antimony film electrode for anodic stripping voltammetry determination of lead and cadmium. Int. J. Electrochem. Sci. 11 (2016) 7507-7518.

[194] A. Chira, B. Bucur, M.P. Bucur, G.L. Radu, Electrode-modified with nanoparticles composed of 4,4′-bipyridine-silver coordination polymer for sensitive determination of Hg(II), Cu(II) and Pb(II). New J. Chem. 38 (2014) 5641-5646.

[195] H. Liu, S. Li, D. Sun, Y. Chen, Y. Zhou, T. Lu, Layered graphene nanostructures functionalized with NH2-rich polyelectrolytes through self-assembly: Construction and their application in trace Cu(II) detection. J. Mat. Chem. B, 2 (2014) 2212-2219.

[196] M.F. Philips, A.I. Gopalan, K.-P. Lee, Development of a novel cyano group containing electrochemically deposited polymer film for ultrasensitive simultaneous detection of trace level cadmium and lead. J. Haz. Mat. 237-238 (2012) 46-54.

[197] K. Tyszczuk-Rotko, I. Sadok, M. Barczak, M. Jabłońska-Czapla, A new voltammetric sensor based on thiol-functionalized polysiloxane film modified by lead nanoparticles for detection of Bi(III) ions. Electrochim. Acta 208 (2016) 102-108.

[198] C. Pérez-Ràfols, N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, Penicillamine-modified sensor for the voltammetric determination of Cd(II) and Pb(II) ions in natural samples. Talanta 144 (2015) 569-573.

[199] C. Pérez-Ràfols, N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, Glutathione modified screen-printed carbon nanofiber electrode for the voltammetric determination of metal ions in natural samples. Talanta 155 (206) 8-13.

[200] B.S. Flavel, M. Nambiar, J.G. Shapter, Electrochemical detection of copper using a Gly-Gly-His modified carbon nanotube biosensor. Silicon 3 (2011) 163-171.

[201] A. Safavia, E. Farjamib, Construction of a carbon nanocomposite electrode based on amino acids functionalized gold nanoparticles for trace electrochemical detection of mercury. Anal. Chim. Acta 688 (2011) 43–48.

[202] B. Viguier, K. Zór, E. Kasotakis, A. Mitraki, C. H. Clausen, W.E. Svendsen, J. Castillo-León, Development of an electrochemical metal-ion biosensor using self-assembled peptide nanofibrils. ACS Appl. Mater. Interfaces 3 (2011) 1594-1600.

[203] S. Krizkova, D. Huska, M. Beklova, J. Hubalek, V. Adam, L. Trnkova, R. Kizek, Protein-based electrochemical biosensor for detection of silver(I) ions. Environ. Toxicol. Chem. 29 (2010) 492-496.

[204] L. Trnkova, S. Krizkova, V. Adam, J. Hubalek, R. Kizek, Immobilization of metallothionein to carbon paste electrode surface via anti-MT antibodies and its use for biosensing of silver. Biosens. Bioelectron. 26 (2011) 2201-2207.

[205] X. Liu, W. Li, Q. Shen, Z. Nie, M. Guo, Y. Han, W. Liu, S. Yao, The Ag+-G interaction inhibits the electrocatalytic oxidation of guanine - A novel mechanism for $Ag^+$ detection. Talanta, 85 (2011) 1603-1608.

[206] N. Wang, M. Lin, H. Dai, H. Ma, Functionalized gold nanoparticles/reduced graphene oxide nanocomposites for ultrasensitive electrochemical sensing of mercury ions based on thymine-mercury-thymine structure. Biosens. Bioelectron. 79 (2016) 320-326.

[207] J. Wu, L. Li, B. Shen, G. Cheng, P. He, Y. Fang, Polythymine oligonucleotide-modified gold electrode for voltammetric determination of mercury(II) in aqueous solution. Electroanalysis, 22 (2010) 479-482.

[208] C.A. Martínez-Huitle, N. Suely Fernandes, M. Cerro-Lopez, M.A. Quiroz, Determination of trace metals by differential pulse voltammetry at chitosan modified electrodes. Portugaliae Electrochim. Acta 28 (2010) 39-49.

[209] E. Khaled, H.N.A. Hassan, I.H.I. Habib, R. Metelka, Chitosan modified screen-printed carbon electrode for sensitive analysis of heavy metals. International J. Electrochem. Sci. 5 (2010) 158-167.

[210] M. Moyo, J.O. Okonkwo, N.M. Agyei, Maize tassel-modified carbon paste electrode for voltammetric determination of Cu(II). Environ. Monit. Assess. 186 (2014) 4807-4817.

[211] M. Moyo, J.O. Okonkwo, Horseradish peroxidase biosensor based on maize tassel-MWCNTs composite for cadmium detection. Sens. Actuators B-Chem. 193 (2014) 515-521.

[212] M. Moyo, J.O. Okonkwo, N.M. Agyei, An amperometric biosensor based on horseradish peroxidase immobilized onto maize tassel-multi-walled carbon nanotubes modified glassy carbon electrode for determination of heavy metal ions in aqueous solution. Enzyme Microb. Technol. 56 (2014) 28-34.

[213] M. Yüce, H. Nazir, G. Dönmez, Using of *Rhizopus arrhizus* as a sensor modifying component for determination of Pb(II) in aqueous media by voltammetry. Bioresour. Technol. 101 (2010) 7551-7555.

[214] M. Yüce, H. Nazir, G. Dönmez, An advanced investigation on a new algal sensor determining Pb(II) ions from aqueous media. Biosens. Bioelectron. 26 (2010) 321-326.

[215] B.B. Prasad, S. Fatma, Electrochemical sensing of ultra trace copper(II) by alga-OMNiIIP modified pencil graphite electrode. Sens. Actuators B-Chem. 229 (2016) 655-663.

[216] B.B. Prasad, K. Singh, An electroconducting copper (II) imprinted sensor using algae as cheap substitute of multiwalled carbon nanotubes. Electrochim. Acta, 187 (2016) 193-203.

[217] V.C. Diculescu, A.-M. Chiorcea-Paquim, A.M. Oliveira-Brett, Applications of a DNA-electrochemical biosensor. Trac- Trends Anal. Chem. 79 (2016) 23-36.

[218] M. Ebrahimi, J.B. Raoof, R. Ojani, Novel electrochemical DNA hybridization biosensors for selective determination of silver ions. Talanta 144 (2015) 619-626.

[219] Z. Li, M. Liu, L. Fan, H. Ke, C. Luo, G. Zhao, A highly sensitive and wide-ranged electrochemical zinc(II) aptasensor fabricated on core–shell $SiO_2$-Pt@meso-$SiO_2$. Biosens. Bioelectron. 52 (2014) 293–297.

[220] N.-N. Bu, C.-X. Tang, X.-W. He, X.-B. Yin, Tetrahedron-structured DNA and functional oligonucleotide for construction of an electrochemical DNA-based biosensor. Chem. Commun. 47 (2011) 7689–7691.

[221] X. Chen, R. Tian, Q. Zhang, C. Yao, Target-induced electronic switch for ultrasensitive detection of $Pb^{2+}$ based on three dimensionally ordered macroporous Au–Pd bimetallic electrode. Biosens. Bioelectron. 53 (2014) 90–98.

[222] S. Tang, P. Tong, H. Li, J. Tang, L. Zhang, Ultra-sensitive electrochemical detection of $Pb^{2+}$ based on rolling circle amplification and quantum dots tagging. Biosen. Bioelec. 42 (2013) 608–611.

[223] D. Hynek, J. Prasek, P. Businova, J. Zak, J. Drbohlavova, J. Chomoucka, J. Kynicky, M. Konecna, M. Brnicky, J. Hubalek, R. Vrba, R. Kizek, V. Adam, Automated voltammetric determination of lead(II) ions using sensor array. Int. J. Electrochem. Sci., 8 (2013) 4441 – 4456.

[224] P. Kanyong, S. Rawlinson, J. Davis, Gold nanoparticle modified screen-printed carbon arrays for the simultaneous electrochemical analysis of lead and copper in tap water. Microchim. Acta 183 (2016) 2361-2368.

[225] F. Davis, S.P.J. Higson, Arrays of microelectrodes: technologies for environmental investigations, Environ. Sci.: Process. Impacts 15 (2013) 1477–1489.

[226] S. Daniele, M.A. Baldo, C. Bragato, Recent developments in stripping analysis on microelectrodes, Curr. Anal. Chem. 4 (3) (2008) 215–228.

[227] G. Herzog, V. Beni, Stripping voltammetry at micro-interface arrays: a review, Anal. Chim. Acta 769 (2013) 10–21.

[228] H. Wan, D. Ha, W. Zhang, H. Zhao, X. Wang, Q. Sun, P. Wang, Design of a novel hybrid sensor with microelectrode array and LAPS for heavy metal determination using multivariate nonlinear calibration. Sens. Actuat. B 192 (2014) 755-761.

[229] C. Kokkinos, A. Economou, I. Raptis, T. Speliotis, Disposable lithographically fabricated bismuth microelectrode arrays for stripping voltammetric detection of trace metals. Electrochem. Comm. 13 (2011) 391-95.

[230] C. Kokkinos, A. Economou, I. Raptis, Microfabricated disposable lab-on-a-chip sensors with integrated bismuth microelectrode arrays for voltammetric determination of trace metals. Anal. Chim. Acta 710 (2012) 1- 8.

[231] C. Kokkinos, A. Economou, Microfabricated chip integrating a bismuth microelectrode array for the determination of trace cobalt(II) by adsorptive cathodic stripping voltammetry. Sens. Actuat. B 229 (2016) 362-369.

[232] A. Mardegan, S. Dal Borgo, P. Scopece, L.M. Moretto, S.B. Hočevar, P. Ugo, Bismuth modified gold nanoelectrode ensemble for stripping voltammetric determination of lead. Electrochem. Comm. 24 (2012) 28-31.

[233] A. Mardegan, P. Scopece, P. Ugo, L.M. Moretto, Ensembles of gold nanowires for the anodic stripping voltammetric determination of inorganic arsenic. J. Nanosci. Nanotech. 15 (2015) 3417-3422.

[234] M. del Valle, Sensor arrays and electronic tongue systems, Int. J. Electrochem. 2012 (2012) 1–12.

[235] J. Zeravik, A. Hlavacek, K. Lacina, P. Skládal, State of the art in the field of electronic and bioelectronic tongues - towards the analysis of wines, Electroanalysis 21 (2009) 2509–2520.

[236] P. Ciosek, W. Wróblewski, Sensor arrays for liquid sensing-electronic tongue systems. Analyst 132 (2007) 963–978.

[237] X. Cetó, N.H. Voelcker, B. Prieto-Simón, Bioelectronic tongues: New trends and applications in water and food analysis, Biosens. Bioelectron. 79 (2016) 608–626.

[238] N. Serrano, B. Prieto-Simón, X. Cetó, M. del Valle, Array of peptide-modified electrodes for the simultaneous determination of Pb(II), Cd(II) and Zn(II). Talanta 125 (2014) 159 - 166.

[239] N. Serrano, A. González-Calabuig, M. del Valle, Crown ether-modified electrodes for the simultaneous stripping voltammetric determination of Cd(II), Pb(II) and Cu(II). Talanta 138 (2015) 130 - 137.

[240] A. González-Calabuig, D. Guerrero, N. Serrano, M. del Valle, Simultaneous voltammetric determination of heavy metals by use of crown ether-modified electrodes and chemometrics. Electroanalysis 28 (2016) 663-670.

[241] C. Pérez-Ràfols, N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, Simultaneous determination of Tl(I) and In(III) using a voltammetric sensor array. Sens. Actuators B-Chem. 245 (2017) 18-24.

[242] C. Pérez-Ràfols, N. Serrano, J.M. Díaz-Cruz, C. Ariño, M. Esteban, A screen-printed voltammetric electronic tongue for the analysis of complex mixtures of metal ions. Sens. Actuators B-Chem. 250 (2017) 393-401.

[243] W. Cai, Y. Li, X.-M. Gao, P. Wang, Full automatic monitor for in-situ measurements of trace heavy metals in aqueous environment. Sensor Lett. 9 (2011) 137–142.

[244] G.Herzog, W. Moujahid, K. Twomey, C. Lyons, V. I. Ogurtsov, On-chip electrochemical microsystems for measurements of copper and conductivity in artificial seawater. Talanta 116 (2013) 26–32

[245] H. Wan, D. Ha, W. Zhang, H. Zhao, X. Wang, Q. Sun, P. Wang, Design of a novel hybrid sensor with microelectrode array and LAPS for heavy metal determination using multivariate nonlinear calibration. Sens. Actuators B-Chem. 192 (2014) 755– 761.

[246] H. Wan, Q. Sun, H. Li, F. Sun, N. Hu, P. Wang, Design of a miniaturized multisensor chip with nanoband electrode array and light addressable potentiometric sensor for ion sensing. Anal. Methods 7 (2015) 9190-9197.

## Figure captions

**Figure 1.** a) Application and working concentration ranges of some analytical techniques compared with the requirements in different fields (adapted from reference 14). b) Different voltammetric modes used in chemical analysis.

**Figure 2.** Possible supports, substracts and strategies of modification of voltammetric sensors for the analysis of metal ions.

Figure 1

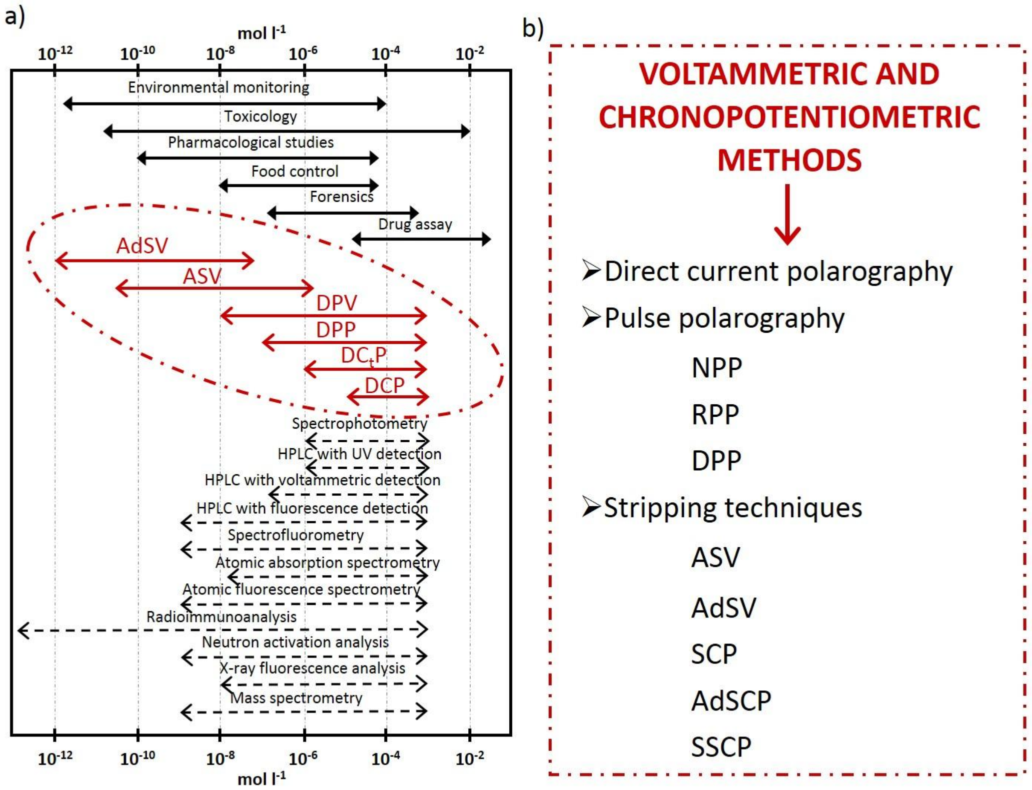
a)
mol l-1
10-12
10-10
10-8
10-6
10-4
10-2
Environmental monitoring
Toxicology
Pharmacological studies
Food control
Forensics
Drug assay
AdSV
ASV
DPV
DPP
DCtP
DCP
Spectrophotometry
HPLC with UV detection
HPLC with voltammetric detection
HPLC with fluorescence detection
Spectrofluorometry
Atomic absorption spectrometry
Atomic fluorescence spectrometry
Radioimmunoanalysis
Neutron activation analysis
X-ray fluorescence analysis
Mass spectrometry
b)
VOLTAMMETRIC AND CHRONOPOTENTIOMETRIC METHODS
➢Direct current polarography
➢Pulse polarography
NPP
RPP
DPP
➢Stripping techniques
ASV
AdSV
SCP
AdSCP
SSCP

Figure 2

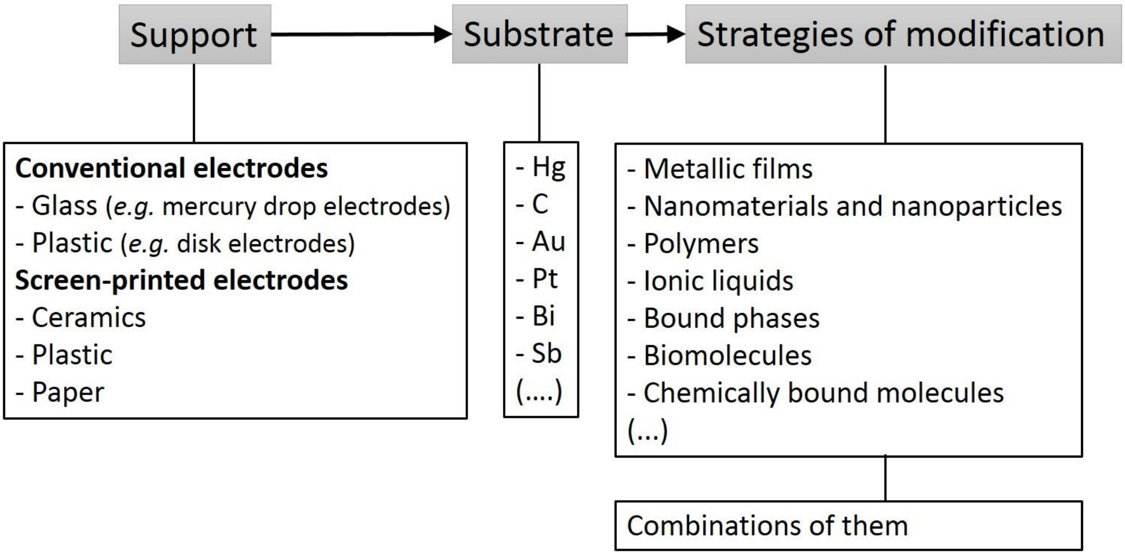
Support
Substrate
Strategies of modification
Conventional electrodes
- Glass (e.g. mercury drop electrodes)
- Plastic (e.g. disk electrodes)
Screen-printed electrodes
- Ceramics
- Plastic
- Paper
- Hg
- C
- Au
- Pt
- Bi
- Sb
(....)
- Metallic films
- Nanomaterials and nanoparticles
- Polymers
- Ionic liquids
- Bound phases
- Biomolecules
- Chemically bound molecules
(...)
Combinations of them

**Table 1.** Maximum levels of some elements in drinking water regulated or recommended by different organizations.

| Element | Maximum levels (µg $L^{-1}$) | | |
|---|---|---|---|
| | EC[a] | EPA[c] | WHO[e] |
| Pb | 10 | 15 | 10 |
| Cd | 5 | 5 | 3 |
| Hg | 1 | 2 | 1 |
| As | 10 | 10 | 10 |
| Sb | 5 | 6 | 20 |
| Cr | 50 | 100 | 50 |
| Cu | 2000 | 1300 | 2000 |
| Se | 10 | 50 | 10 |
| Tl | - | 2 | - |
| Mo | - | - | 70 |
| Ni | 20 | - | 20 |
| Zn | - | 5000 | 3000 |
| Mn | 50[b] | 50[d] | - |
| Fe | 200[b] | 300[d] | - |
| Ag | - | 100[d] | - |

a: Council Directive 98/83/EC of 3rd November 1998 on the quality of water intended for human consumption, amended by Commission Directive (EU) 2015/1787 of 6 October 2015.

b: Indicator parameters (non-compulsory).

c: When not otherwise indicated, USA Environmental Protection Agency (EPA) National Primary Drinking Waters Regulation (compulsory)

d: EPA National Secondary Drinking Waters Regulation (non-enforceable guidelines)

e: Guidelines for Drinking-water Quality, 3rd Ed. Vol. 1: Recommendations. World Health Organization (WHO), Geneva, 2004.

**Table 2.** Maximum levels of some elements in food regulated or recommended by different organizations.

| Element | Wine (μg L$^{-1}$) | | Raw milk (μg kg$^{-1}$) | | Meat (bovine, sheep, pig and poultry) (μg kg$^{-1}$) | | Fish muscle (μg kg$^{-1}$) | | Bivalve molluscs (μg kg$^{-1}$) | | Cereals, legumes and pulses (μg kg$^{-1}$) | | Fruit (except small fruits & berries) (μg kg$^{-1}$) | | Vegetables (μg kg$^{-1}$) | | Fats and oils (including milk fat) (μg kg$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ | EC$^{a}$ | FAO/ WHO$^{b}$ |
| Pb | 200 | 200 | 20 | 20 | 100 | 100 | 300 | 300 | 1500 | | 200 | 50-300$^{c}$ | 200 | 100 | 100-300$^{c}$ | | 100 | 100 |
| Cd | | | | | 50 | | 50-300$^{c}$ | | 1000 | 2000 | 100-200$^{c}$ | 100-400$^{c}$ | | | 50-200$^{c}$ | 50-200$^{c}$ | | |
| Hg | | | | | | | 1000 | 500$^{d}$ | | | | | | | | | | |
| As | | | | | | | | | | | | | | | | | | 100 |

a: Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, modified by Commission Regulation (EC) No 629/2008 of 2 July 2008

b: General Standard for Contaminants and Toxins in Food and Feed (CODEX STAN 193-1995) Adopted in 1995 Revised in 1997, 2006, 2008, 2009. Amended in 2010, 2012, 2013, 2014, 2015. FAO/WHO.

c: depending on the type of fish, cereal or vegetable

d: As methylmercury

**Table 3.** Mercury based electrodes.

| Electrode | Analyte | Technique | Sample | Detection limit | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| HMDE | Cd(II)<br>Pb(II)<br>Cu(II)<br>Zn(II) | DPASV | Poultry feeds | Zn(II): 0.69 μg kg$^{-1}$<br>Cd(II): 0.35 μg kg$^{-1}$<br>Pb(II): 0.68 μg kg$^{-1}$<br>Cu(II): 0.24 μg kg$^{-1}$ | --- | - Measurements in an acetate buffer (pH 5) media.<br>- $E_d$ = -1.05 V, $t_d$ = 120 s, potential scan from -1.2 V to 0.15 V (scan rate 10 mV s$^{-1}$).<br>- Objective: control of metal content.<br>- Levels of Cd(II) and Pb(II) found are greater than the maximum tolerable which could be harmful for poultries. | [41] |
| HMDE | Cd(II)<br>Pb(II) | DPASV | Soil, plants, air particulate, water, phosphate ore (raw and treated) and fertilizer samples | --- | --- | - Measurements in an acetate buffer (pH 4) media.<br>- Control analysis of different materials close to a Syrian phosphate industry and in the vicinity of phosphogypsum piles.<br>- Other metal ions were also analyzed: Zn(II), Cr(III) and Cu(II) by AAS; Se(IV), Ni(II), As(III) and Hg by NAA. | [42] |
| HMDE | Cd(II)<br>Cu(II)<br>Zn(II) | ASV | Muscle, gill and liver tissues of fish species | --- | --- | - Measurements in an acetate buffer media.<br>- $E_d$(Cd(II)) = -0.75 V, $E_d$(Zn(II)) = -1.0 V, $E_d$(Cu(II)) = -0.25 V.<br>- Concentrations of Cu(II), Cd(II), and Zn(II) are significantly lower than the permissible FAO/WHO levels. | [43] |
| HMDE | Pb(II)<br>Cd(II)<br>Zn(II)<br>Cu(II) | ASV | Water, sediments and fish | --- | --- | -The objective is the evaluation of the quality of the aquatic environment of the Plitvice Lakes National Park based on the analysis of ecotoxic metal ions in different compartments.<br>- Hg is determined by cold vapor AAS. | [44] |
| HMDE | Cd(II)<br>Pb(II)<br>Cu(II)<br>Zn(II) | SWASV | Environmental and food samples | --- | --- | - $E_d$ = -1.15 V, $t_d$ = 210 s, potential scan from -1.15 V to 0.10 V (scan rate 100 mV s$^{-1}$).<br>- Analysis of Hg(II) is performed with gold electrode. | [45-50] |
| HMDE | Pb(II)<br>Cd(II)<br>Zn(II)<br>Cu(II)<br>Se(IV) | DPASV:<br>(Pb(II), Cd(II), Zn(II), Cu(II))<br>DPCSV:<br>(Se(IV)) | Milk and dairy products | Pb(II): 0.25 μg L$^{-1}$<br>Cd(II): 0.12 μg L$^{-1}$<br>Zn(II): 0.05 μg L$^{-1}$<br>Cu(II): 0.04 μg L$^{-1}$<br>Se(IV): 0.14 μg L$^{-1}$ | Pb(II): 0. 5-200 μg L$^{-1}$<br>Cd(II): 0.3-220 μg L$^{-1}$<br>Zn(II): 0.1- 500 μg L$^{-1}$<br>Cu(II): 0.1-450 μg L$^{-1}$<br>Se(IV): 0.4-120 μg L$^{-1}$ | For Pb(II), Cd(II), Zn(II):<br>- Measurements in a 0.3 mol L$^{-1}$ phosphate buffer (pH 6) media.<br>- $E_d$ = -1.10 V, $t_d$ = 20 s, potential scan from -1.15 V to 0 V (scan rate 40 mV s$^{-1}$).<br>For Cu(II):<br>- Measurements in a 0.3 mol L$^{-1}$ ammonia buffer (pH 9. 5) media. | [51] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | - $E_d$ = -0.2 V, $t_d$ = 20 s, potential scan from -0.5 V to 0 V (scan rate 40 mV $s^{-1}$).<br>For Se(IV):<br>- Measurements in a phosphate buffer (pH 2) media.<br>- $E_d$ = -0.3 V, $t_d$ = 20 s, potential scan from -0.1 V to -0.9 V (scan rate 40 mV $s^{-1}$).<br>- The objective is to determine metal ion concentrations in dairy products in different industrial areas of Iran.<br>- In all cases levels found were below the permissible limits.<br>- The order of metal concentrations in all milk and other dairy products is Zn > Cu > Pb > Se > Cd. | |
| HMDE | Pb(II)<br>Cd(II)<br>Zn(II)<br>Co(II) | DPASV | Milk and water samples | Pb(II): 0.006 μg $L^{-1}$<br>Cd(II): 0.007 μg $L^{-1}$<br>Co(II): 0.047 μg $L^{-1}$<br>Zn(II): 0.013 μg $L^{-1}$ | --- | - Measurements in a 0.1 mol $L^{-1}$ potassium chloride/acetate buffer (pH 4.0) media.<br>- $E_d$ = -1.3 V, $t_d$ = 60 s, potential scan from -1.1 V to 0.0 V (scan rate 50 mV $s^{-1}$).<br>- Analysis of Hg(II), As(II) is performed with gold electrode. | [52] |
| HMDE | Cd(II)<br>Pb(II)<br>Cu(II)<br>Zn(II) | DPASV<br>Over-potential deposition | --- | --- | --- | - Measurements in an acetate buffer (pH 4.8) media.<br>- $E_d$ = -2.20 V, $t_d$ = 10 s, potential scan from -1.4 V to 0.1 V (scan rate 20 mV $s^{-1}$).<br>- Use of very cathodic accumulation potentials at which solvent reduction occurs.<br>- A 5-10 fold signal increase respect to classical methodology ($E_d$ = -1.40 V). | [54] |
| TMFE | Cd(II)<br>Pb(II)<br>Cu(II) | SWASV | Sea water and particulate fraction | Cd(II), Pb(II), Cu(II): 0.001 μg $L^{-1}$ (at $t_d$ 5 min) | --- | - Measurements in a hydrochloric acid media.<br>- $E_d$ = -0.975 V, $t_d$ = 3 - 10 s, potential scan from -0.90 V to 0.0 V.<br>- Metal contamination related with a shipwreck lying (Coastal Adriatic sea).<br>- Concentrations of Cd(II) and Pb(II) will exceed the legal limits after 2015 if the hulk is not removed. | [53] |
| HMDE | Sb(III) | SWAdSV | Tap and commercial mineral water | 0.0036 μg $L^{-1}$ | up to 10.0 μg $L^{-1}$ | - Ligand considered: quercetin-5′-sulfonic acid.<br>- Measurements in a Britton-Robinson buffer (pH 5.5) media.<br>- $E_d$ = -0.10 V, $t_d$ = 60 s, potential scan from -0.05 V to -1.4 V. | [55] |
| HMDE | Sb(III) | SWAdSV | Mineral water | 0.1 μg $L^{-1}$ (HQ),<br>0.014 μg $L^{-1}$ (HQS) | | - Ligand considered: 8-hydroxyquinoline (HQ) and 8-hydroxyquinoline-5-sulfonic acid (HQS).<br>- Measurements in an acetate buffer (pH 5.4) media for HQ and phosphate buffer (pH 2.2) media for HQS. | [56] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| HMDE | V(V) | DPAdASV | Tap, purified drinking and river water | 0.23 μg $L^{-1}$ | up to 0.35 μg $L^{-1}$ | - $E_d$ = -0.10 V, $t_d$ = 30 s, potential scan from -0.15 V to -1.0 V.<br>- Effect of the presence of a sulfonic acid group in the ligand structure.<br>- Sensitivity is higher when HQS is used.<br>- Ligand considered: quercetin-5′-sulfonic acid.<br>- Measurements done in the presence of $KBrO_3$ (35 mmol $L^{-1}$) in the media as an oxidant to increase the vanadium reduction signal.<br>- Measurements in a Britton-Robinson buffer (pH 7) media.<br>- $E_d$ = -0.0 V, $t_d$ = 30 s, potential scan from -0.1 V to -1.0 V (scan rate 50 mV $s^{-1}$). | [57] |
| HMDE | As(III) | DPAdSV | Drinking and river water | 0.08 μg $L^{-1}$ (APDTC)<br>0.27 μg $L^{-1}$ (ADDTP) | 0.50-3.00 μg $L^{-1}$ (APDTC)<br>2.50-15.00 μg $L^{-1}$ (ADDTP) | - Ligands considered: ammonium pyrrolidine dithiocarbamate (APDTC) and ammoniumdiethyl dithiophosphate (ADDTP).<br>- Measurements in a 2.00 mol $L^{-1}$ hydrochloric acid media.<br>- $E_d$ = -0.40 V, $t_d$ = 80 s for APDTC, and $E_d$ = -0.30 V, $t_d$ = 80 s for ADDTP, potential scan from -0.3 V to -1.9 V (scan rate 10 mV $s^{-1}$).<br>- Adsorption process based on the formation of complexes with APDTC or ADDTP prior to the formation of an intermetallic compound with Cu(II). | [58] |
| HMDE | Co(III) | SWAdSV | Different waters | 0.02 μg $L^{-1}$ | 0.0-40.0 μg $L^{-1}$ | - The presence of a cationic surfactant (cetylpyridiniumbromide) improved the sensitivity.<br>- Ligand considered: pyrogallol red.<br>- Measurements in a 0.05 mol $L^{-1}$ HEPES buffer (pH 7.8) media.<br>- $E_d$ = -0.40 V, $t_d$ = 60 s, potential scan from -0.4 V to -1.3 V (scan rate 126 mV $s^{-1}$).<br>- The interference of Ni(II) and Zn(II) is considered.<br>- This method considerably exceeds the separation obtained with DMG and others ligands for Co(III), Ni(II) and Zn(II) signals. | [59] |
| HMDE | Co(III)<br>Fe(III)<br>Ni(II) | DPAdSV | Human serum | --- | --- | - Ligand considered: dimethylglyoxime for Ni(II) and Co(III) and 5-Br-PADP for Fe.<br>- Measurements in an ammonium acetate buffer (pH 8.3) media.<br>- Ni(II) and Co(III): $E_d$ = -0.90 V, $t_d$ = 180 s, potential scan from -0.9 V to -1.3 V (scan rate 4 mV $s^{-1}$); Fe(III): $E_d$ = -0.65 V, $t_d$ = | [60] |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | 180 s, potential scan from -0.65 V to -0.76 V (scan rate 2 mV $s^{-1}$).<br>- Correlation study between metal content in serum and hepatitis B and C is considered. |  |
| HMDE | Co(III)<br>Cu(II)<br>Fe(III)<br>Ni(II)<br>V(V) | DPAdSV | Pore water | Co(III): 0.0023 µg $L^{-1}$<br>Cu(II): 0.0057 µg $L^{-1}$<br>Fe(III): 0.07 µg $L^{-1}$<br>Ni(II): 0.03 µg $L^{-1}$<br>V(V): 0.13 µg $L^{-1}$ | Co(III): up to 3.53 µg $L^{-1}$<br>Cu(II): up to 5.1 µg $L^{-1}$<br>Fe(III): up to 11.2 µg $L^{-1}$<br>Ni(II): up to 11.7 µg $L^{-1}$<br>V(V): up to 15.3 µg $L^{-1}$ | - Ligand considered: a mixture of DMG and catechol.<br>- Measurements in a HEPES buffer (pH 7.0) media.<br>- $E_d$ = -0.35 V, $t_d$ = 60 s, potential scan from 0 V to -1.15 V (scan rate 20 mV $s^{-1}$).<br>- Method also suitable for estuarine and coastal waters. | [61] |
| HMDE | Zr(IV) V(V) | DPAdSV | River and estuary water, and coastal and sea water | --- | --- | - Sequential determination of Zr(IV) and V(V).<br>- Ligand considered: cupferron-oxalic acid-1,3-diphenylguanidine.<br>- Measurements in an ammonium acetate (pH 4.8) media.<br>- For Zr(IV): $E_d$ = -0.6 V, $t_d$ = 400 s, potential scan from -0.6 V to -1.2 V (scan rate 10 mV $s^{-1}$). For V(V): $E_d$ = -0.2 V, $t_d$ = 30 s, potential scan from -0.2 V to -1.0 V (scan rate 60 mV $s^{-1}$). | [62] |
| HMDE | Fe(III) | SWAdSV | Sea water | 0.6 ng $L^{-1}$ (ultrapure water)<br>0.3 ng $L^{-1}$ (seawater) | up to 33.5 ng $L^{-1}$ (ultrapure water)<br>up to 56 ng $L^{-1}$ (seawater) | - Determinations performed in a laminar flow hood in a cell specially designed.<br>- Measurements done in the presence of oxygen which has a catalytic effect in the reduction of the Fe-complex.<br>- Ligand considered: 2,3-dihydroxynaphthalene.<br>- Measurements in a HEPPS buffer (pH 8.15) media.<br>- $E_d$ = -0.1 V, $t_d$ = 30 s, potential scan from -0.35 V to -0.75 V. | [63] |
| HMDE | Cu(II)<br>Cd(II) | DPAdSV | Food and water | Cu(II): 0.04 µg $L^{-1}$<br>Cd(II): 0.02 µg $L^{-1}$ | Cu(II): 0.5-105.0 µg $L^{-1}$<br>Cd(II): 0.8–70.0 µg $L^{-1}$ | - Ligand considered: luminol.<br>- Measurements in 0.1 mol $L^{-1}$ borate buffer (pH 7.5) media.<br>- $E_d$ = -0.1 V, $t_d$ = 60 s, potential scan from -0.3 V to -0.85 V (scan rate 100 mV $s^{-1}$). | [64] |
| *Ex-situ* HgSPE | Cd(II) | SWASV | River water | 0.2 µg $L^{-1}$ | 0.2-40 µg $L^{-1}$ | - Electrode modification from a 0.2 mol $L^{-1}$ acetate buffer (pH 4.5) solution of 170 mg $L^{-1}$ Hg(II) ions.<br>- Measurements in a 0.2 mol $L^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$ = -1.0 V, $t_d$ = 60 s, potential scan from -1.0 V to -0.1 V.<br>- In order to completely remove the residual Cd(II) from the electrode, -0.1 V for 60 s is applied.<br>- Semicontinuous monitoring of Cd(II) in waters. | [65,66] |
| HgSPE | Pb(II) | DPASV | --- | 8.9 µg $L^{-1}$ | 29.8–229.2 µg $L^{-1}$ | - $E_d$ = -1.0 V, $t_d$ = 120 s, potential scan from -1.0 V to -0.4 V. | [67] |
| Hg(Ag)FE | Cd(II)<br>Pb(II) | SWASV | --- | --- | --- | - Measurements in a 0.1 mol $L^{-1}$ ammonium citrate media.<br>- PLS regression was applied to resolve quantitatively the | [68] |

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| | Cu(II)<br>Bi(III) | | | | | strongly overlapping peaks of Cu(II) and Bi(III) ions. | |
| Hg(Au)MEA | Cd(II)<br>Pb(II)<br>Cu(II)<br>Zn(II) | ASV | Water | --- | --- | - Good linearity was obtained for Cd(II), Pb(II) and Cu(II) ions, but Zn(II) shows poor linearity. | [69] |
| Hg(Ag)FE | Zn(II)<br>Cu(II) | DPASV | Gastric juice and mucosa of rats | --- | --- | - Measurements in a 0.05 mol $L^{-1}$ potassium nitrate media.<br>- Zn(II): $E_d$ = -1.10 V, $t_d$ = 30 s, potential scan from -1.1 V to -0.7 V; Cd(II): $E_d$ = -0.25 V, $t_d$ = 30 s, potential scan from -0.25 V to -0.15 V. | [70] |
| Mercury oxide /GCE | Cd(II)<br>Pb(II) | SWASV | Milk | Pb(II): 0.08 µg $L^{-1}$<br>Cd(II): 0.05 µg $L^{-1}$ | 0.5 to 50 µg $L^{-1}$ | - Mercuric oxide was adsorbed onto the surface of GC and further electrochemically reduced to form a mercury film on the electrode surface. | [71] |
| Hg/Nafion/ FE | Zn(II)<br>Cd(II)<br>Pb(II) | DPAdSV | Tap, sea, lake and mineral waters | Pb(II): 0.10 µg $L^{-1}$<br>Cd(II): 0.06 µg $L^{-1}$<br>Zn(II): 0.06 µg $L^{-1}$ | Pb(II) and Cd(II): until 15.0 µg $L^{-1}$<br>Zn(II): until 25.0 µg $L^{-1}$ | - Ligand considered: clioquinol (5-chloro-7-iodo-8-hydroxyquinoline, CQ).<br>-Measurements in a 0.3 mol $L^{-1}$ Britton-Robinson buffer (pH 5.3) media.<br>- $E_d$ = -0.65 V, $t_d$ = 30 s, potential scan from -0.2 V to -1.2 V (scan rate 50 mV $s^{-1}$).<br>- Comparison with a HMDE is carried out. | [72] |
| Hg/Nafion/ FE | Pb(II)<br>Cd(II) | SWAdSV | Mineral water | Pb(II): 0.05 µg $L^{-1}$<br>Cd(II): 0.01 µg $L^{-1}$ | Pb(II): 1.0 - 16.0 µg $L^{-1}$,<br>Cd(II): 1.0 - 13.0 µg $L^{-1}$ | - Ligand considered: pyrogallol red.<br>- Measurements in an acetate buffer (pH 4.0) media.<br>- $E_d$ = -0.4 V, $t_d$ = 100 s, potential scan from -0.2 V to -1.2 V.<br>- Pyrogallol red forms 1:1 and 1:2 (metal:ligand) complexes with Pb(II) and Cd(II) respectively. | [73] |
| Hg/Nafion/ FE | Pb(II)<br>Cd(II) | AdSV | Different reference water materials | 0.2 µg $L^{-1}$ | until 18.0 µg $L^{-1}$ | - Ligand considered: quercetin-5′-sulfonic acid.<br>- Measurements in a Britton-Robinson buffer (pH 6.1) media.<br>- $E_d$ = -0.1 V, $t_d$ = 30 s, potential scan from -0.1 V to -1.0 V (scan rate 248 mV $s^{-1}$).<br>- Comparison with a HMDE is done. | [74] |
| G-GC-*in-situ* HgFE | Pb(II)<br>Cd(II)<br>Zn(II) | SWASV | Tap water | Zn(II): 0.04 µg $L^{-1}$<br>Cd(II): 0.11 µg $L^{-1}$<br>Pb(II): 0.14 µg $L^{-1}$ | 0 - 60 µg $L^{-1}$ | - Graphene is coated onto the GCE surface followed by the *in-situ* deposition of Hg.<br>- Measurements in a 0.2 mol $L^{-1}$ acetate buffer (pH 4.6) media.<br>- $E_d$ = 1.3 V, $t_d$ = 120 s, potential scan from -1.4 V to -0.2 V (scan rate 297 mV $s^{-1}$).<br>- Conditioning step: 0.3 V along 60 s is applied between | [75] |

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| | | | | | | measurements. | |
| Hg nano-droplets-MWCNTs-CHIT/SPE | Cd(II)<br>Pb(II)<br>Cu(II) | SWASV | River water | Cd(II): 1.35 µg $L^{-1}$<br>Pb(II): 4.77 µg $L^{-1}$<br>Cu(II): 1.27 µg $L^{-1}$ | --- | - Electrode prepared with a mixture of MWCNTs and chitosan, followed by adsorption of Hg.<br>- Measurements in an acetate buffer/ 0.1 mol $L^{-1}$ potassium chloride (pH=4.8) media.<br>- $E_d$ = -1.2 V, $t_d$ = 300 s, potential scan from -1.0 V to -0.15 V.<br>- Conditioning step: -0.1 V along 30 s is applied between measurements. | [76] |
| Hg-AuNPs-SPCE | Cd(II) | --- | Water samples | 2.6 µg $L^{-1}$ | 8.4 µg $L^{-1}$ to 500 mg $L^{-1}$ | - Portable analytical system developed for *in-situ* environmental metal ion detection. | [77] |
| Hg-Bi/SWNT/GCE | Cd(II)<br>Pb(II)<br>Zn(II) | SWASV | River water | --- | Zn(II) and Cd(II): < 2 µg $L^{-1}$<br>Pb(II): 0.12 ng $L^{-1}$ | - Measurements in a 0.1 mol $L^{-1}$ acetate buffer/0.1 mol $L^{-1}$ potassium chloride (pH 6.0) media.<br>- $E_d$ = -1.3 V, $t_d$ = 300 s, potential scan from -1.3 V to -0.3 V.<br>- Conditioning step: -0.3 V along 60 s is applied between measurements. | [78] |

HMDE: hanging mercury drop electrode; ASV: anodic stripping voltammetry; TMFE: thin mercury film electrode; HgSPE: mercury screen printed electrode; Hg(Ag)FE: silver amalgam film electrode; Hg(Au)MEA: gold microelectrode array plated with mercury; G-GC-*in-situ* HgFE: graphene modified *in-situ* mercury film glassy carbon electrode; Hg/MWCNT-chitosan/SPE: mercury multiwallet carbon nanotubes chitosan screen printed electrode; Hg nanodroplets-MWCNTs-CHIT/SPE: mercury nanodroplets modified multi-walled carbon nanotubes chitosan screen printed electrode; Hg-AuNPs-SPCE: gold nanoparticles amalgam modified screen printed carbon electrode; Hg-Bi/SWNT/GCE: mercury bismuth single walled carbon nanotubes composite electrode.

**Table 4.** Gold based electrodes.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| AuE | Hg(II)<br>Cu(II) | SWASV | Food and environmental | --- | --- | - $E_d$ = -0.05 V, $t_d$ = 300 s, scan from -0.05 V to 0.85 V.<br>- Two-step sequential analysis employing two working electrodes: an AuE for Hg(II) (and Cu(II)), and subsequently, an HMDE for Cu(II), Pb(II), Cd(II) and Zn(II). | [45-50] |
| AuRDE | Hg(II)<br>As(III) | DPASV | Milk and water | Hg(II): 1 ng L$^{-1}$<br>As(III): 3 ng L$^{-1}$ | --- | - $E_d$ = -0.3 V, $t_d$ = 60 s, scan from -0.2 V to 0.8 V (scan rate 50 mV s$^{-1}$).<br>- Two-step sequential analysis employing two working electrodes: an AuRDE for Hg(II) and As(III), and subsequently, a HMDE for Co(II), Pb(II), Cd(II) and Zn(II). | [52] |
| SPAuE | Hg(II) | SWASV | Waste water and rain water | 1.1 ng mL$^{-1}$ | 5 to 30 ng L$^{-1}$ | - Commercial gold SPE.<br>- Measurements in a 0.1 mol L$^{-1}$ hydrochloric acid media.<br>- $E_d$ = 0.3 V, $t_d$ = 60 s, potential scan from 0.1 V to 0.7 V.<br>- Conditioning step: 0.7 V along 15 s is applied after each measurement. | [79] |
| SPAuE | Hg(II) | SWASV | --- | 0.8 µg L$^{-1}$ | 16-280 µg L$^{-1}$ and 1.2 - 8 µg L$^{-1}$ | - SPE build in a PET support | [80] |
| AuNPs/GC | Hg(II) | SWASV | Spiked real waters | 0.01 µg L$^{-1}$ | 0.2 – 10 µg L$^{-1}$ | - Sample prepared employing electromembrane extraction (60 V for 12 min) previous to ASV measurement.<br>- $E_d$=0 V, $t_d$= 300 s, scan from 0.3 V to 0.7 V (scan rate 500 mV s$^{-1}$).<br>- Measurements in a 1.0 mol L$^{-1}$ hydrochloric acid media.<br>- Conditioning step: A conditioning potential of 0.5 V during 5 s and a desorption potential of -0.8 V during 60 s are applied before and after measurements. | [81] |
| AuNPs-GC | Hg(II) | DPASV | Tap water | 0.02 µg L$^{-1}$ | 0.2 – 100 µg L$^{-1}$ | - Electrode is prepared by casting the AuNPs on the GCE using Nafion.<br>- Measurements in a 0.1 mol L$^{-1}$ hydrochloric acid media.<br>- $E_d$= -0.9 V, $t_d$=200 s, scan from -0.8 V to -0.2 V (scan rate 10 mV s$^{-1}$).<br>- Comparison with electrochemical impedance spectroscopy (EIS).<br>- LODs below the corresponding guideline value from WHO. | [82] |
| AuNPs/SPC | Hg(II) | SWASV | Urine | ≈ 1 µg L$^{-1}$ | until 20 µg L$^{-1}$ | -Samples prepared by vortex-assisted ionic liquid dispersive liquid-liquid microextraction and microvolume back-extraction.<br>- $E_d$ = 0.3 V, $t_d$ = 240 s, scan from 0.3 V to 0.55 V.<br>- LODs allowed are significantly lower than those establish by the WHO for normal urine samples. | [83] |

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| AuNPs/SPCE | Hg(II) | SWASV | Dust and water | μg $L^{-1}$ range | --- | - $E_d$ = 0.2 V, $t_d$ = 120 s, scan from 0.1 V to 0.7 V.<br>- A conditioning potential of 0.7 V during 15 s was applied between measurements.<br>- No stirring for the deposition step is needed.<br>- Voltammetric measurement combined with a high-throughput bath ultrasonic extraction and potential applicability to decentralized atmospheric pollution assessment in the case of dust samples. | [84,85] |
| AuNPs-MWCNTs/SPCE | Hg(II)<br>Pb(II) | SWASV | Tap water and river water | Hg(II): 0.2 μg $L^{-1}$<br>Simultaneous analysis:<br>Hg(II): 1.9 μg $L^{-1}$,<br>Pb(II): 2.0 μg $L^{-1}$ | Hg(II): 0.5 - 50 μg $L^{-1}$<br>Simultaneous analysis:<br>Hg(II): 2- 60 μg $L^{-1}$<br>Pb(II): 2- 100 μg $L^{-1}$ | - Modification of SPE MWCNTs, followed by electrolytical deposition of AuNPs.<br>- Comparison between an AuNPs-GO-SPCE and an AuNPs- SPAuE is performed.<br>- Competition between Pb(II) and Hg(II) for gold sites may be the main cause for higher LOD for Hg(II) in the simultaneous analysis than in the separate analysis of Hg(II).<br>- Measurements in a 0.1 mol $L^{-1}$ hydrochloric acid media.<br>- Hg(II): $E_d$ = 0.3 V, $t_d$ = 200 s, potential scan from 0.3 V to 0.5 V.<br>- Simultaneous analysis: $E_d$ = -0.5 V, $t_d$ = 120 s, potential scan from -0.5 V to 0.55 V. | [86] |
| RGO-Au/GC | Hg(II) | DCASV | Tap water | 0.12 μg $L^{-1}$ | 0.2 - 30 μg $L^{-1}$ | - A RGO-gold nanocomposite film is directly and homogeneously deposited on a GCE by one-step electrodeposition.<br>- Measurements in a 0.01 mol $L^{-1}$ hydrochloric acid media.<br>- $E_d$ = 0.3 V, $t_d$ = 600 s, scan from 0.2 V to 0.8 V (scan rate 250 mV $s^{-1}$).<br>- LOD below WHO guidelines for drinking water (5 nmol $L^{-1}$). | [87] |
| AuNEEs | As(III) | SWASV | Sea water | 5 ng $L^{-1}$ | 0.2 - 3 μg $L^{-1}$ | - The correct selection of ratio between the active and geometric area of the electrodes should improve the signal/background current ratio, further lowering LODs.<br>- Measurements in a 0.2 mol $L^{-1}$ hydrochloric acid / 62 mmol $L^{-1}$ hydrazine media.<br>- $E_d$ = -0.4 V, $t_d$ = 180 s, potential scan from -0.4 V to 0.45 V. | [88] |
| CNTs-AuNPs vibrating SPE | As(III) | LSASV | --- | 0.5 μg $L^{-1}$ | 10 - 550 μg $L^{-1}$ | - The novelty is the attachment of a vibrating motor to the SPE with the aim of avoiding external agitation of the solution.<br>- Commercial modified SPE (110 CNT–GNP by Dropsens) is used.<br>- Measurements in a 0.1 mol $L^{-1}$ sulphuric acid media.<br>- $E_d$ = -0.4 V, $t_d$ = 120 s, potential scan from -0.4 V to 0.0 V (scan rate 300 mV $s^{-1}$). | [89] |
| AuNPs-CB/SPE | As(III) | SWASV | Drinking water | 0.4 μg $L^{-1}$ | 2 -30 μg $L^{-1}$ | - Carbon black is presented as a sensitive and cost-effective | [90] |

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| | | | | | | alternative to CNTs to create a nanocomposite with the AuNPs.<br>- SPE was modified with a CB dispersion prior to AuNPs modification.<br>- Measurements in a 0.1 mol L$^{-1}$ hydrochloric acid/0.01% ascorbic acid media.<br>- $E_d$ = -0.4 V, $t_d$ = 300 s, potential scan from -0.3 V to 0.5 V.<br>- Regeneration step: a potential of 0.2 V along 10 s after each measurement. | |
| AuMWE | Zn(II)<br>Cu(II)<br>Pb(II)<br>Hg(II) | DPASV | Saline and fresh waters | Hg(II): 0.2 μg L$^{-1}$<br>Pb(II): 0.3 μg L$^{-1}$<br>Zn(II) and Cu(II): 0.4 μg L$^{-1}$ | --- | - Measurements in a 0.5 mol L$^{-1}$ sodium chloride/1 mol L$^{-1}$ hydrochloric acid media.<br>- $E_d$ = -1.0 V, $t_d$ = 32 s, scan from -0.8 V to -0.7 V (scan rate 80 mV s$^{-1}$).<br>- Vibrating working electrode during the deposition step.<br>- Oxygen is not removed during measurements.<br>- Between measurements a standby potential of 0.55 V is applied. | [91] |
| SPAuE | Cu(II)<br>Pb(II) | SWASV | Atmospheric depositions | < ng mL$^{-1}$ range | --- | - Measurements in a 0.1 mol L$^{-1}$ hydrochloric acid media.<br>- $E_d$ = -0.5 V, $t_d$ = 600 s, scan from -0.5 V to 0.5 V.<br>- Conditioning step: 0.5 V during 60 s is applied between measurements.<br>- Coupling of a semiautomatic measurement system to an atmospheric elemental fractionation sampler. | [92] |
| GS-Nafion-AuNPs/SPCE | Pb(II),<br>Cd(II) | DPASV | Water | Pb(II): 0.23 μg L$^{-1}$<br>Cd(II): 0.35 μg L$^{-1}$ | Pb(II): 0.5 - 60 μg L$^{-1}$<br>Cd(II): 0.8 - 50 μg L$^{-1}$ | - Electrode is prepared by dropping a GS-Nafion dispersion onto the surface of a SPCEs and subsequent electroless plating of AuNPs.<br>- Nafion is used to stabilize disperse GS into an aqueous solution.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH=4.5) media.<br>- $E_d$ = -1.3 V, $t_d$ = 240 s, potential scan from -1.1 V to -0.1 V. | [93] |
| AuNPs-CFs/Au | Pb(II)<br>Cu(II) | DPASV | --- | Pb(II): 1.1 μg L$^{-1}$<br>Cu(II): 0.06 μg L$^{-1}$ | --- | - The monodispersion of gold nanoparticles inside the carbon foam is performed by an emulsion polymerization and carbonization approach.<br>- AuNPs–CFs are bound onto the electrode surface using chitosan as a binder.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH=5.0) media.<br>- $E_d$ = -1.3 V, $t_d$ = 180 s, potential scan from -0.7 V to 0.6 V. | [94] |
| GNDs-encaged-porous AuE | Cu(II)<br>Pb(II) | SWV | --- | --- | Cu(II): 0.6 - 254 μg L$^{-1}$<br>Pb(II): 1.3 - 500 μg L$^{-1}$ | - Graphene nanodots-encaged porous gold electrodes are fabricated via ion beam sputtering deposition.<br>- The enhanced answer of these devices is due to the entrapped graphene nanodots in 3-D porous structure. | [95] |

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| AuNP-SWCNT/PETE | Pb(II)<br>Cu(II) | SWASV | --- | Pb(II): 0.546 μg $L^{-1}$<br>Cu(II): 0.613 μg $L^{-1}$ | 3.31 μg $L^{-1}$ to 22.29 μg $L^{-1}$ | - Measurements in an acetate buffer (pH=5) media.<br>- AuNPs are deposited electrochemically on SWCNT film applying CV scans.<br>- The SWCNT thin film is fabricated onto a flexible PET support using a vacuum filtration method. | [96] |
| AuFC-composite E | Cr(VI) | LSV | River water | 4.4 μg $L^{-1}$ | 20 - 2000 μg $L^{-1}$ | - Measurements in a 0.02 mol $L^{-1}$ hydrochloric acid media.<br>- $E_d$ = -0.4 V, $t_d$ = 150 s, potential scan from -0.6 V to 0.6 V.<br>- Regeneration step: a potential of 0.8 V along 30 s after each measurement in a 0.02 mol $L^{-1}$ hydrochloric acid media.<br>- Determination based on direct reduction of Cr(VI) to Cr(III) in highly acidic media.<br>- Scan from 0 V to 0.7 V (scan rate 50 mV $s^{-1}$).<br>- LOD in agreement with guideline values given by WHO and EPA for contaminated waters. | [97] |

SPAuE: screen-printed gold electrode; AuNPs/GCE: gold nanoparticles modified glassy carbon electrode; AuNPs/SPCE: gold nanoparticles modified screen printed carbon electrode; AuNPs-MWCNTs/SPCE: gold nanoparticles multiwallet carbon nanotubs modified screen-printed carbon electrode; RGO-Au/GCE: reduced graphene oxide gold nanocomposite modified glassy carbon electrode; AuNEEs: gold nanoelectrode ensembles; CNTs-AuNPs vibrating SPE: carbon nanotubs gold nanoparticles modofied vibrating screen-printed electrode; AuNPs-CB/SPE: gold nanoparticles carbon black modified screen-printed electrode; AuMWE: gold microwire electrode; GS-Nafion-AuNPs/SPCE: graphene sheets-Nafion-gold nanoparticles modified screen-printed carbon; AuNPs-CFs/Au: gold nanoparticles-doped carbon foam gold modified electrode; GNDs-encaged- porousAuE: graphene nanodots-encaged porous gold electrode; AuNP-SWCNT/PETE: gold nanoparticles patterned on single-walled carbon nanotube PET electrode; AuFC-composite E: gold film modified carbon composite electrode.

**Table 5.** Carbon based electrodes.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| GCE | Pb(II)<br>Cd(II) | SWASV | Poultry and bird game meat | LOQ < 10 ng g$^{-1}$ | 10 - 100 ng g$^{-1}$ (meat)<br>50 - 500 ng g$^{-1}$ (liver) | - Determination of metal ions after acidic digestion.<br>- Figures of merit established with reference materials. | [100] |
| MWCNTs/GCE<br>MWCNTs/PIGE | Pb(II) | DCV | --- | --- | 2 - 10 mg L$^{-1}$ | - Electrodes presented as an alternative to HMDE for metal ion determination.<br>- Measurements in an acetate buffer (pH 5) media.<br>- Potential scan from -0.7 V to -0.2 V, scan rate 25 mV s$^{-1}$. | [101] |
| MWCNTs-Nafion/GCE | Pb(II)<br>Cd(II) | ASV | Water | Pb(II): 0.1 μg L$^{-1}$<br>Cd(II): 0.15 μg L$^{-1}$ | --- | - MWCNTs/Nafion composite film electrode exhibited a synergistic effect for trace Pb(II) and Cd(II) detection with enhanced sensitivity and stability. | [102] |
| Graphene ultrathin film electrode | Pb(II) | SWASV | --- | 1.45 μg L$^{-1}$ | --- | - Comparison with a conventional diamond-like carbon electrode.<br>- A layer of Ni was created to act as a catalyst.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer/0.1 mol L$^{-1}$ $KNO_3$ (pH 5.3) media.<br>- $E_d$= -1.0 V, $t_d$ = 180 s, potential scan from -0.8 to 0.0 V.<br>- Pre-cleaning step: 0.2 V along 180 s before each measurement. | [103] |
| GO/GCE | Pb(II)<br>Cd(II) | DPASV | Rice, soya, milk, and tap water | Pb(II): 0.05 ng L$^{-1}$<br>Cd(II): 0.03 ng L$^{-1}$ | 0.4 ng L$^{-1}$ - 1 μg L$^{-1}$ | - GO covalently modified carbon electrode (GC-O-GO) surface shows very ultrasensitive response for these cations.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$= -1.0 V, $t_d$= 10 s, potential scan from -0.95 V to 0.05 V. | [104] |
| BDDE | Pb(II) | SWASV | Tap water | 0.3 μg L$^{-1}$ | 2 – 30 μg L$^{-1}$ | - Measurements in a 0.2 mol L$^{-1}$ potassium nitrate / 0.05 mol L$^{-1}$ nitric acid (pH 1.26) media.<br>- $E_d$= -1.3 V, $t_d$ = 600 s, potential scan from -0.8 to 0.0 V.<br>- Conditioning step: 0.6 V along 120 s prior to next measurement. | [107] |
| BDDE | Cd(II)<br>Pb(II)<br>Cu(II)<br>Hg(II) | DPASV | Waste water | Cd(II): 3.5 μg L$^{-1}$<br>Pb(II): 2.0 μg L$^{-1}$<br>Cu(II): 0.1 μg L$^{-1}$<br>Hg(II): 0.7 μg L$^{-1}$ | --- | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 6.0) media.<br>- $E_d$ = -1.5 V, $t_d$ = 300 s, potential scan from -1.5 V to 0.6 V, scan rate 50 mV s$^{-1}$. | [108] |
| BDDE | Zn(II) | DPASV | Environm | 0.03 μg L$^{-1}$ | 0.033 - 327 μg L$^{-1}$ | - Commercial BDDE (Windsor Scientific Ltd.). | [109] |

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| | | | ental rubber industry samples | | | - Measurements in a 0.1 mol $L^{-1}$ potassium chloride media.<br>- $E_d$= -1.7 V, $t_d$= 120 s, potential scan from -1.7 V to -0.85 V. | |
| EPPGE, BDDE, SPCE | Sb(III) | DPASV | --- | 0.47 µg $L^{-1}$ (EPPG) | --- | - Comparison study of unmodified non-classical carbon electrodes. | [110] |
| BD-NCDE | Pb(II)<br>Cu(II)<br>Hg(II) | DPASV/SWASV | --- | Pb(II): 290 µg $L^{-1}$<br>Cu(II): 7 µg $L^{-1}$<br>Hg(II): 134 µg $L^{-1}$ | Pb(II): 0.2 - 4.6 mg $L^{-1}$<br>Cu(II): 0.06- 1.4 mg $L^{-1}$<br>Hg(II): 0.2 - 2 mg $L^{-1}$ | - BD-NCDE pretreated via electrochemical dynamic polarization by applying incremental voltage anodically and cathodically alternately to improve its electrochemical properties.<br>- The BDD film is formed on the surface of a Ti substrate.<br>- Measurements in a 0.2 mol $L^{-1}$ acetate buffer (pH 5) media.<br>- $E_d$= -1.5 V, $t_d$= 300 s, potential scan from -0.6 V to 0.6 V. | [111] |
| BD-NDE | Pb(II) | SWASV | Mineral and river water | Pb(II): 0.57 µg $L^{-1}$ | 1 – 10 µg $L^{-1}$ | - Measurements in an ammonium acetate buffer (pH 4.5) media.<br>- $E_d$= -1.0 V, $t_d$ = 60 s, potential scan from -0.8 to 0.0 V.<br>- Conditioning step: 0.9 V along 45 s before each measurement. | [112] |
| $NH_3$-plasma-MWCNTs | Zn(II)<br>Cd(II)<br>Cu(II)<br>Hg(II) | SWASV | Water | Zn(II): 0.02 µg $L^{-1}$<br>Cd(II): 0.03 µg $L^{-1}$<br>Cu(II): 0.014 µg $L^{-1}$<br>Hg(II): 0.029 µg $L^{-1}$ | Zn(II): 13 - 183 µg $L^{-1}$<br>Cd(II): 0.28 - 2.5 µg $L^{-1}$<br>Cu(II): 12 - 178 µg $L^{-1}$<br>Hg(II): 4 - 120 µg $L^{-1}$ | - $NH_3$ plasma was used to introduce $NH_2$ groups onto the surface of MWCNTs<br>- Measurements in a 0.1 mol $L^{-1}$ ammonium buffer media.<br>- $E_d$ = −1.3 V, $t_d$ = 150 s, potential scan from -1.3 to 0.6 V.<br>- LODS lower than the guideline values in drinking water given by the WHO. | [113] |

MWCNTs/GCE: multi-walled carbon nanotubes glassy carbon electrode; MWCNTs/PIGE: multi-walled carbon nanotubes paraffin impregnated glassy carbon electrode; MWCNTs-Nafion/GCE: multi-walled carbon nanotubes Nafion modified glassy carbon electrode; GO/GCE: graphene oxide modified glassy carbon electrode; BDDE: boron doped diamond electrode; EPPGE: edge plane pyrolytic graphite electrode; SPCE: screen-printed carbon electrode; Bd-NCDE: boron-doped nanocrystalline diamond electrode; $NH_3$-plasma-MWCNTs: $NH_3$-plasmamultiwallet carbon nanotubs modified electrode.

**Table 6.** Bismuth based electrodes.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| BiE | Pb(II)<br>Cd(II)<br>Zn(II) | SWASV | River water | Pb(II): 93 ng L$^{-1}$<br>Cd(II): 54 ng L$^{-1}$<br>Zn(II): 396 ng L$^{-1}$ | 10 - 100 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 5) media.<br>- $E_d$ = -1.4 V, $t_d$ = 180 s, potential scan from -1.4 V to -0.35 V. | [114] |
| BiRDE | Pb(II)<br>Cd(II)<br>Zn(II) | SWASV | Rainwater and sewage sludge (only Pb(II)) | Pb(II): 5.85 μg L$^{-1}$<br>Cd(II): 5.64 μg L$^{-1}$<br>Zn(II): 59.1 μg L$^{-1}$ | Pb(II) and Cd(II): 10 - 160 μg L$^{-1}$<br>Zn(II): 50 - 800 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- Zn(II): $E_d$ = -1.4 V, $t_d$ = 60 s, potential scan from -1.4 V to -0.3 V.<br>- Pb(II), Cd(II): $E_d$ = -1.0 V, $t_d$ = 120 s, potential scan from -1.0 V to -0.3 V. | [115] |
| BiRDE | Zn(II) | SWASV | Rain and tap water, urine | 8.1 μg L$^{-1}$ | 20 - 160 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ phosphate buffer (pH 7.5) media.<br>- $E_d$ = -1.4 V, $t_d$ = 120 s, potential scan from -1.4 V to -0.3 V. | [116] |
| Bi-CE | Pb(II),<br>Cd(II),<br>Zn(II) | SWASV | Drinking water | --- | --- | - Different Bi-modified carbon surfaces (GC, CP, and G pencil) are considered.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 3.5) media.<br>- $E_d$ = -1.4 V, potential scan from -1.5 V to 0.0 V. | [117] |
| *ex-situ* BiFE | Ni(II) | SWAdSV | Certified and lake water | 0.1 μg L$^{-1}$ | 10.0 - 70.0 μg L$^{-1}$ | - 1-Nitroso-2-napthol as chelating agent (6.5 μmol L$^{-1}$).<br>- Measurements in a 0.10 mol L$^{-1}$ Britton-Robinson buffer (pH 7.5) media.<br>- $E_d$ = -0.30 V, $t_d$ = 60 s, potential scan from -0.3 V to -1.2 V. | [118] |
| *ex-situ* BiSPCE | Sb(III) | DPAdSV | Groundwater | 1.2 μg L$^{-1}$ | up to 100.0 μg L$^{-1}$ | - Quercetin-5'-sulfonic acid as chelating agent.<br>- Measurements in an acetate buffer (pH 4.6) media.<br>- $E_d$ = -0.5 V, $t_d$ = 60 s, potential scan from -0.5 V to -1.1 V.<br>- Conditioning step: -1.1 V along 3 s is applied between measurements. | [119] |
| Bi-C tapeE | Pb(II) | SWASV | Toys | 2 μg L$^{-1}$ | 10 - 500 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- Pb(II), Cd(II), Zn(II) can be differentiated in a sample volume of 15 μL.<br>- For Pb(II) analysis: $E_d$ = -1.5 V, $t_d$ = 300 s, potential scan from -1.5 to 0.1 V. | [120] |
| $BiF_4$-CPE | Pb(II)<br>Cd(II) | SWASV | Water | Pb(II): 93 μg L$^{-1}$<br>Cd(II): 54 μg L$^{-1}$<br>($t_d$=240 s) | | - Favorable performance in acidic solutions (pH 0.5 - 2.5) in the presence of dissolved oxygen.<br>- $E_d$ = -1.0 V, $t_d$ = 120 s, potential scan from -1.0 V to -0.2 V. | [121] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *In-situ* Bi-porousSPCE | Pb(II)<br>Cd(II) | SWASV | River | Pb(II): 0.03 μg L$^{-1}$<br>Cd(II): 0.34 μg L$^{-1}$ | Pb(II): 1 - 30 μg L$^{-1}$<br>Cd(II): 0.05 - 30 μg L$^{-1}$ | - Measurements in an acetate buffer (pH 4.5) media.<br>- E$_d$ = -1.2 V, t$_d$ = 300 s, potential scan from -1.0 V to -0.45 V. | [122] |
| *In-situ* Bi-GO/GCE | Zn(II)<br>Cd(II)<br>Pb(II) | DPASV | Tap water | Zn(II): 1.80 μg L$^{-1}$<br>Cd(II): 0.18 μg L$^{-1}$<br>Pb(II): 0.11 μg L$^{-1}$ | 1 - 100 μg L$^{-1}$ | - Direct electrochemical reduction of GO on the GCE.<br>- Measurements in a 0.1 mol $^{-1}$ acetate buffer (pH 4.5) media.<br>- E$_d$ = -1.4 V, t$_d$ = 300 s, potential scan from -1.4 V to 0 V.<br>- Conditioning step: Prior to the next cycle, 0.3 V along 60 s in fresh supporting electrolyte. | [123] |
| *In-situ* Bi-SbFGCE | Cd(II) | SWASV | Tap water | 0.15 μg L$^{-1}$ | 1.0 - 220 μg L$^{-1}$ | - Measurements in a hydrochloric acid (pH 2.0) media.<br>- E$_d$ = -1.3 V, t$_d$ = 210 s, potential scan from -1.2 V to 0.2 V.<br>- A cleaning step (0.3 V along 30 s) is done after each measurement. | [124] |
| *In-situ* Sn-BiFGCE | Cd(II)<br>Zn(II) | DPASV | Tap water | Zn(II): 0.31 μg L$^{-1}$,<br>Cd(II): 0.86 μg L$^{-1}$ | 2 - 80 μg L$^{-1}$ | - Measurements in an acetate buffer (pH 4.7) media.<br>- E$_d$=-1.4 V, t$_d$=270 s, potential scan from -1.4 V to 0 V. | [125] |
| BiNPs/GCE | Pb(II)<br>Cd(II) | SWASV | Water | Pb(II): 0.8 μg L$^{-1}$<br>Cd(II): 0.4 μg L$^{-1}$ | 5.0 - 60.0 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- E$_d$ = -1.2 V, t$_d$ = 120 s, potential scan from -1.1 to -0.4 V. | [126] |
| BiNPs/AgPE | Pb(II)<br>Cd(II)<br>Zn(II) | --- | Drinking and river waters | 0.1 μg L$^{-1}$ | --- | --- | [127] |
| BiNPs-NPC-GS/GCE | Pb(II)<br>Cd(II)<br>Tl(I) | SWASV | Lake and tap water | Pb(II): 0.66 μg L$^{-1}$<br>Cd(II): 0.46 μg L$^{-1}$ | Pb(II): 12 - 124 μg L$^{-1}$<br>Cd(II): 9 - 90 μg L$^{-1}$ | --- | [128] |
| RGO-BiNPs/CPE | Pb(II)<br>Cd(II)<br>Zn(II)<br>Cu(II) | DPASV | --- | Cd(II): 2.8 μg L$^{-1}$<br>Pb(II): 0.55 μg L$^{-1}$<br>Zn(II): 17 μg L$^{-1}$<br>Cu(II): 26 μg L$^{-1}$ | --- | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer media.<br>- Cd(II) and Pb(II): E$_d$ = -1.05 V, potential scan from -0.9 to -0.35 V.<br>- Zn(II): E$_d$ = -1.25 V, potential scan from -1.25 to -0.8 V.<br>- Cu(II): E$_d$ = -0.6 V, potential scan from -0.6 to -0.07 V. | [129] |
| *in situ* Bi-ERGO/SPE | Pb(II)<br>Cd(II) | SWASV | Milk samples | Cd(II): 0.5 μg L$^{-1}$<br>Pb(II): 0.8 μg L$^{-1}$ | 1.0 - 60.0 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer media.<br>- E$_d$ = -1.2 V, t$_d$ = 150 s, potential scan from -1.2 to -0.3 V.<br>- Conditioning step: 0 V along 60 s after each measurement. | [130] |
| *in-situ* BiF-ERGO/PCE | Pb(II)<br>Cd(II)<br>Zn(II) | SWASV | Tap water | Zn(II): 0.19 μg L$^{-1}$<br>Cd(II): 0.09 μg L$^{-1}$<br>Pb(II): 0.12 μg L$^{-1}$ | --- | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.6) media.<br>- E$_d$ = -1.4 V, t$_d$ = 120 s, potential scan from -1.4 to 0.3 V.<br>- A cleaning step (0.3 V along 30 s) is applied after each measurement.<br>- LODs below the EPA values prescribed for drinking water. | [131] |
| *in-situ* BiF- | Pb(II), | DPASV | Tap water | Cd(II): 1.5 μg L$^{-1}$ | Two linear ranges, | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) | [135] |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| NMC-NA/ GCE | Cd(II) |  |  | Pb(II): 0.05 µg L$^{-1}$ | Cd(II): 2 - 10 µg L$^{-1}$ and 10 - 100 µg L$^{-1}$ Pb(II): 0.5 - 10 µg L$^{-1}$ and 10 - 100 µg L$^{-1}$ | media.<br>- $E_d$ = -1.2 V, $t_d$ = 150 s, potential scan from -1.0 to 0.0 V.<br>-LODs lower than the guideline values of drinking water given by WHO. |  |
| *ex-situ* Bi-CNTsNafion-/CPE | Pb(II)<br>Cd(II)<br>Zn(II) | ASV | Tap and lake water | Zn(II): 17.3 µg L$^{-1}$<br>Cd(II): 16.9 µg L$^{-1}$<br>Pb(II): 11.9 µg L$^{-1}$ |  | - Measurements in a sodium acetate (pH 6.5) media.<br>- $E_d$ = -1.25 V, $t_d$ = 300 s, potential scan from -1.25 V to -0.35 V. | [136] |
| *In-situ* Bi-GO-MWCNTs-Nafion/GCE | Pb(II)<br>Cd(II) | DPASV | Electroplating effluents | Pb(II): 0.2 µg L$^{-1}$<br>Cd(II): 0.1 µg L$^{-1}$ | 0.5 - 30 µg L$^{-1}$ | - Nafion was considered to improve film stability and anions-resistant permselectivity.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$ = -1.4 V, $t_d$ = 10 s (static conditions), potential scan from -1.4 V to 0.4 V.<br>- Conditioning step: 0.4 V along 60 s before each measurement. | [137] |
| Nafion-Bi-PPF/alumina E | Pb(II)<br>Cd(II)<br>Zn(II) | SWASV | Tap and river water | Pb(II): 0.33 µg L$^{-1}$<br>Cd(II): 0.55 µg L$^{-1}$<br>Zn(II): 0.63 µg L$^{-1}$ | 1 - 10 µg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$ = -1.3 V, $t_d$ = 120 s, potential scan from -1.3 V to 0.2 V. | [138] |
| Nafion-Bi-PPF/alumina E | Pb(II)<br>Cd(II)<br>Zn(II) | SWASV | --- | Pb(II): 0.62 µg L$^{-1}$<br>Cd(II): 0.72 µg L$^{-1}$<br>Zn(II): 1.57 µg L$^{-1}$ | --- | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media. | [139] |
| *In situ* Bi-PPCE | Ni(II) | SWAdSV | Spring water | 20 ng L$^{-1}$ | --- | - Ni(II) can be determined even in the presence of Co(II).<br>- Ligand considered: dimethylglioxime.<br>- Measurements in a 0.1 mol L$^{-1}$ ammonium buffer and 0.01 mol L$^{-1}$ tartrate media.<br>- Two-step protocol:<br>*In situ* Bi deposition: $E_d$ = -1.1 V, $t_d$ = 60 s.<br>Complex deposition: $E_d$ = -0.8 V, $t_d$ = 120 s, potential scan from -0.8 V to -1.3 V.<br>- Conditioning step: 120 s at 0.5 V. | [140] |
| *Ex situ* Bi-PPCE | Cr(VI) | SWAdSV | Waste and tap water | 0.2 µg L$^{-1}$ | 5 – 25 µg L$^{-1}$ | - Ligand considered: pyrocatechol violet.<br>- Measurements in a 0.1 mol L$^{-1}$ sodium nitrate and 0.o1 mol L$^{-1}$ acetate buffer (pH 6) media.<br>- $E_d$ = -0.2 V, $t_d$ = 60 s, potential scan from –0.2 V to -1.2 V.<br>- Conditioning step: 20 s at -1.4 V. | [141] |
| *In-situ* Bi-GPSS/ SPE | Pb(II)<br>Cd(II) | DPASV | Deionized, lake and tap water | Cd(II): 0.042 µg L$^{-1}$<br>Pb(II): 0.089 µg L$^{-1}$ | 0.5 - 120 µg L$^{-1}$ | - The SPE surface is modified by addition of a suspension of graphene and PSS and the subsequent evaporation of the solvent at room temperature. | [142] |

- Measurements in a 0.1 mol $L^{-1}$ acetate buffer (pH 4.5) media.
- $E_d$ = -1.3 V, $t_d$ = 120 s, potential scan from -1.15 to -0.35 V.
- A cleaning step (0.8 V along 30 s) is applied after each measurement.

BiE: bismuth electrode; BiRDE: bismuth rotating disk electrode; Bi-CE: bismuth modified carbon electrodes; *ex-situ* BiFE: *ex-situ* bismuth film electrode; Bi-C tape: bismuth carbon tape electrode; $BiF_4$-CPE: tetrafluorobismuthate modified carbon paste electrode; *in-situ* Bi-porousSPCE: *in-situ* bismuth porous screen-printed carbon electrode; *in-situ* Bi-SbFGCE: *in-situ* bismuth-antimony film glassy carbon electrode; *in-situ* Sn-BiFGCE: *in-situ* stannum-bismuth composite film glassy carbon electrode; BiNPs/GCE: bismuth nanoparticles modified glassy carbon electrode; BiNPs/AgPE: bismuth nanoparticles modified silver paste electrode; BiNPs-NPC-GS/GCE: bismuth-nanoparticles enriched nano-porous carbon on graphene sheet modifie glassy carbon electrode; RGO-BiNPs/CPE: reduced graphene oxide bismuth nanoparticle modified carbon paste electrode; *in situ* Bi-ERGO/SPE: *in-situ* bismuth film electrochemical reduced graphene oxide modified screen printed electrode; *in-situ* BiF-ERGNO/PCE: *in-situ* bismuth-film electrochemically reduced graphene oxide modified pencil-graphite electrode; *in-situ* BiF-NMC-NA/GCE: *in-situ* bismuth film nitrogen-doped microporous carbon Nafion modified glassy carbon electrode; *ex-situ* Bi-CNTsNA/CPE: *ex-situ* bismuth film carbon nanotubs Nafion modified carbon paste electrode; *in-situ* Bi-GO-MWCNTs-Nafion/GCE: in-situ bismuth film graphene oxide multiwallet carbon nanotubs Nafion modified glassy carbon electrode; Nafion-Bi-PPF/alumina E: bismuth film on pyrolyzed photoresist alumina electrode modified with Nafion; *in situ* Bi-PPCE: *in-situ* bismuth modified pyrolyzed photoresist electrode; *ex situ* Bi-PPCE: *ex-situ* bismuth modified pyrolyzed photoresist electrode; *in-situ* Bi-GPSS/SPE: i*n-situ* bismuth graphene-poly(sodium 4-styrenesulfonate) composite film screen printed electrode.

**Table 7.** Antimony based electrodes.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| *In-situ* SbSPCE | Cd(II)<br>Pb(II)<br>Cu(II) | DPASV | Groundwater | Cd(II): 3.4 µg L$^{-1}$<br>Pb(II): 5.0 µg L$^{-1}$<br>Cu(II): 1.6 µg L$^{-1}$ | Cd(II): 115.5 - 72.4 µg L$^{-1}$<br>Pb(II): 16.8 - 62.6 µg L$^{-1}$<br>Cu(II): 5.3 - 99.8 µg L$^{-1}$ | - Measurements in a 0.01 mol L$^{-1}$ acetate buffer (pH 4.5) and 0.01 mol L$^{-1}$ KNO$_3$.<br>- E$_d$ = -1.2 V, t$_d$ =-120 s, potential scan from -1.2 V to 0.2 V. | [144] |
| *In-situ* Sb-NaMM/CPE | Cd(II) | SWASV | Tap water | Cd(II): 0.25 ng L$^{-1}$ | 4 - 150 µg L$^{-1}$ | - The chemically modified CPE is prepared by mixing NaMM, graphite powder, and paraffin oil in the presence of ethanol in a mortar. After ethanol evaporation, the CP is packed into a piston-driven CPE Shell.<br>- Mesuraments in a hydrochloric acid (pH 3) media.<br>- E$_d$ = -1.2 V, t$_d$ =-260 s, potential scan from -1.2 V to 0.2 V. | [145] |
| *In-situ* Sb-CNF/SPCE | Pb(II)<br>Cd(II) | DPASV | Estuarine water | Pb(II): 2.1 µg L$^{-1}$<br>Cd(II): 1.1 µg L$^{-1}$ | Pb(II): 6.9 - 100.9 µg L$^{-1}$<br>Cd(II): 3.7 - 100.3 µg L$^{-1}$ | - Modifications are performed in a commercial SPCE.<br>- Mesuraments in a 0.01 mol L$^{-1}$ hydrochloric acid media.<br>- E$_d$ = -1.5 V, t$_d$ = 120 s, potential scan from -1.5 V to -0.15 V. | [146] |
| *Ex-situ* SbSPCE | Ni(II) | DPAdSV | Wastewater | 0.9 µg L$^{-1}$ | 3.1 - 197 µg L$^{-1}$ | - Dimethylglyoxime as chelating agent (5 10$^{-5}$ mol L$^{-1}$).<br>- Mesuraments in a 0.1 mol L$^{-1}$ ammonia buffer (pH 9.2) media.<br>- E$_d$ = -0.7 V, t$_d$ = 120 s, potential scan from -0.7 V to -1.25 V.<br>- Cleaning step: -1.25 V along 30 s before each measurement. | [147] |
| *In-situ* SbGCE | Ce(III)<br>La(III)<br>Pr(III) | AdSV | Tap water | Ce(III): 0.06 µg L$^{-1}$<br>La(III): 0.42 µg L$^{-1}$<br>Pr(III): 0.71 µg L$^{-1}$ | 1 - 25 µg L$^{-1}$ | - Alizarin as chelating agent (10$^{-6}$ mol L$^{-1}$).<br>- Mesuraments in an acetate buffer (pH 5.8) media.<br>- E$_d$ = -0.1 V, t$_d$ = 360 s, potential scan from -0.2 V to 1.1 V. | [148] |
| SbNPs-RGO/GCE | Pd(II)<br>Pt(II)<br>Rh(III) | DPAdSV | Dust | Pd(II): 0.45 pg L$^{-1}$<br>Pt(II): 0.49 pg L$^{-1}$<br>Rh(III): 0.49 pg L$^{-1}$ | 40 - 400 pg L$^{-1}$ | - Dimethylglyoxime as chelating agent (10$^{-5}$ mol L$^{-1}$).<br>- Mesuraments in a 0.2 mol L$^{-1}$ sodium acetate (pH 5.2) media.<br>- E$_d$ = -1.2 V, t$_d$ = 120 s. | [149] |
| *Ex-situ* SbSPCE | Pd(II) | DPAdSV | Spiked tap water | 2.7 µg L$^{-1}$ | 1 - 100 µg L$^{-1}$ | - Dimethilglyoxime as chelating agent (2 10$^{-4}$ mol L$^{-1}$).<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- E$_d$ = -0.6 V, t$_d$ = 180 s, potential scan from -0.5 V to -1.2 V.<br>- Conditioning step: -1.0 V along 30s before each measurement. | [150] |

*In-situ* SbSPCE: *in-situ* antimony modified screen-printed carbon electrode; *in-situ* Sb-NaMM/CPE: *in-situ* antimony film sodium montmorillonite modified carbon paste electrode; *in-situ* Sb-CNF/SPCE: *in-situ* antimony film carbon nanofiber modified screen-printed carbon electrode; *in-situ* SbGCE: *in-situ* antimony modified glassy carbon electrode; SbNPs-RGO/GCE: antimony nanoparticles reduced graphene oxide modified glassy carbon electrode; *ex-situ* SbSPCE: *ex-situ* antimony modified screen-printed carbon electrode.

**Table 8.** Miscellaneous material based electrodes.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| CuGCE | Pb(II)<br>Hg(II) | SWASV | --- | Pb(II): 0.06 μg L$^{-1}$<br>Hg(II): 0.1 μg L$^{-1}$<br>(t$_d$ = 300 s) | Pb(II): 5 - 70 μg L$^{-1}$<br>Hg(II): 10 - 100 μg L$^{-1}$<br>(t$_d$ = 120 s) | - Measurements in a 0.1 mol L$^{-1}$ hydrochloric acid / 0.4 mol L$^{-1}$ sodium chloride media.<br>- E$_d$ = -0.6 V, t$_d$ = 120 s, potential scan from -0.6 V to 0.15 V.<br>- Cleaning step: 0.4 V along 30 s before each measurement. | [151] |
| SPCuE | Zn(II) | ASV | Blood serum | 9.0 μg L$^{-1}$ | until 325 μg L$^{-1}$ | - Fabricated using a combination of lithographic and deposition onto glass slides.<br>- Measurement in a 0.1 mol L$^{-1}$ acetate buffer (pH 6) media.<br>- E$_d$ = -1.0 V, t$_d$ = 300 s, potential scan from -1.0 V to -0.3 V. | [152] |
| Ce-ZCPME | Cd(II)<br>Pb(II) | SWASV | --- | Cd(II): 0.07 μg L$^{-1}$<br>Pb(II): 0.46 μg L$^{-1}$ | --- | - In-house fabricated electrode.<br>- Ce-impregnated zeolites are prepared from a Ce(III) ethanolic solution and zeolite. The formed slurry is dried and calcined.<br>- The CPEs is prepared by mixing the carbon graphite, the Ce-zeolite and paraffin oil.<br>- Measurements in a 0.1 mol L$^{-1}$ phosphate buffer (pH 4) media.<br>- E$_d$ = -1.2 V, t$_d$ = 120 s, potential scan from -1.6 V to 0.0 V. | [153] |
| SnNPs-RGO/GCSE | Pb(II)<br>Cd(II)<br>Cu(II) | SWASV | Tap water | Cd(II): 0.07 μg L$^{-1}$<br>Pb(II): 0.12 μg L$^{-1}$<br>Cu(II): 0.03 μg L$^{-1}$ | 1 - 100 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 5) media.<br>- E$_d$ = -1.0 V, t$_d$ = 150 s, potential scan from -1.0 V to -0.2 V.<br>- LODs below values stipulated by WHO. | [154] |
| NiNPs-CPM/GCE | Hg(II) | DPV | Fish | 0.42 μg L$^{-1}$ | Until 10 mg L$^{-1}$ | - Measurement in a 0.05 mol L$^{-1}$ acetate buffer (pH 5.0) media.<br>- Potential scan from -0.2 V to 0.6 V. | [155] |
| Sn-Pb-MPC/GCE | Cd(II) | SWASV | River water | 0.36 μg L$^{-1}$ | 0 - 140 μg L$^{-1}$ | - Measurement in a 0.1 mol L$^{-1}$ acetate buffer and 0.1 mol L$^{-1}$ potassium chloride (pH = 6) media.<br>- E$_d$ = -1.4 V, t$_d$ = 360 s, potential scan from -1.0 to -0.7 V. | [156] |
| RGO-Fe$_3$O$_4$/GCE | Pb(II) | SWASV | Soils | 1.2 μg L$^{-1}$ | 41.5 - 600 μg L$^{-1}$ | - Measurements in 0.1 mol L$^{-1}$ acetate buffer media.<br>- E$_d$ = -1.0 V, t$_d$ = 120 s, potential scan from -1.0 to 0.0 V. | [157] |
| α-Fe$_2$O$_3$/GCE | Pb(II) | SWASV | --- | --- | --- | - Comparison of different α-Fe$_2$O$_3$ structures: nanocubes, nanoplates and nanorods.<br>- Measurements in 0.1 mol L$^{-1}$ acetate buffer (pH 5.0) media.<br>- E$_d$ = -1.2 V, t$_d$ = 120 s.<br>- Devices meet the requirements of WHO for lead in drinking water (10 μg L$^{-1}$). | [158] |
| AlOOH-RGO/GCE | Pb(II)<br>Cd(II) | SWASV | Drinking water | Cd(II): 0.004 μg L$^{-1}$<br>Pb(II): 0.07 μg L$^{-1}$ | Cd(II): 22.5 - 90 μg L$^{-1}$<br>Pb(II): 41.5 - 166 μg L$^{-1}$ | - Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 6.0) media.<br>- E$_d$= -1.2 V, t$_d$ = 120 s, potential scan from -1.0 to 0.4 V.<br>- Regeneration step: 0.3 V along 140 s after each measurement in fresh supporting electrolyte. | [150] |

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| MgO-nanoflowers /GCE | Pb(II)<br>Cd(II) | SWASV | Reservoir water | Cd(II): 9 ng $L^{-1}$<br>Pb(II): 0.4 ng $L^{-1}$ | Cd(II): 4.5 - 16 μg $L^{-1}$<br>Pb(II): 0.66 - 4.4 μg $L^{-1}$ | - A homogeneous MgO nanoflowers/Nafion suspension is pipetted onto the surface of GCE.<br>- Measurements in a 0.1 mol $L^{-1}$ acetate buffer media.<br>- $E_d$ = -0.8 V, $t_d$ = 120 s, scan potential from -1.4 V to 0.4 V | [160] |
| NiO-nanosheets/ GCE | Hg(II) | DPV | --- | 8 μg $L^{-1}$ | 160 μg $L^{-1}$ - 100 mg $L^{-1}$ | - Mesoporous NiO nanosheets dissolved in chitosan are dropped onto the surface of a GCE<br>- Measurements in a phosphate buffer (pH 6.0) media. | [161] |
| CoO/EGrE | Cu(II) | SWASV | Water | 94 μg $L^{-1}$ | --- | - $E_d$ -0.5 V | [162] |
| $MnO_2$-carbon composites /GCE | Cd(II)<br>Pb(II) | ASV | --- | Pb(II): 5.6 μg $L^{-1}$<br>Cd(II): 5.8 μg $L^{-1}$ | --- | - $MnO_2$ with different carbonaceous materials is considered.<br>- Measurements in 0.020 mol $L^{-1}$ sulphuric acid 0.030 mol $L^{-1}$ potassium chloride media.<br>- Ed = -1.3 V, td = 120 s, potential scan from -1.3 V to 0.6 V. | [163] |
| $ZrO_2$-$TiO_2$/CPE | In(III) | SWASV | --- | ---- | --- | - Determination of In(III) in the presence of Pb(II). | [164] |
| $ZrO_2$-$TiO_2$/CPE | Cd(II)<br>Pb(II) | CV | --- | Cd(II): 1.2 mg $L^{-1}$<br>Pb(II): 1.6 mg $L^{-1}$ | Cd(II): 5.6 - 1120 mg $L^{-1}$<br>Pb(II): 2 - 2010 mg $L^{-1}$ | - Work devoted to the preparation of the electrode. | [165] |
| Mg-Al LDHs/GCE | Cd(II) | SWASV | Reservoir water | 0.02 μg $L^{-1}$ ($t_d$ 120s)<br>0.6 ng $L^{-1}$ ($t_d$ 30 min) | 11 – 112 μg $L^{-1}$ ($t_d$ 120s)<br>2.24 - 6.7 μg $L^{-1}$ ($t_d$ 30 min) | - Nafion is used as binder of Mg–Al LDHs with electrode surface.<br>- Measurements in a 0.1 mol $L^{-1}$ phosphate buffer (pH 5.0) media.<br>- $E_d$ = -1.4 V, $t_d$ = 120 s (or 30 min), potential scan from -1.0 V to -0.6 V. | [166] |
| 3C-SiCFE | Cu(II)<br>Ag(I) | DPASV | --- | Cu(II): 0.006 μg $L^{-1}$<br>Ag(I): 0.004 μg $L^{-1}$ | 0.01 - 1.0 μg $L^{-1}$ | - Analyzed separately.<br>- $E_d$ = -0.4 V for Cu(II) and 0 V for Ag(I), $t_d$ = 180 s<br>- Cleaning step: 0.6 V for at least 8 min after each measurement. | [167] |
| $MgSiO_3$ hollow spheres /GCE | Cd(II)<br>Pb(II)<br>Cu(II)<br>Hg(II) | SWASV | Water | Cd(II): 0.02 μg $L^{-1}$<br>Pb(II): 0.06 μg $L^{-1}$<br>Cu(II): 0.006 μg $L^{-1}$<br>Hg(II): 0.030 μg $L^{-1}$ | Cd(II): 11 - 110 μg $L^{-1}$<br>Pb(II): 20 - 200 μg $L^{-1}$<br>Cu(II): 6 - 63 μg $L^{-1}$<br>Hg(II): 20 - 200 μg $L^{-1}$ | - Nafion is used as binder of $MgSiO_3$ hollow spheres and the electrode surface.<br>- Measurements in 0.1 mol $L^{-1}$ acetate buffer (pH 5.0) media.<br>- $E_d$ = 1.4 V, $t_d$ = 180 s, potential scan from -1.4 V to 0.5 V.<br>- LODs much lower than the guideline values in drinking water given by WHO. | [168] |

CuGCE copper film modified glassy carbon electrode; SPCuE: screen-printed copper electrode; Ce-ZCPME: Cerium-incorporated zeolite modified carbon paste electrode; SnNP-RGO/GCSE: tin nanoparticles reduced graphene oxide modified glassy carbon sheet electrode; NiNPs-CPM/GCE: nickel nanoparticles carbon porous material modified glassy carbon electrodes; Sn-Pb-MPC/GCE: tin and lead hybrid nanoparticles mesoporous carbon modified glassy carbon electrode; RGO-$Fe_3O_4$ /GCE: reduced graphene iron oxide nanocomposite modified glassy carbon electrode; α-$Fe_2O_3$/GCE: α-$Fe_2O_3$ nanostructures modified glassy carbon electrode; AlOOH-RGO/GCE: aluminium oxide reduced graphene modified glassy carbon electrode; MgO-nanoflowers/GCE: magnesium oxide nanoflower modified glassy carbon electrode; NiO-nanosheets/GCE: nickel oxide-nanosheets modified glassy carbon electrode; CoO/EGrE: cobalt oxide modified exfoliated graphite electrode; $MnO_2$-carbon composite/GCE: manganese oxide carbon composite glassy carbon electrode; glassy carbon electrode NiO-nanosheets/GCE: nickel oxide-nanosheets modified glassy carbon electrode; CoO/EGrE: cobalt oxide modified exfoliated graphite electrode; Mg-Al LDH/GCE: magnesium and aluminium layered double hydroxides modified glassy carbon electrode; $ZrO_2$-$TiO_2$/CPE: zirconium dioxide titanium dioxide modified carbon paste electrode; 3C-SiCFE: cubic silicon carbide film electrode; $MgSiO_3$ hollow spheres/GCE: hollow spheres of $MgSiO_3$ modified the glassy carbon electrode.

**Table 9.** Electrodes modified with molecules.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| EDTA-CN-NS-Nafion/GCE | Pb(II) | DPASV | Water | 0.12 ng L$^{-1}$ | two linear ranges:<br>0.4 ng L$^{-1}$ - 0.23 µg L$^{-1}$<br>0.23 - 343 µg L$^{-1}$ | - EDTA is covalently immobilized onto CN-NS using N-(trimethoxysilylpropyl) ethylene-diamine triacetic acid sodium salt as a coupling reagent.<br>- GCE is modified by dropping a mixture of EDTA-CN-NS and Nafion onto the electrode surface.<br>- Measurement in a phosphate buffer media.<br>- $E_d$ = -0.6 V, $t_d$ = 350 s, potential scan from -0.9 V to -0.2 V. | [169] |
| MTU-GO-AuNPs/ITOE | Hg(II) | DPV | Tap, bottled and lake waters | 0.16 µg L$^{-1}$ | 1 - 22 µg L$^{-1}$ | - MTU is dropped on the electrodes surface of the modified GO-AuNPs /ITO electrode.<br>- MTU is fixed on the surface via strong S–Au interactions.<br>- Measurement in a 0.2 mol L$^{-1}$ phosphate buffer (pH 1) media.<br>- A previous accumulation step at open circuit is performed along 5 min before DPV scan.<br>- Potential scan from 0 V to +1.0 V. | [170] |
| AP-GO/GCE | Cd(II)<br>Cu(II) | SWASV | Tap water and human urine | Cd(II): 0.4 ng L$^{-1}$<br>Cu(II): 0.2 ng L$^{-1}$ | Cd(II): 1 - 56 ng L$^{-1}$ Cu(II): 0.6 - 32 ng L$^{-1}$ | - A negative reduction potential is applied to a p-nitrophenyl modified GCE to reduce the nitro groups to amine forming the p-aminophenyl modified electrode.<br>- Measurements in an acetate buffer (pH 4.5) media.<br>- Accumulation is performed at open circuit along 15 min at 30$^{o}$C.<br>- $E_d$ = -1.0 V, potential scan from -1.0 V to 0 V. | [171] |
| L-SNPs/CPE | Cd(II)<br>Cu(II)<br>Hg(II) | SWASV | Tap water, Persian Gulf water, tobacco, fish and shrimp tissues, human hair and rice | Cd(II): 0.3 µg L$^{-1}$<br>Cu(II): 0.1 µg L$^{-1}$<br>Hg(II): 0.05 µg L$^{-1}$ | Cd(II): 1.5 - 1000 µg L$^{-1}$<br>Cu(II): 0.6 - 1100 µg L$^{-1}$<br>Hg(II): 0.5 - 1000 µg L$^{-1}$ | - Electrode is prepared by mixing the ligand modified silica nanoparticles and the graphite powder paraffin in a mortar.<br>- Measurements in a Britton-Robinson buffer (pH 2.0) media.<br>- $E_d$ = −1.1 V, $t_d$ = 60 s, potential scan from -1.1 V to 0.7 V.<br>- After each measurement a renewed CP surface is obtained by polishing of the electrode on a paper. | [172] |
| L-MWCNTs/CPE | Pb(II)<br>Hg(II) | SWASV | sea water, waste | Hg(II): 0.18 µg L$^{-1}$<br>Pb(II): 0.12 µg L$^{-1}$ | 0.5 -140 µg L$^{-1}$ | - Electrode is prepared introducing the ligand into the matrix of CPE modified with MWCNTs. | [173] |

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| | | | water, tobacco, marine and human teeth | | | - Measurements in a hydrochloric acid (pH = 3) media.<br>- $E_d$ = −1.2 V, $t_d$ = 90 s, potential scan from -0.8 V to 0.7 V.<br>- Conditioning step: 0.9 V along 45 s is applied before each measurement. | |
| 2-HBBH/CPE | Ag(I) | DPASV | Estuarine waters | 1.1 ng L$^{-1}$ | 0.001-100 µg L$^{-1}$ | - 2-HBBH together with paraffin oil are incorporated in the CPE.<br>- Measurement in a 0.1 mol L$^{-1}$ phosphate buffer (pH 5.5) media (pH 1 in real samples).<br>- Accumulation step: 180 s at open circuit.<br>- $E_d$ = 0.0 V, $t_d$ = 180 s, potential scan from -0.4 V to 0.7 V. | [174] |
| AcAcNH$_2$-HMS/CPE | Cd(II)<br>Pb(II)<br>Cu(II) | SWASV | waste water | Pb(II): 5.4 µg L$^{-1}$<br>Cd(II): 47.4 µg L$^{-1}$<br>Cu(II): 4.2 µg L$^{-1}$ | Cd(II): 0.1 - 1.3 µg L$^{-1}$<br>Pb(II): 0.03 - 0.9 µg L$^{-1}$<br>Cu(II): 0.01 - 1.1 µg L$^{-1}$ | - Electrode is prepared by homogeneous mixing AcAcNH$_2$ and mesoporous silica with carbon powder and paraffin oil.<br>- Measurement in a Britton-Robinson buffer (pH 5.02) media.<br>- $E_d$ = -1.1 V, $t_d$ = 210 s, potential scan from -1.2 V to 0.25 V, scan rate 50 mV s$^{-1}$. | [175] |
| In situ Bi-L-Nafion/GCE | Cd(II) | DPASV | | 0.014 µg L$^{-1}$ | 0.056 - 1.12 µg L$^{-1}$<br>($t_d$ = 180 s) | - Electrode prepared by coating the GCE with the cadmium ionophore N,N,N′,N′-tetrabutyl-3,6-dioxaoctanedi(thioamide) and Nafion composite.<br>- Bismuth is deposited *in situ* on the electrode surface.<br>- Measurement in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) solution.<br>- $E_d$ = -1.4 V, $t_d$ = 180 s; potential scan from -1.4 V to -0.3 V.<br>- Cleaning step: electrolysis at 0.3 V along 60 s in fresh supporting electrolyte prior to the next cycle. | [176] |
| IL-GR-L/CPE | Tl(I)<br>Pb(II)<br>Hg(II) | SWASV | Tap water, river water and soil samples | Tl(I): 0.07 µg L$^{-1}$<br>Pb(II): 0.09 µg L$^{-1}$<br>Hg(II): 0.08 µg L$^{-1}$ | 0.25 – 40 µg L$^{-1}$ | - Measurements in a 0.2 mol L$^{-1}$ acetate buffer (pH 4.0) media.<br>- $E_d$ = -1.1 V, $t_d$ = 90 s, potential scan -1.0 to 0.4 V.<br>- Pre-conditioning step: 0.9 V along 45 s before each measurement. | [177] |
| IIP-IL/CPE | Hg(II) | DPSAV | Waste water | 0.02 µg L$^{-1}$ | two linear ranges:<br>0.1 – 2 µg L$^{-1}$<br>16 - 400 µg L$^{-1}$ | - Accumulation step: 20 min (stirring 400 rpm) in a phosphate buffer (pH 4.5) media at open circuit.<br>- Measurement step in a 0.1 mol L$^{-1}$ hydrochloric acid media.<br>- $E_d$ = -0.9 V, $t_d$ = 35 s, potential scan -0.9 to -0.4 V.<br>- Cleaning step: after each experiment the electrode surface is removed with a paper sheet. | [178] |
| IIP-RGO/GCE | Hg(II) | SWASV | --- | 0.02 µg L$^{-1}$ | 0.07–80 µg L$^{-1}$ | - The IIP-RGO is prepared by surface imprinted method. | [179] |

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| | | | | | | - The GCE modification is performed by dropping a Nafion/IIP-RGO suspension on the electrode surface.<br>- Accumulation step: 13 min at open circuit in a 0.1 mol $L^{-1}$ acetate buffer (pH 4.5) media.<br>- Reduction and measuring step in a medium changed (0.1 mol $L^{-1}$ nitric acid / 0.5 mol $L^{-1}$ potassium chloride): $E_d$ = -0.7 V, $t_d$ = 50 s, potential scan -0.1 to 0.7 V (scan rate 100 mV $s^{-1}$).<br>- Conditioning step: 0.8 V along 70 s in a 0.2 mol $L^{-1}$ nitric acid media after each measurement. | |
| IIP and multi-walled carbon nanotubes (MWCNTs) | Ag(I) | DPASV | Tap, ground and river waters | 0.013 µg $L^{-1}$ | 0.05 - 30 µg $L^{-1}$ | - The electrode is prepared by mixing the graphite powder, the nanosized silver IIP and the MWCNTs.<br>- Measurements in a 0.1 mol $L^{-1}$ acetate buffer solution (pH 5.0) media.<br>- $E_d$ = -0.4 V, $t_d$ = 180 s, potential scan from .0.2 V to 0.2 V (scan rate 30 mV $s^{-1}$). | [180] |
| NMP-IL-/HF-GCE | Cd(II)<br>Pb(II) | DPV | Tap river, and waste water | Cd(II): 0.61 µg $L^{-1}$<br>Pb(II): 0.19 µg $L^{-1}$ | Cd(II): 2 - 13000 µg $L^{-1}$<br>Pb(II): 0.6 - 6500 µg $L^{-1}$ | - Accumulation step: 1800 s (stirring 200 rpm) at open circuit.<br>- Measurements in a 0.1 mol $L^{-1}$ hydrochloric acid and 30 mg $L^{-1}$ mercury acetate media.<br>- $E_d$ = -0.85 V, potential scan -0.85 to -0.4 V.<br>- Tentative study in which further investigation is needed. | [181] |
| P123-SH-IL/GCE | Cd(II) | DCASV | Water | 0.11 µg $L^{-1}$ | 3.25 µg $L^{-1}$ - 97 mg $L^{-1}$ | - The GCE is coated with a P123-SH/ILs suspension and the solvent is evaporated at room temperature.<br>- Measurements in a 0.1 mol $L^{-1}$ acetate buffer (pH 5.5) media.<br>- $E_d$ = -1.1 V, $t_d$ = 240 s, potential scan from -1.1 V to -0.4 V.<br>- Conditioning and activation steps: 0.5 V along 120 s, and 10 successive cyclic potential scans from -1.1 V to -0.4 V at 100 mV $s^{-1}$ in a 0.1 mol $L^{-1}$ sodium hydroxide media. | [182] |
| kryptofix 21-capped AuNP-RGO/CPE | Cu(II) | DPASV | River, tap, dam waters | 0.1 µg $L^{-1}$ | 0.5 - 75 µg $L^{-1}$ | - The modified CPE is prepared by mixing graphite powder, kryptox 21-capped GNPs and RGO with paraffin oil.<br>- Measurement in a 0.1 mol $L^{-1}$ hydrochloric acid media.<br>- $E_d$ = -0.4 V, $t_d$ = 180 s, potential scan from -0.5 V to 0.2 V (scan rate 50 mV $s^{-1}$). | [183] |
| Crown-ether-MWCNT/CPE | Hg(II) | LSV | Blood, urine or tab-water | 0.25 mg $L^{-1}$ | 5 - 110 mg $L^{-1}$ | - The modified CPE is prepared by mixing the crown ether, the MWCNTs and the graphite powder.<br>- Measurements in a 0.25 mol $L^{-1}$ phtalic acid media.<br>- Accumulation along 300 s at open circuit.<br>- Potential scan from -0.2 V to 1.0 V (scan rate 50 mV $s^{-1}$). | [184] |

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| | | | | | | - Activation step: the electrode is activated in phthalic acid applying 10-cyclic scans | |
| Dicyclohexyl-18-crown-6/CPE | Tl(I) | DPASV | Water, hair | 0.86 µg L$^{-1}$ | 3.0 - 250 µg L$^{-1}$ | - The modified CPE is prepared by mixing the graphite powder, the crown and silicon oil.<br>- Measurements in a 0.10 mol L$^{-1}$ acetate buffer (pH 5.0) media.<br>- $E_d$ = -1.2 V, $t_d$ = 300 s, potential scan from -1.4 to -0.7 V (scan rate 20 mV s$^{-1}$).<br>- Regeneration step: after every measurement a thin layer of the surface is removed with a spatula and replaced by fresh paste. | [185] |
| PDMS-PA-DB18C6/SPCE | Pb(II) | DPASV | Waste water | 3.5 µg L$^{-1}$ | 20 - 700 µg L$^{-1}$ | - Modification of SPCE by drop coating.<br>- Measurements in a 0.05 mol L$^{-1}$ hydrochloric acid media.<br>- Accumulation step: -1.1 V along 120 s at open circuit.<br>- $E_d$ = -1.1 V, $t_d$ = 90 s, potential scan from -1.1 V to 0 V (scan rate 7.5 mV s$^{-1}$).<br>- Accumulation and deposition steps are carried out in still solution (a drop covering the SPCE surface). | [186] |
| *In situ* Bi-3DAGN-STP/GCE | Cd(II),<br>Pb(II) | DPASV | --- | Cd(II): 0.1 µg L$^{-1}$<br>Pb(II): 0.2 µg L$^{-1}$ | Cd(II): 1 - 70 µg L$^{-1}$ Pb(II): 1 - 80 µg L$^{-1}$ | - 3DAGN–STP nanocomposite is prepared by *in situ* chemical co-polymerization of m-aminobenzene sulfonic acid and aniline in the presence of graphene nanosheets.<br>- Modification of the GCE by drop coating.<br>- Formation of an *in situ* Bi film.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.0) media.<br>- $E_d$ = -1.1 V, $t_d$ = 300 s, potential scan from -1.1 V to 0.1 V (scan rate 7.5 mV s$^{-1}$). | [187] |
| *In-situ* Bi-P*m*PD /GCE | Cd(II)<br>Pb(II) | SWASV | --- | Cd(II): 0.02 µg L$^{-1}$<br>Pb(II): 0.04 µg L$^{-1}$ | 6 - 240 µg L$^{-1}$ | - Modification of the GCE by electropolymerization.<br>- Formation of an *in situ* Bi film.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.0).<br>- $E_d$ = -1.0 V, $t_d$ = 150 s, potential scan from -1.2 V to -0.2 V.<br>- Cleaning step: 0.5 V along 60 s prior to the next cycle. | [188] |
| *In-situ* Bi G-PANI/SPCE | Zn(II)<br>Cd(II)<br>Pb(II) | SWASV | Human serum | Zn(II): 1.0 µg L$^{-1}$<br>Cd(II): 0.1 µg L$^{-1}$<br>Pb(II): 0.1 µg L$^{-1}$ | 1 - 300 µg L$^{-1}$ | - Graphene-polyaniline nanocomposite is prepared by reverse-phase polymerization in the presence of polyvinylpyrrolidone.<br>- Modification of the SPCE surface by electrospray.<br>- Formation of an *in situ* Bi film.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) | [189] |

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| | | | | | | media.<br>- $E_d$ = -1.6 V, $t_d$ = 240 s, potential scan from -0.8 V to 0.7 V (scan rate 100 mV s$^{-1}$). | |
| *In situ* Bi-PANI/GCE | Cd(II)<br>Pb(II) | SWASV | | Cd(II): 0.12 µg L$^{-1}$<br>Pb(II): 3.4 µg L$^{-1}$ | Cd(II): 2.8 - 16.8 µg L$^{-1}$<br>Pb(II): 5.2 - 31 µg L$^{-1}$ | - Measurements in a 0.020 mol L$^{-1}$ sulfuric acid and 0.030 mol L$^{-1}$ potassium chloride media.<br>- $E_d$ = -1.3 V, $t_d$ = 120 s, potential scan from -1.3 V to -0.25 V.<br>- Conditioning step: 0.6 V along 30 s. | [190] |
| *In situ* Sn-poly(p-ABSA)-G/GCE | Cd(II) | SWASV | Industrial waste water, lake water, farm-land irrigation water | 0.05 µg L$^{-1}$ | 1.0 - 70.0 µg L$^{-1}$ | - Prepared by successive electrodeposition of exfoliated graphene oxide and electropolymerization of p-aminobenzene sulfonic acid.<br>- Formation of an *in situ* stannum film.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer media.<br>- $E_d$ = -1.2 V, $t_d$ = 120 s, potential scan from -1.2 V to 0 V.<br>- Conditioning step: 0.3 V along 30 s under stirring condition before next cycle. | [191] |
| *Ex-situ* Sb-SPAN-EGSPE | Pb(II)<br>Cd(II) | DPASV | River and tap water | Pb(II): 0.2 µg L$^{-1}$<br>Cd(II): 0.41 µg L$^{-1}$ | 2 - 70 µg L$^{-1}$ | - Mesuraments in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$= -1.1 V, $t_d$= 180 s, potential scan from -1.1 V to -0.3 V. | [192] |
| *Ex-situ* Sb-PEDOTSDS-GCE | Pb(II)<br>Cd(II) | SWASV | Mineral and river water | Pb(II): 0.5 µg L$^{-1}$<br>Cd(II): 0.8 µg L$^{-1}$ | 4.5 - 140 µg L$^{-1}$ | - Mesuraments in an acetate buffer (pH 4.0) media.<br>- $E_d$= -1.0 V, $t_d$ = 60 s, potential scan from -0.8 to 0.0 V. | [193] |
| Ag-dipy-CP-PMB/GCE | Hg(II)<br>Cu(II)<br>Pb(II) | DPASV | Fish and plants | Hg(II): 0.09 µg L$^{-1}$<br>Cu(II): 0.71 µg L$^{-1}$<br>Pb(II): 2.3 µg L$^{-1}$ | Hg(II): 0.2 - 10 µg L$^{-1}$<br>Cu(II): 1.3 - 6.4 µg L$^{-1}$<br>Pb(II): 4.1 - 20.7 µg L$^{-1}$ | - Coordination polymer immobilized on the GCE surface via an organic electrodeposited layer.<br>- Accumulation step: $E_d$ =-0.6 V, $t_d$ = 300 s.<br>- Measurements in a new cell in an acetate buffer media: potential scan from -0.65 V to 0.55 V (scan rate 10 mV s$^{-1}$).<br>- Regeneration: 0.8 V along 100 s in acetate buffer media. | [194] |
| [PAH–GS]$_{12}$/GCE | Cu(II) | DPASV | --- | 22 µg L$^{-1}$ | 32 µg L$^{-1}$ - 3.2 mg L$^{-1}$ | - Modification is done by layer by layer self-assembly methodology.<br>- Measurements in 0.1 mol L$^{-1}$ ammonium buffer (pH 7.0) media.<br>- $E_d$ =-0.4 V, $t_d$ = 420 s, potential scan from -0.4 V to 0.3 V. | [195] |
| (P(DPA-co-2ABN)/GCE) | Cd(II)<br>Pb(II) | DPASV | Tap water | Cd(II): 0.255 µg L$^{-1}$<br>Pb(II): 0.165 µg L$^{-1}$ | Cd(II): 1.26 - 907.8 µg L$^{-1}$<br>Pb(II): 0.26 - 58.73 µg L$^{-1}$ | - Modification is performed through electrodeposition of P(DPA-co-2ABN) film onto the surface of GCE by CV.<br>- Measurements in a pH 2 media.<br>- $E_d$ = -1.0 V, $t_d$ = 60 s, potential scan from -1.1 V to -0.2 V (scan rate 30 mV s$^{-1}$). | [196] |
| *in situ* PbNPs- | Bi(III) | SWASV | River | 0.5 ng L$^{-1}$ | 2 -41 ng L$^{-1}$ (30 min) | - SH-PF is deposited and electrochemically activated onto the | [197] |

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| SH-PF/GCE |  |  | water |  |  | electrode surface.<br>- Lead nanoparticles are *in-situ* electroplated on the modified GCE.<br>- Accumulation step in a 0.1 mol $L^{-1}$ nitric acid media along 30 min at open circuit in the absence of PbNPs.<br>- Reduction and measurement steps in a 3 mol $L^{-1}$ hydrochloric acid (containing lead): $E_d$ = -1.35 V, $t_d$ = 180 s, potential scan from -0.7 V to 0.3 V. |  |

EDTA-CN-NS-Nafion/GCE: EDTA-immobilized graphene-like carbon nitride nanosheets Nafion modified glassy carbon electrode;2-HBBH/CPE: 2-hydroxybenzaldehyde benzoylhydrazone modified carbon paste electrode; MTU-GO-AuNPs/ITOE: 5-methyl-2-thiouracil graphene oxide gold nanoparticles modified indium tin oxide electrode; AP-GO/GCE: p-aminophenyl graphene oxide modified glassy carbon electrode; L-SNPs/CPE: N,N'-bis(3-(2-thenylidenimino)propyl)piperazine coated silica nanoparticles modified carbon paste electrode; L-MWCNTs/CPE: 3-(4-methoxybenzylideneamino)-2-thioxothiazolodin-4-one multi-walled carbon nanotubes modified carbon paste electrode; AcAcNH$_2$-HMS/CPE: acetyl-acetone hexagonal mesoporous silica modified carbon paste electrode; *in situ* Bi-L-Nafion/GCE: *in situ* bismuth N,N,N′,N′-tetrabutyl-3,6-dioxaoctanedi(thioamide)-Nafion modified glassy carbon electrode; IL-GR-L/CPE: 1-n-octylpyridinum hexafluorophosphate, graphene and [2,4-$Cl_2C_6H_3C(O)CHPPh_3$] composite carbon paste electrode; IIP-IL/CPE: ion imprinted polymer ionic liquid composite carbon paste electrode; IIP-RGO/GCE: ion imprinted polymer reduced graphene oxide modified glassy carbon electrode; IIP-MWCNTs/CPE: ion imprinted polymer multi-walled carbon nanotubes modified carbon paste electrode; NMP-IL-/HF-GCE: nanomagnetic particles 1-butyl-3-methylimidazolium hexafluorophosphate modified hollow fiber-graphite electrode; P123-SH-IL/GCE: thiol-functionalized mesoporous molecular sieve 1-butyl-3-methylimidazolium tetrafluoroborate modified glassy carbon electrode; kryptofix 21-capped AuNP-RGO/CPE: kryptofix 21 capped gold nanoparticles reduced graphene oxide modified carbon paste electrode; crown ether-MWCNT/CPE: crown ether multi-walled carbon nanotubes modified carbon paste electrode; dicyclohexyl-18-crown-6/CPE: dicyclohexyl-18-crown-6 modified carbon paste electrode; PDMS-PA-DB18C6/SPCE : siloxane-crown ether polyamide copolymer modified screen-printed carbon electrode; *in situ* Bi-3DAGN-STP/GCE: *in situ* bismuth film three-dimensional activated graphene networks sulfonate-terminated polymer modified glassy carbon electrode; *in-situ* Bi-P*m*PD/GCE: *in situ* bismuth film thiolated poly(*m*-phenylenediamine) modified glassy carbon electrode; *in-situ* Bi G-PANI/SPCE: *in situ* bismuth film graphene-polyaniline modified screen printed carbon electrode; *in situ* Bi/PANI/GCEs: *in situ* bismuth filmpolyanilinemodified glassy carbon electrode; Sn-poly(p-ABSA)-G/GCE: stannum film poly(p-aminobenzene) sulfonic acid graphene composite modified glassy carbon electrode; *ex-situ* Sb-SPAN-EGSPE: *ex-situ* antimony film sulfonated polyaniline expanded graphite paper based electrode; *ex-situ* Sb-PEDOTSDS-GCE: *ex-situ* antimony film poly(3,4-ethylenedioxythiophene)-sodium dodecyl sulfate modified glassy carbon electrode; Ag-dipy-CP-PMB/GCE: 4,4′-bipyridine silver coordination polymer phenylmethyl-4,4′-bipyridinium modified glassy carbon electrode; [PAH–GS]$_{12}$/ GCE: multilayer polyallylamine hydrochloride graphene oxide modified glassy carbon electrode; P(DPA-co-2ABN)/GCE: poly(diphenylamine-co-2-aminobenzonitrile) modified glassy carbon electrode; *in situ* PbNPs-SH-PF/GCE: *in situ* lead nanoparticles thiol-functionalized polysiloxane modified glassy carbon electrode.

**Table 10.** Electrodes modified with biomolecules and biomaterials.

| Electrode | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
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|---|---|---|---|---|---|---|---|
| D-penicillamine /GCE | Cd(II)<br>Pb(II) | DPASV | Waste water | Cd(II): 4.30 µg L$^{-1}$<br>Pb(II); 3.02 µg L$^{-1}$ | Until 115 µg L$^{-1}$ | - D-penicillamine immobilized via electrografting on aryldiazonium salt monolayer anchored to the GCE surface.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$ = -1.25 V, $t_d$ = 120 s, potential scan from -1.25 V to -0.5 V.<br>- Cleaning step: -0.5 V along 30 s after each measurement. | [198] |
| GSH/SPCNFE | Cd(II)<br>Pb(II) | DPASV | Waste water | Cd(II): 3.2 µg L$^{-1}$<br>Pb(II): 3.0 µg L$^{-1}$ | Cd(II): 10.8 - 150.1 µg L$^{-1}$<br>Pb(II): 10.1 - 150.1 µg L$^{-1}$ | - The commercial CNFs-SPCE is modified with glutathione via electrografting.<br>- Comparison with a glutathione modified SPCE.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 4.5) media.<br>- $E_d$ = -1.4 V, $t_d$ = 120 s, potential scan from -1.4 V to -0.45 V.<br>- Cleaning step: -0.3 V along 15 s in a 0.1 mol L$^{-1}$ $HClO_4$ media after each measurement. | [199] |
| Gly-Gly-His/SWCNT-SiE | Cu(II) | DPV | --- | --- | --- | - An eletrografting aminophenyl film is created on the H-terminated silicon substrate in which carboxyl functionalized CNTs are immobilized. The tripeptide Gly-Gly-His is then covalently attached.<br>- Accumulation step: 10 min at open circuit.<br>- Measurement step (medium change) in ammonium acetate buffer (pH 7.0) media. Potential scan from 0.1 V to -0.6 V.<br>- Cleaning step: by immersion in 0.1 mol L$^{-1}$ $HClO_4$ solution along 30 s at open circuit after each measurement. | [200] |
| thiolated amino acid-AuNP-IL/CPE | Hg(II) | SWV | Waste and tap water | 0.46 µg L$^{-1}$ (Cys) | 2 µg L$^{-1}$ - 4 mg L$^{-1}$ | - Electrode prepared by hand-mixing the graphite powder, the ionic liquid and the thiolate amino acid-capped AuNPs.<br>- Thiolate amino acid-capped AuNPs prepared by mixing and stirring solutions of the amino acids and AuNPs.<br>- Study of the influence of the amino acid considered (Cys, HCys and GSH).<br>- Measurements in a 0.1 mol L$^{-1}$ phosphate buffer (pH 7.0) media.<br>- Accumulation step: at open circuit.<br>- Measurement step: potential scan from 0.5 V to 0.1 V. | [201] |
| PeptideNF /AuE | Cu(II) | SWV | --- | --- | Until 3.2 mg L$^{-1}$ | - The electrode is prepared by self-assembled peptide nanofibers with AuE.<br>- Accumulation 2 min at open circuit, potential scan from 0.25 V to -0.05 V in an ammonium acetate buffer (pH 6.8) media.<br>- Regeneration of the electrode is required after each measurement. | [202] |
| MT/HMDE | Ag(I) | DPV | --- | 53.5 µg L$^{-1}$ | Until 53 mg L$^{-1}$ | - Indirect analysis of Ag(I) ions. Ag(I) is determined analyzing the decrease of the metallothionein oxidation peak due to the complexation with Ag(I) ions.<br>- Steps: Adsorption of metallothionein on the HMDE surface at open circuit (120 s). Rinsing of the electrode. Interaction with analyte ions in a drop of the sample solution at open circuit. Rinsing of the electrode. DPV scan from -1.2 V to -0.3 V. | [203] |
| MT- | Ag(I) | SWV | Water | 53.5 ng L$^{-1}$ | Two linear ranges: | - Immobilization of metallothionein into the surface of CPE via anti-MT- | [204] |

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| antibody/CPE | | | | | 1.07 - 1600 µg L$^{-1}$<br>1.6 - 53 mg L$^{-1}$ | antibodies.<br>- Accumulation step: electrode surface in contact with the sample along 300 s.<br>- Measuring step in a 0.2 mol L$^{-1}$ borate buffer (pH 9.6): potential scan from 0.0 V to 1.6 V.<br>- Signal related with the oxidation of a Ag-MT complex.<br>- Interferences of Cu(II), Hg(II), Pt(II), Cd(II), Zn(II), Fe(II), and Ni(II) are tested. | |
| Guanine-CNT/GCE | Ag(I) | DPV | --- | 3.21 µg L$^{-1}$ | 10.7 - 268 µg L$^{-1}$ | - Indirect analysis of Ag(I) ions. Ag(I) is determined analyzing the decrease of the guanine oxidation peak due to the influence of Ag(I) in the formation of oxidation intermediate and the electrocatalytic oxidation activity of guanine.<br>- Guanine is deposited on the electrode surface via *in situ* with the analyte.<br>- Incubation step: a solution of guanine in a 0.1 mol L$^{-1}$ acetate buffer (pH 5.0) solution and the Ag(I) ions (from standards o samples) incubated along 20 min at room temperature.<br>- Accumulation step: The CNTs/GCE is dipped into the above solution to accumulate the Ag-guanine at 0.3V for 240 s.<br>- Measurement step: DP potential scan from 0.6 V to 1.1 V. | [205] |
| T-AuNP-RGO/GCE | Hg(II) | DPASV | Tap water | <1.5 ng L$^{-1}$ | 10 ng L$^{-1}$ - 1.0 µg L$^{-1}$ | -Thymine is covalently coupled through its carboxyl group to the AuNP-RGO/GCE modified by self-assembled monolayer of cysteamine.<br>- Accumulation step: immersion in the sample solution during 15 min at open circuit.<br>- Measuring step in a 0.01 mol L$^{-1}$ phosphate buffer/0.5 mol L$^{-1}$ sodium chloride (pH=7.0) solution: reduction at $E_d$ = -0.4 V, $t_d$ = 120 s; potential scan from -0.5 V to 0.5 V.<br>- Regeneration step: by washing in an EDTA solution.<br>- Excellent selectivity against Zn(II), Cd(II), Pb(II), Cu(II), Ni(II), and Co(II). | [206] |
| PTO/AuE | Hg(II) | DPASV | --- | 12 ng L$^{-1}$ | 40 - 200 ng L$^{-1}$ | - Electrode prepared by self-assembly of thiolated polythymine oligonucleotide on the AuE via Au-S bonds, and then passivated with 1-mercaptohexanol.<br>- Accumulation step: immersion in the sample solution along 15 min at open circuit.<br>- Measuring step in a 0.01 mol L$^{-1}$ HEPES buffer and 1 mol L$^{-1}$ sodium perchlorate (pH 7.2) media: reduction at $E_d$ = -0.2 V, $t_d$ = 60 s; potential scan -0.2 V to 1.0 V.<br>- High selectivity, which allows determination of Hg(II) even in the presence of excess (200-fold) of other metal ions. | [207] |
| Chitosan | Cu(II), | DPASV | --- | Pb(II): 12.8 µg L$^{-1}$ | Pb(II): 412 - 3270 µg L$^{-1}$ | - The electrode is coated by dropping some µL of chitosan solution. | [208] |

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| /GCE | Pb(II),<br>Cd(II),<br>As(IV),<br>Pt(IV) |  |  | Cu(II): 57 µg L$^{-1}$<br>Cd(II): 263 µg L$^{-1}$<br>As(IV): 50 µg L$^{-1}$<br>Pt(IV): 6.8 µg L$^{-1}$ | Cu (II): 253 - 2484 µg L$^{-1}$<br>Cd(II): 1781 - 6977 µg L$^{-1}$<br>As(IV): 599 - 3780 µg L$^{-1}$<br>Pt(IV): 1597 - 7000 µg L$^{-1}$ | - Measurement in a phosphate buffer (pH 7) media.<br>- Pre-concentration between -1.0 to -0.1 V, depending on the metal ion, $t_d$ = 180 s, potential scan depending on the metal ion (scan rate of 10 mV s$^{-1}$)<br>- Each experiment in a newly prepared CT-GCE.<br>- The possibility of simultaneous detection of more than a metal ion is also introduced. |  |
| Chitosan /SPCE | Pb(II),<br>Cu(II),<br>Cd(II),<br>Hg(II) | DPASV | --- | Pb(II): 3.4 µg L$^{-1}$<br>Cu(II): 5 µg L$^{-1}$<br>Cd(II): 5 µg L$^{-1}$<br>Hg(II): 2 µg L$^{-1}$ | Pb(II): 20 - 160 µg L$^{-1}$<br>Cu(II): 10 - 200 µg L$^{-1}$<br>Cd(II): 10 - 200 µg L$^{-1}$<br>Hg(II): 20 - 80 µg L$^{-1}$ | - The electrode is prepared by printing the support with a homemade carbon ink prepared by mixing chitosan, a PVC solution and carbon powder.<br>- Measurement in a 0.1 mol L$^{-1}$ hydrochloric acid and potassium chloride media.<br>- $E_d$ = -1 V, $t_d$ = 30 s, potential scan from -1 V to -0.4 V (scan rate 50 mV s$^{-1}$).<br>- Non electrode regeneration is needed. | [209] |
| Maize tassel/CPE | Cu(II) | SWV | Waters | 8.3 µg L$^{-1}$ | 78 µg L$^{-1}$ - 25.4 mg L$^{-1}$ | - The electrode is prepared by hand mixing of maize tassel powder, graphite powder and a mineral oil.<br>- Accumulation step: immersion in the sample solution along at open circuit.<br>- Measuring step in a 0.05 mol L$^{-1}$ sodium nitrate solution and application of a potential scan from 0.6 V to -0.8 V. | [210] |
| HRP-maize tassel-MWCNT/GCE | Cd(II) | CV |  | 0.51 µg L$^{-1}$ | 2 - 30 µg L$^{-1}$ | - Indirect analysis of Cd(II) ions (inhibitor biosensor). Current generated (after incubation of the biosensor in the sample solution) as a result of the reduction of $H_2O_2$ is correlated to Cd(II) concentrations.<br>- The electrode is prepared by dropping and drying a dispersion of maize tassel and MWCNT in DMF on the surface of a GCE;<br>later it is coated with HRP and Nafion which act as a binder.<br>- Measurement steps in a 0.1 mol L$^{-1}$ phosphate buffer and 0.1 mol L$^{-1}$ potassium chloride (pH 7.0) media containing a controlled concentration of $H_2O_2$: i) the reduction of $H_2O_2$ is measured and recorded (potential scan from 0.6 to -0.6 V (scan rate 100 mV s$^{-1}$), ii) incubation of the biosensor in the Cd(II) sample solution along 20 min, iii) measure of the sensor response to $H_2O_2$ (potential scan from 0.6 to -0.6 V (scan rate 100 mV s$^{-1}$)), iv) response of biosensor to $H_2O_2$ before and after its interaction with Cd(II) is considered.<br>- The electrode must be stored at 4◦C when it is not in use. | [211] |
| HRP-maize tassel-MWCNT/GCE | Cu(II),<br>Pb(II) | Amperometry | --- | Pb(II): 2.5 µg L$^{-1}$<br>Cu(II): 4.2 µg L$^{-1}$ | Pb(II): 0.092 -0.55 mg L$^{-1}$<br>Cu(II): 0.068 - 2 mg L$^{-1}$ | - Inhibition in reduction signals of $H_2O_2$ is proportional to metal ion concentration.<br>- Same procedure than [8].<br>- Amperometric measurements at -0.3 V. | [212] |
| *Rhizopus arrhizus*/CPE | Pb(II) | DPV | --- | 1 µg L$^{-1}$ | 20.7 - 2587 µg L$^{-1}$ | - The electrode is prepared by making a homogeneous paste with dried nonliving fungal tissue.<br>- Accumulation step in a 0.01 mol L$^{-1}$ of Tris–HCl media along 12 min at open | [213] |

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| | | | | | | circuit.<br>- Measurement step in a medium changed (0.01 mol L$^{-1}$ Tris-HCl buffer pH 7), potential scan from 1.5 V to -1.5 V | |
| *Phormidium*/ CPE | Pb(II) | DPV | --- | 5.2 µg L$^{-1}$ | 0.01 - 4.0 mg L$^{-1}$ | - The electrode is prepared by making a homogeneous paste with heat dried algal biomass, graphite powder, and paraffin.<br>- Accumulation step in a 0.05 mol L$^{-1}$ of Tris–HCl media along 10 min at open circuit.<br>- Measurement step in a changed media (0.05 mol L$^{-1}$ Tris-HCl buffer pH 8), potential scan from 1.5 V to -1.5 V<br>- Cleaning step: after each determination, electrode was treated with HCl (0.1 mol L$^{-1}$) and distilled water. | [214] |
| Algae-OMNiIIP/PGE | Cu(II) | DPASV | --- | 0.0018 µg L$^{-1}$ | 0.008 - 7.807 µg L$^{-1}$ | - Accumulation step: 210 s at open circuit under dynamic condition.<br>- Reduction and measurement (step in the same media): $E_d = -1.2$ V, $t_d = 15$ s, scan potential from -0.4 V to 0.3 V (10 mV s$^{-1}$). | [215] |
| Algae-MIP/PGE | Cu(II) | DPASV | --- | 0.004 µg L$^{-1}$ | --- | - $E_d = -1.2$ V, $t_d = 180$ s, potential scan from -0.4 V to 0.4 V (scan rate 10 mV s$^{-1}$) | [216] |
| DNA/CPE<br>DNA-AuNPs/CPE | Ag(I) | DPV | --- | CPE: 11 ng L$^{-1}$<br>AuNPs/CPE: 2 ng L$^{-1}$ | --- | - Analysis based in the decrease of the reduction peak of ethyl green (EG) dye used as electroactive label.<br>- DNA is electro-immobilized on the CPE or AuNPs/CPE surfaces (0.5 V along 5 min). Subsequent accumulation of EG is performed (along 5 min at open circuit).<br>- Hybridization is performed by immersing the probe-modified CPE in a media containing the target DNA and Ag(I) along 5 min at 0.50 V. | [218] |
| Aptamer-SPMS NPs/FTO | Zn(II) | DPASV | Human blood and disrupted human cells | 4.2 ng L$^{-1}$ | 6.5 ng L$^{-1}$ - 3269 µg L$^{-1}$ | - Aptamer with the sequence of 5'-GCATCAGTTAGTCATTACGC TTACGGCGGCTCTATCCTAACTGATATATTGTGAAGTCGTGTCCC- 3'.<br>- Measurements in a 0.1 mol L$^{-1}$ acetate buffer (pH 5.6) media.<br>- $E_d = -1.7$ V, $t_d = 200$ s, potential scan from -1.6 V to -1.0 V.<br>- Cleaning step: 0.4 V in a 0.1 mol L$^{-1}$ acetate buffer with 0.01 mol L$^{-1}$ EDTA and 0.05 mol L$^{-1}$ NaCl after each measurement. | [219] |
| Ts-DNA/AuE | Hg(II) | DPV | tap, lake and river water | 0.02 µg L$^{-1}$ | 0.02 - 4 µg L$^{-1}$ | - ts-DNA is immobilized onto the AuE surface including a T5 DNA (T: thymine) section for Hg(II) identification<br>- Accumulation step: incubation of Hg(II) ions in the presence of functional oligonucleotide and methylene blue.<br>-Potential scan from 0 V to -0.4 V. | [220] |
| DNAzyme based | Pb(II) | DPV | | 1 10$^{-19}$ mol L$^{-1}$ | 110$^{-17}$ - 110$^{-4}$ mol L$^{-1}$ (logarithmic dependence) | - The DNA biosensor is fabricated by immobilizing capture probe DNA on three dimensional ordered macroporous Au–Pd bimetallic electrode, which is | [221] |

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| electrode |  |  |  |  | further hybridized with the DNA loaded on the methylene blue-SWCNTs adduct.<br>- Under optimal conditions, the electrochemical signal of the MB is related with Pb(II) concentration.<br>- Measurement in a 0.05 mol $L^{-1}$ Tris-acetate buffer and 0.5 mol $L^{-1}$ sodium chloride (pH 8.0) media. |  |
| DNAzyme based electrode | Pb(II) | SWV | 7.8 pM | 0.01 to 1000 nM (logarithmic dependence) | - The goodness is due to the combination of DNAzyme as a recognition element and the rolling circle amplification (RCA) (a unique enzymatic process) as a signal amplification tool. | [222] |

D-penicillamine/GCE: D-penicillamine modified glassy carbon electrode; GSH/SPCNFE: glutathione modified carbon nanofibers screen printed electrode; thiolated amino acid-AuNP-IL/CPE: thiolated amino acid capped Au nanoparticle ionic liquid modified carbon paste electrode; Gly-Gly-His/SWCNT-SiE: Gly-Gly-His modified single wallet carbon nanotubes silicon electrode; peptideNF/AuE: peptide nanofibers modified gold electrode; MT/HMDE: metallothionein modified hanging mercury drop electrode; MT-antibody/CPE: metallothionein antibodymodified carbon paste electrode; Guanine-CNT/GCE: guanine carbon nanotubes modified glassy carbon electrode; T-AuNP-RGO/GCE: thymine modified gold nanoparticles/reduced graphene oxide nanocomposite glassy carbon electrode; PTO/AuE: thiolated polythymine oligonucleotide modified gold electrode; Chitosan/GCE: chitosan modified glassy carbon electrode; Chitosan/SPCE: chitosan modified screen-printed carbon electrode; PTO/AuE: thiolated polythymine oligonucleotide modified gold electrode; D-penicillamine/GCE: D-penicillamine modified glassy carbon electrode; Chitosan/GCE: chitosan modified glassy carbon electrode; Chitosan/SPCE: chitosan modified screen-printed carbon electrode; Maize tassel/CPE: maize tassel modified carbon paste electrode; HRP-maize tassel-MWCNT/GCE： horseradish peroxidase maize tassel multiwalled carbon nanotube modified glassy carbon; *Phormidium*/CPE: *Phormidium* modified carbon paste electrode; *Rhizopus arrhizus*/CPE: *rhizopus arrhizus* modified carbon paste electrode; algae-OMNiIIP/PGE: algae- one monomer ion imprinted polymer modified pencil graphite electrode; algae-MIP/PGE: algae molecular imprinted polymer modified pencil graphite electrode; Aptamer- SPMS NPs/FTO: aptamer $SiO_2$-Pt@meso-$SiO_2$ core–shell nanoparticles modified graphene fluorine doped tin oxide electrode; Ts-DNA-FO-MB/AuE: Tetrahedron-structured DNA functionalized oligonucleotide methylen blue modified gold electrode.

**Table 11.** Arrays of electrodes.

| Electrode | Analyte | Technique | Sample | Detection limit | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| SPAuEA | Pb(II) | DPASV | Rain water | 0.882 μg mL$^{-1}$ | 2.941 - 100 μg mL$^{-1}$ | - System formed by 96 individual SPAuE, each one with working, reference and counter electrodes.<br>- This three-electrode screen-printed planar electrode system could be used for fully automated electrochemical detection of selected species. | [223] |
| AuNP-SPCEA | Pb(II)<br>Cu(II) | SWASV | Tap water | Pb(II): 2.1 ng L$^{-1}$ Cu(II): 1.4 ng L$^{-1}$ | Pb(II): 10 μg L$^{-1}$ - 100 μg L$^{-1}$<br>Cu(II): 10 μg L$^{-1}$ - 150 μg L$^{-1}$ | - In house manufactured array of 8 SPCE modified with AuNPs.<br>- Measurements in a Briton Robinson buffer (pH 9.2) media.<br>- $E_d$ = -0.5 V, $t_d$ = 250 s, potential scan from -0.2 V to 0.6 V. | [224] |
| Au-MEA | Zn(II)<br>Pb(II)<br>Cu(II) | DPASV | --- | --- | 10 – 50 μg L$^{-1}$ | - A light addressable potentiometric sensor for pH is also included in the device.<br>- MEAs with different diameters and number of microelectrodes are considered.<br>- Measurements in an acetate buffer and 0.5 mol L$^{-1}$ potassium chloride (pH 4) media.<br>- $E_d$ = -1.35 V, $t_d$ = 120 s, potential scan from -1.35 V to 0.0 V. | [228] |
| Bi-MEA | Pb(II)<br>Cd(II)<br>Ni(II) | SWASV (Pb(II) and Cd(II))<br>AdSV (Ni(II)) | Lake and mineral water | Pb(II): 0.6 μg L$^{-1}$<br>Cd(II): 0.7 μg L$^{-1}$<br>Ni(II): 0.7 μg L$^{-1}$ | 2.2 - 15 μg L$^{-1}$ | For Pb(II) and Cd(II):<br>- Ferrocyanide ions are added in the sample solutions to alleviate the interference by Cu(II).<br>- Measurements in 0.1 mol L$^{-1}$ acetate buffer and 0.01 mol L$^{-1}$ potassium chloride (pH 4.5) media.<br>- $E_d$ = -1.2 V, $t_d$ = 120 s, potential scan from -1.2 V to -0.3 V.<br>For Ni(II):<br>- Complexing ligand: dimethylglyoxime.<br>- Measurements in 0.1 mol L$^{-1}$ ammonia buffer and 0.01 mol L$^{-1}$ potassium chloride (pH 9.2) media.<br>- $E_d$ = -0.7 V, $t_d$ = 60 s, potential scan from -0.7 V to -1.3 V. | [230] |
| Bi-MEA | Co(II) | AdASV | Lake and mineral water | 0.18 μg L$^{-1}$ | 1.0 - 16.0 μg L$^{-1}$ | - 3 electrode microdevice, in which working electrode is a bismuth microelectrode array constituted by 625 Bi disks.<br>- Microdevice fabricated through sputtering and photolithography.<br>- Complexing ligand: dimethylglyoxime.<br>- Measurements in 10$^{-3}$ mol L$^{-1}$ ammonia buffer (pH 9.2) | [231] |

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| | | | | | | media.<br>- $E_d$ = -1 V, $t_d$ = 30 s, potential scan from -0.7 V to -1.4 V. | |
| BiNEEs | SWASV | Pb(II) | --- | 60 ng $L^{-1}$ (*in-situ* Bi deposition)<br>30 ng $L^{-1}$ (*ex-situ* Bi deposition) | 1 - 14 µg $L^{-1}$ | - Measurements in 0.01 mol $L^{-1}$ hydrochloric acid media.<br>- $E_d$ = -1.1 V, $t_d$ = 180 s, potential scan from -0.8 V to -0.3 V.<br>- Conditioning step: 90 s at 0.5 V for *in-situ* Bi electrode and 60 s at –0.3 V for *ex-situ* Bi electrode. | [232] |
| AuNWEEs | ASV | As(III) | River water | 0.08 µg $L^{-1}$ | until 20 µg $L^{-1}$ | - As(V) is determined by difference between As(III) and total arsenic, which is determined after reduction of As(V) with cysteine. | [233] |

SPAuEA : screen-printed gold electrode array; AuNP-SPCEA: gold nanoparticles modified screen-printed carbon electrode array; Bi-MEA: bismuth film microelectrode array; BiNEES: bismuth modified ensembles of gold nanoelectrodes; AuNWEEs: ensembles of gold nanowires electrodes

**Table 12.** Voltammetric electronic tongues.

| Electrodes | Analyte | Technique | Sample | LOD | Linear range | Comments | Reference |
|---|---|---|---|---|---|---|---|
| GSH–GEC<br>Cys-Gly-GEC<br>ɣ-Glu-Cys-GEC | Pb(II)<br>Cd(II)<br>Zn(II) | DPASV | --- | For all the electrodes:<br>Pb(II): 6.2 μg $L^{-1}$,<br>Cd(II): 3.4 μg $L^{-1}$,<br>Zn(II): 2.0 μg $L^{-1}$ | 0.1 to 1.5 μmol $L^{-1}$ for Pb(II), Cd(II) and Zn(II). | - Peptides immobilized respectively through aryl diazonium electrochemical grafting onto the surface of GEC.<br>- The information provided by one single modified electrode at both fixed and multiple pH values (pH 6.8, 7.5 and 8.2) is compared with those supplied by the three-sensor array at multiple pH values.<br>- Fast Fourier transform coupled with an ANN is selected for the processing of the voltammograms. | [238] |
| CB-15-crown-5<br>CB-18-crown-6 | Pb(II)<br>Cd(II)<br>Cu(II) | DPASV | --- | CB-15-crown-5<br>Pb(II): 3.3 μg $L^{-1}$,<br>Cd(II): 4.7 μg $L^{-1}$,<br>Cu(II): 2.3 μg $L^{-1}$<br>CB-18-crown-6<br>Pb(II): 1.5 μg $L^{-1}$,<br>Cd(II): 2.4 μg $L^{-1}$,<br>Cu(II): 1.5 μg $L^{-1}$ | CB-15-crown-5<br>Pb(II): 10.9 – 186.5 μg $L^{-1}$,<br>Cd(II): 15.7 – 191.1 μg $L^{-1}$,<br>Cu(II): 7.7 – 177.3 μg $L^{-1}$<br>CB-18-crown-6<br>Pb(II): 5.0 – 186.5 μg $L^{-1}$,<br>Cd(II): 7.9 – 191.1 μg $L^{-1}$,<br>Cu(II): 5.1 – 177.3 μg $L^{-1}$ | - CB-18-crown-6 and CB-15-crown-5 assisted by lysine are immobilized respectively through aryl diazonium electrochemical grafting onto the surface of GEC.<br>- Pb(II) shows a more favorable complex forming ability with CB-18-crown-6 whereas Cu(II) fits snugly into CB-15-crown-5. For Cd(II), CB-15-crown-5 is a little bit more selective than CB-18-crown-6.<br>- Discrete Wavelet Transform and Causal Index coupled with an ANN is selected for the processing of the voltammograms. | [239] |
| GEC<br>CB-15-crown-5<br>CB-18-crown-6 | Pb(II)<br>Cd(II)<br>Hg(II) | DPASV | Certified metal solutions | For Pb(II) and Cd(II) see Ref [219]<br>For Hg(II):<br>GEC: 11 μg $L^{-1}$<br>CB-15-crown-5: 12 μg $L^{-1}$<br>CB-18-crown-6: 13 μg $L^{-1}$ | For Pb(II) and Cd(II) see Ref [219]<br>For Hg(II):<br>GEC: 37 - 200 μg $L^{-1}$<br>CB-15-crown-5: 40 - 200 μg $L^{-1}$<br>CB-18-crown-6: 43 - 200 μg $L^{-1}$ | - CB-18-crown-6 and CB-15-crown-5 assisted by lysine are immobilized respectively through aryl diazonium electrochemical grafting onto the surface of GEC.<br>- Hg(II) shows a similar interaction for the three considered sensors, however it can be seen that CB-18-crown-6-GEC is a little bit more selective than CB-15-crown-5-GEC.<br>- Discrete Wavelet Transform coupled with an ANN is selected for the processing of the voltammograms. | [240] |
| Crown-6-SPCNFE<br>*Ex-situ*-SbSPCNFE | Tl(I)<br>In(III) | DPASV | Tap water | Crown-6-SPCNFE<br>Tl(I): 10.9 μg $L^{-1}$,<br>In(III): 13.7 μg $L^{-1}$<br>*Ex-situ*-SbSPCNFE<br>Tl(I): 8.6 μg $L^{-1}$,<br>In(III): 6.3 μg $L^{-1}$ | Crown-6-SPCNFE<br>Tl(I): 36.3 – 270.3 μg $L^{-1}$,<br>In(III): 45.7 – 300.4 μg $L^{-1}$<br>*Ex-situ*-SbSPCNFE<br>Tl(I): 28.7 – 270.3 μg $L^{-1}$,<br>In(III): 21.0 – 300.4 μg $L^{-1}$ | - CB-18-crown-6 assisted by lysine is immobilized respectively through aryl diazonium electrochemical grafting onto the surface of SPCNFE.<br>- Sb is *ex-situ* coated onto the surface of SPCNFE.<br>- Baseline correction, smoothing Savitzky-Golay, 1st derivative Savitzky-Golay, reference correction and | [241] |

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| | | | | | | autoscale coupled with a PLS model are selected for the processing of the voltammograms. | |
| SPCE-CNF<br>GSH-SPCE-CNF<br>Cys-SPCE-CNF<br>*Ex-situ*-SbSPCE-CNF | Zn(II)<br>Cd(II)<br>Pb(II)<br>Bi(III)<br>In(III)<br>Tl(I) | DPASV | Tap water | SPCE-CNF<br>Zn(II): 5.1 µg L$^{-1}$,<br>Cd(II): 3.4 µg L$^{-1}$,<br>Pb(II): 2.6 µg L$^{-1}$<br>Bi(III): 16.8 µg L$^{-1}$,<br>In(III): 3.0 µg L$^{-1}$,<br>Tl(I): 6.5 µg L$^{-1}$<br>GSH-SPCE-CNF<br>Zn(II): 7.4 µg L$^{-1}$,<br>Cd(II): 3.5 µg L$^{-1}$,<br>Pb(II): 3.2 µg L$^{-1}$<br>Bi(III): 8.7 µg L$^{-1}$,<br>In(III): 7.9 µg L$^{-1}$,<br>Tl(I): 12.5 µg L$^{-1}$<br>Cys-SPCE-CNF<br>Zn(II): 7.9 µg L$^{-1}$,<br>Cd(II): 3.3 µg L$^{-1}$,<br>Pb(II): 3.1 µg L$^{-1}$<br>Bi(III): 11.4 µg L$^{-1}$,<br>In(III): 5.5 µg L$^{-1}$,<br>Tl(I): 17.4 µg L$^{-1}$<br>Ex-situ-SbSPCE-CNF<br>Zn(II): 4.5 µg L$^{-1}$,<br>Cd(II): 3.2 µg L$^{-1}$,<br>Pb(II): 4.0 µg L$^{-1}$<br>Bi(III): 5.2 µg L$^{-1}$,<br>In(III): 6.3 µg L$^{-1}$,<br>Tl(I): 8.6 µg L$^{-1}$ | SPCE-CNF<br>Zn(II): 16.9 – 198.3 µg L$^{-1}$,<br>Cd(II): 11.3 – 200.0 µg L$^{-1}$,<br>Pb(II): 8.7 – 200.8 µg L$^{-1}$<br>Bi(III): 56.1 – 200.7 µg L$^{-1}$,<br>In(III): 10.0 – 200.4 µg L$^{-1}$,<br>Tl(I): 21.7 – 274.9 µg L$^{-1}$<br>GSH-SPCE-CNF<br>Zn(II): 24.5 – 198.3 µg L$^{-1}$,<br>Cd(II): 11.6 – 200.0 µg L$^{-1}$,<br>Pb(II): 10.8 – 200.8 µg L$^{-1}$<br>Bi(III): 29.1 – 200.7 µg L$^{-1}$,<br>In(III): 26.4 – 200.4 µg L$^{-1}$,<br>Tl(I): 41.8 – 274.9 µg L$^{-1}$<br>Cys-SPCE-CNF<br>Zn(II): 26.3 – 198.3 µg L$^{-1}$,<br>Cd(II): 10.9 – 200.0 µg L$^{-1}$,<br>Pb(II): 10.3 – 200.8 µg L$^{-1}$<br>Bi(III): 38.0 – 200.7 µg L$^{-1}$,<br>In(III): 18.2 – 200.4 µg L$^{-1}$,<br>Tl(I): 57.8 – 274.9 µg L$^{-1}$<br>Ex-situ-SbSPCE-CNF<br>Zn(II): 14.9 – 198.3 µg L$^{-1}$,<br>Cd(II): 10.7 – 200.0 µg L$^{-1}$,<br>Pb(II): 13.2 – 200.8 µg L$^{-1}$<br>Bi(III): 17.2 – 200.7 µg L$^{-1}$,<br>In(III): 21.0 – 200.4 µg L$^{-1}$,<br>Tl(I): 28.5 – 274.9 µg L$^{-1}$ | - The tongue is successfully applied to the analysis of a complex mixture of metal ions (4 analytes and 2 interferences)<br>- Sb is *ex-situ* coated onto the surface of SPCNFE.<br>- GSH and Cys are immobilized on aryl diazonium salt monolayers anchored to the surface of SPCE-CNF<br>- An orthogonal signal correction coupled with a hierarchical PLS model is selected for the processing of the voltammograms. | [242] |
| MEA and MLAPS | Zn(II),<br>Cd(II),<br>Pb(II),<br>Cu(II)<br>with<br>MEA<br>Fe(III)<br>and | DPASV | --- | Zn(II): 3.4 µg L$^{-1}$,<br>Cd(II): 0.2 µg L$^{-1}$,<br>Pb(II): 0.5 µg L$^{-1}$,<br>Cu(II): 1.8 µg L$^{-1}$<br>Fe(III): 280 µg L$^{-1}$<br>Cr(IV): 26 µg L$^{-1}$ | Zn(II): 10 – 600 µg L$^{-1}$,<br>Cd(II): 1 – 100.0 µg L$^{-1}$,<br>Pb(II): 1 – 200 µg L$^{-1}$<br>Cu(II): 2 – 300 µg L$^{-1}$,<br>$FeCl_3$: $10^{-5} – 10^{-3}$ M<br>$K_2Cr_2O_7$: $10^{-5} – 10^{-3}$ M | - Combining MEA with MLAPS, the full automatic monitor realize stand-alone real-time and in-situ measurements of trace heavy metals.<br>- The working electrode is the mercury coated AuMEA | [243] |

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| | Cr(VI) with MLAPS | | | | | | |
| MEA and an interdigitated electrode pair | Cu(II) | UPD-SV | Artificial Sea water | 0.115 µmol L$^{-1}$ | 0.48 – 3.97 µmol L$^{-1}$ | - A microelectrochemical sensor array for Cu(II) and conductivity suitable for operation in the marine environment are presented.<br>- Two types of sensors are implemented: i) a three-electrode cell made of a platinum working microelectrode array, a Ag\|AgCl reference electrode and a platinum counter electrode; and ii) the impedimetric sensor made of platinum interdigitated electrodes. | [244] |
| MEA and LAPS | Zn(II)<br>Pb(II)<br>Cu(II) | SWASV | --- | --- | 10 to 50 µg L$^{-1}$for Zn(II), Pb(II) and Cu(II). | - A novel hybrid chemical sensor array for heavy metal detection and pH detection with gold MEA and LAPS integrated on the same silicon wafer is presented.<br>- A self-calibration process by multivariate nonlinear regression is used | [245] |
| NEA and LAPS | Pb(II)<br>Cu(II) | SWASV | --- | --- | 20 to 100 µg L$^{-1}$for Pb(II) and Cu(II). | – A novel miniaturized multisensor chip for lead and copper detection and for pH sensing is presented.<br>- This multisensor chip is a simplification and improvement to the previous fabricated integrated sensor [212]. | [246] |

GEC: graphite–epoxy composite electrodes; CB-18-crown-6: 4-carboxybenzo-18-crown-6; CB-15-crown-5: 4-carboxybenzo-15-crown-5; PLS: partial Least Squares; *Ex-situ*-SbSPCNFE: *ex-situ* antimony film electrode; Crown-6-SPCNFE: 4-carboxybenzo-18-crown-6 modified electrode; SPCNFE: screen-printed carbon nanofiber-modified electrode; SPCE: screen-printed carbon electrode; CNF: carbon nanofiber; GSH: glutathione; Cys: L-cysteine; AE: auxiliary electrode; RE: reference electrode; WE: working electrode; MEA: microelectrode array; MLAPS: multiple light-addressable potentiometric sensor; UPD-SV: underpotential deposition-stripping voltammetry; LAPS: light addressable potentiometric sensor; NEA: nanoband electrode array.