

Screen-printed electrodes for environmental monitoring of heavy metal ions: a review

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Abstract Heavy metals such as lead, mercury, cadmium, zinc and copper are among the most important pollutants because of their non-biodegradability and toxicity above certain thresholds. Here, we review methods for sensing heavy metal ions (HMI) in water samples using screen-printed electrodes (SPEs) as transducers. The review (with 107 refs.) starts with an introduction into the topic, and this is followed by sections on (a) mercury-coated SPEs, (b) bismuth-coated SPEs, (c) gold-coated SPEs (d) chemically modified and non-modified carbon SPEs, (e) enzyme inhibition-based SPEs, and (f) an overview of commercially available electrochemical portable heavy metal analyzers. The review reveals the significance of SPEs in terms of decentralized and of in situ analysis of heavy metal ions in environmental monitoring.

Keywords Screen-printed electrodes · Electrochemical detection · Heavy metal ions · Environmental monitoring · Water framework directive · Marine strategy framework directive

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Introduction

Water pollution is a worldwide problem affecting developing and developed countries alike [1] since rapid economic growth has been accompanied by considerable environmental side effects, especially pollution by metals. Heavy metal contaminants are one prevalent type of water pollutant [2] and are among the most important because of their non-biodegradability. The main threats to human health from heavy metal ions are associated with exposure to lead, cadmium, mercury and arsenic [3]. They are persistent in the environment once discharged and removal from source waters is necessary to ensure a clean drinking water supply. The problem of heavy metal pollution arises from several sources. Lead can be present as a result of lead solder in copper piping. Mercury and cadmium can be a result of power plant emissions. Heavy metal ions (HMI) in seas come from both natural processes and anthropogenic activities. Natural processes like atmospheric inputs and aeolian processes set the background values for HMI. With the rapid industrialization and urbanization in coastal regions, anthropogenic inputs are the main sources of pollution in the marine environment, and HMI are increasingly introduced to agricultural land as well as inland and coastal marine ecosystems [4, 5]. Important sources of seawater pollution by HMI in the coastal and bay areas include industrial wastes and liquid effluents and paint degradation of naval ships [6].

Metal ions such as copper, zinc and cadmium at the low concentrations are necessary for both plants and animals as micronutrients and are involved in several biochemical processes [7]. However, at slightly higher concentrations they become toxic for the aquatic ecosystem [5, 8], e.g., copper and zinc are used as a toxicant in antifouling coatings [9].

Therefore, simultaneous and real-time detection of the content and bioavailability of multiple heavy metals in the coastal areas and industrial effluents is required [10].

Two types of water quality criteria are employed for the evaluation of the element toxicity to the biota namely acute and chronic water criteria [11]. Acute criterion is defined as concentration associated with 50 % mortality for a fixed exposure. Chronic values are usually defined as the geometric mean of the highest concentration of a toxic substance at which no adverse effect is observed and the lowest concentration of the toxic substance that causes an adverse effect. The significance of the observed effects is determined by statistical tests comparing responses of organisms exposed to the low-level (control) concentrations of the toxic substance against responses of organisms exposed to elevated concentrations. Data from several species are necessary for the definition of both criteria.

Though water criteria are usually presented as total concentrations of an element in question, it has been established that free concentrations or activities of HMI and not their total concentrations primarily determine their biological availability and consequently toxicity [12, 13]. Such metal ions as copper, zinc, lead and cadmium possess high affinity to the inorganic and organic ligands and sorptive surfaces abundant in the seawater and sediments [5]. Due to this property, activity of these metal ions in natural waters is several orders of magnitudes lower than their total concentrations and controlled by the “metal buffering capacity” of the system [14]. Therefore, activity of the metal cations in the seawater is an indispensable parameter for the evaluation of their toxicity. Currently toxicity of a particular metal is estimated using several parameters such as total metal concentration, pH, total organic carbon, etc.

Monitoring the status of the environment has become a priority in the context of international legislations worldwide, including Europe [15, 16]. Because of their non-biodegradability and toxicity above certain thresholds, HMI such as lead, mercury, cadmium, zinc and copper have been identified as hazardous substances of priority concern for the European marine environment by the Water Framework Directive and are included in Descriptor 8 of the Marine Strategy Framework Directive. Conventional underwater sampling and research has assumed the cost of traditional sampling methodologies (sample return and/or scientist onsite), which tend to be expensive and in addition are not sustainable. Usually, the presence of trace amounts of HMI in environmental samples is determined by spectrophotometric techniques [17, 18]. However, the direct analysis of some complex samples like seawater presents some difficulties due to the high salt content, causing matrix interference and insufficient precision. In such cases, a typical dilution of the

sample may be necessary before the analysis, which in turn can aggravate the problem and leads to poor results. Therefore, the use of in situ new generation sensors in different marine platforms will be necessary in order to reduce sampling and monitoring costs. Thus, there are optical sensors usually based on thin indicator-loaded polymer films or membranes, intrinsic optical properties of the HMI or sensors based on conventional chromogenic and fluorogenic reagents, among others. Oehme and Wolfbeis [19] have treated in detail the basis and analytical characteristics of optical sensors for heavy metal ions. Despite the big potential that optical sensing devices offers, their selectivities and limits of detection should be improved. This can be done through the use of biosensors (i.e., sensors based on enzymes, antibodies, other biomolecules, or even whole cells), and also by making use of new methods of micro-electronics and improved opto-electronic components, which allow minute signal changes to be detected even above a large background.

There are many techniques employed in metal determination (electrochemical techniques, atomic absorption spectrometry, atomic emission spectrometry with inductively coupled plasma excitation, X-ray fluorescence, optical sensors, etc.). Among these, electrochemical analysis can be considered the most powerful technique for in-field analysis, due to the small size of the equipment, easy installation and the possibility of multi-element detection.

Electrochemical detection of heavy metal ions in water samples

A broad overview of electrochemical detection of HMI, mainly lead, cadmium, zinc, copper and mercury among others, in water samples is reviewed. Although there is a great variety of electrodes that have been used as transducers, this report is only focused on the use of screen-printed electrodes (SPEs). The need for decentralised testing of trace metals in connection with environmental field screening and the remarkable sensitivity of electroanalytical procedures, coupled with their compact instrumentation and low power requirements, make them very attractive for the task of in situ metal analysis.

Traditionally, stripping voltammetric techniques, combined with the use of hanging mercury drop electrodes (HMDEs) or mercury film electrodes (MFEs), were the most used for the detection of trace levels of HMI. The anodic stripping voltammetry (ASV) is a very sensitive technique because the accumulation step on the working electrode carried out before the anodic stripping allows pre-concentration of the metals, and the application of voltage pulses during the stripping generates a high signal-to-background ratio. Thus the sensitivity of these methodologies is usually very high. The most common pulse wave forms used to obtain the stripping scan are square wave (SWASV) or differential pulse

(DPASV) (Fig. 1) although another electrochemical technique, potentiometric stripping analysis (PSA), is becoming very popular. Moreover, mercury-based conventional electrodes, such as HMDE [20–22] and MFE [23–28] have traditionally been used in stripping techniques because of their advantages, such as high sensitivity, reproducibility, purity of the surface, high hydrogen over potential, and possibility of amalgam formation. Despite all these advantages, problems remain, related to the use of conventional electrochemical cells and to the need for a de-aeration step. Improvements can be achieved by the elimination of classical bulky electrodes and cells and the use of electrochemical methods less influenced by oxygen interference.

The coupling of disposable SPEs (Fig. 2) with stripping techniques presents an attractive alternative to overcome these drawbacks. The screen-printing microfabrication technology is nowadays well established for the production of thick-film electrochemical transducers. The screen-printing technique uses a woven mesh to support an ink-blocking stencil, and a roller or squeegee is moved across the screen stencil to force or pump ink or other printable materials past the threads of the woven mesh in the open areas. In general, a series of woven meshes is prepared to print the different parts of the electrode. Between printing two ink layers on a substrate, the ink needs to first be solidified through a thermal treatment. Finally, a protective ink coating is used to insulate the conductive track from the electrodes. This technology allows the mass

production of reproducible yet inexpensive and mechanically robust solid strip electrodes. Other important features that these electrodes exhibit are related to the miniaturization of the corresponding device along with their ease of handling and manipulation in a disposable manner. Advantages include the versatility of the design and the possibility of using different inks (carbon, silver, gold, platinum...) that can include nanomaterials, organic compounds or mediators, and the easy modification of their surface. This makes them good candidates as transducers in a wide variety of biosensors: chemical sensors, enzymatic sensors, immuno- and genosensors and aptasensors among others. Several reviews have been published recently where the methodologies and designs of different biosensors based on screen-printed electrodes are discussed [29, 30].

Other advantages of a single-use disposable sensor include elimination of the problems associated with carryover of contamination or biofouling and reducing the fear of expensive damage associated with a reusable sensor. The combination of these devices with portable instruments (Fig. 3) can provide analysers that can be relatively cheap, easy to use, suitable for in field use, and sensitive enough to perform heavy metal traces analysis for an in situ control of pollution.

So this review will focus on the use of screen printed electrodes (SPEs) in the environmental monitoring of HMI. Many kinds of SPEs have been used as transducers, including mercury-coated SPEs, bismuth-coated SPEs, gold SPEs and

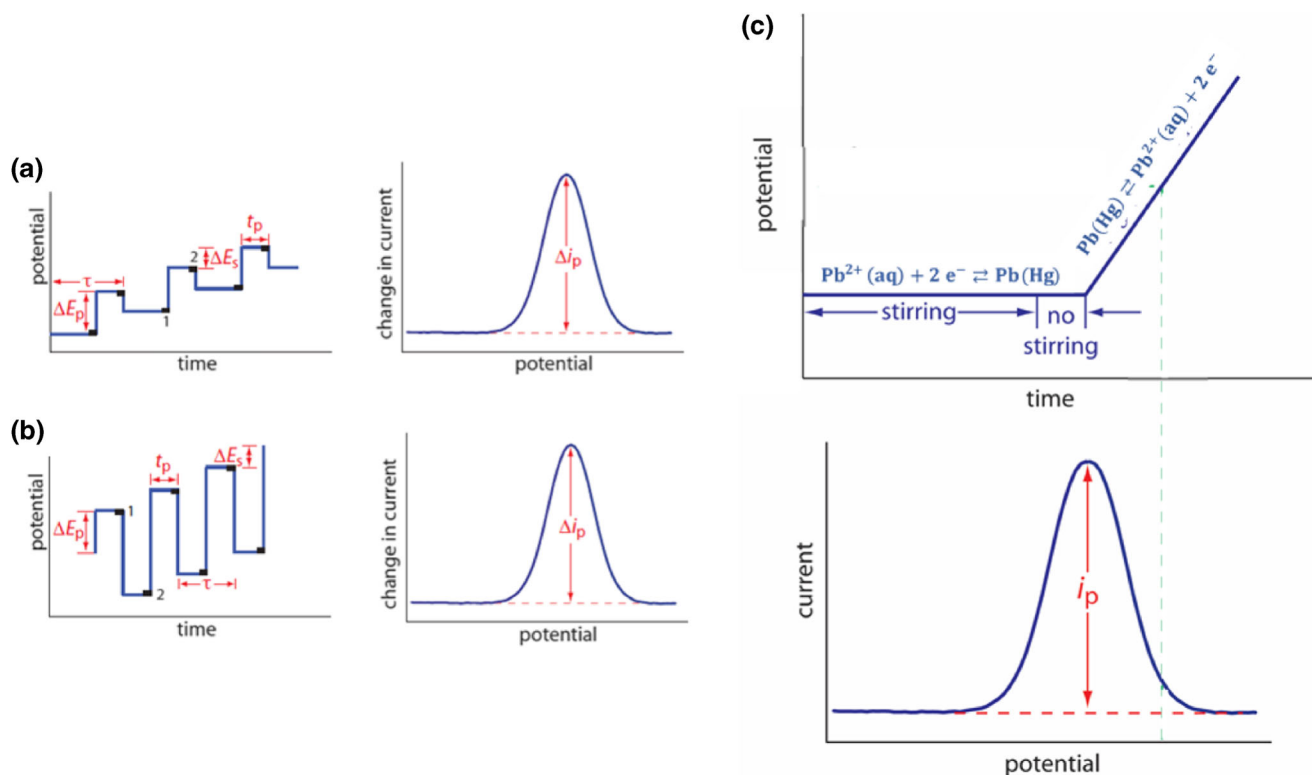


Fig. 1 Potential-excitation signals and typical voltammograms obtained for: **a** differential pulse; **b** square-wave and **c** anodic stripping voltammetry

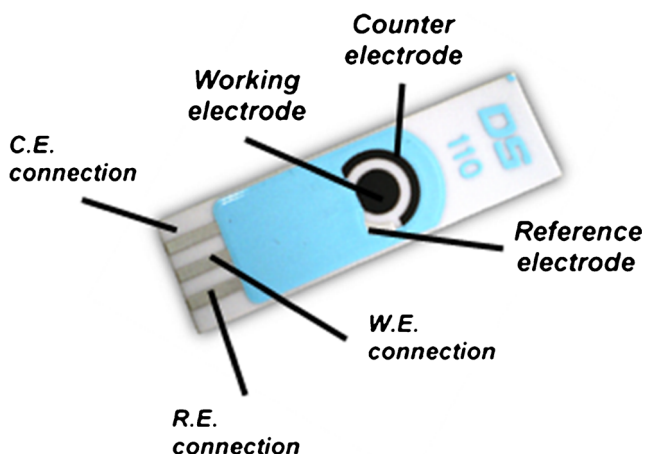


Fig. 2 Screen-printed electrode. *WE* working electrode, *RE* reference electrode, *CE* counter electrode

gold and/or carbon nanostructured SPEs. These are the most common in the literature, but other examples such as unmodified carbon electrodes, chemical-modified SPEs or enzymatic inhibition-biosensors, although less used, will be also included.

Mercury-coated SPEs

Mercury-coated SPEs consist of a very thin layer of Hg atoms adsorbed onto the electrode surface, usually a carbon electrode. So the mechanisms of accumulation and the stripping are the same as those occurring at conventional Hg electrodes. That is, two separate stages are performed, a pre-concentration step to accumulate the analyte at the working electrode, and then electrochemically stripped back into the solution in the current measurement step.

Table 1 provides some examples of the use of mercury-coated screen printed sensors for HMI detection. Some



Fig. 3 Portable hand-held electrochemical instrument to obtain the heavy metal levels

characteristics such as limits of detection and electrochemical techniques used in the anodic stripping are given. SWASV is the most common electrochemical technique and the mercury film can be formed *ex situ* (with medium exchange) [31–36] or *in situ* (the same medium than the accumulation of the metals) [37–39]. In both cases the addition of mercury salts is necessary, usually mercury chloride compounds, so the presence of chloride ions can affect the potential of the pseudo-reference electrode and consequently change the potential of the stripping peak of the HMI. To avoid the handling, transport and disposal of toxic mercury(II) solutions during decentralized measurements, the use of mercury-coated screen-printed sensors, prepared beforehand in the lab and ready to use, was suggested since the coating is pre-deposited on the electrode surface through a mercury oxide precursor containing the working electrode ink [40] or using a membrane as a mercury entrapping system [41, 42].

On the other hand, from Table 1 it can be concluded that the metals more commonly detected in water samples using these kind of electrodes are lead and cadmium, followed by copper and zinc. The main drawback found when a simultaneous determination of lead, cadmium, copper and zinc is carried out [37, 38, 42] comes from the formation of Zn Cu intermetallic compounds that gives a decrease of the Zn stripping peak and at the same time an increase of the Cu stripping peak, and consequently giving failed results. One strategy to solve this problem is the addition of gallium that forms a stronger intermetallic compound with Cu and releases the Zn presented in solution.

Another strategy to improve the sensitivity and the selectivity of the Hg-coated SPEs is the modification with crown-ether compounds for the metal detection [43, 44]. In addition, chitosan can be used for the homogeneous dispersion of MWCNTs [45] for modified SPEs where after mercury is deposited, forming a random array of mercury nano-droplets. This sensor was used for the simultaneous determination of lead, cadmium and copper in river water.

Finally, based on femto second laser ablation technologies, square arrays of 64 microelectrodes (8×8) were made in a polymer substrate and then screen-printed carbon ink [36] (Fig. 4). Because of the small overall surface of screen printed microelectrode arrays (SP μ EA), only a low quantity of mercury (less than 1 μ g) was *ex situ* deposited, and the devices were sufficient to perform a trace analysis of river water close to a zinc mine.

Bismuth-coated SPEs

Despite the excellent performance of mercury based electrodes, because of the inconvenience of the well-known toxicity of mercury, their use is discouraged and may be banned in future regulations and occupational health considerations. In order to overcome this problem, bismuth film electrodes

Table 1 Applications of mercury-coated SPEs to detection of HMI

Metals	L.O.D. ($\mu\text{g L}^{-1}$)	Preconcentration time/s	Electrochemical technique	Sample	Comments	Reference
Pb ²⁺	0.030	600	DPASV or PSA	Urine and drinking water	Hg is preplated ex situ during 15 min at the beginning of each day	[31]
Pb ²⁺ , Cd ²⁺ , Cu ²⁺	0.4, 1, 8	180	SWASV or PSA	–	Hg is preplated ex situ during 2 min	[32]
Cd ²⁺	0.2	60	SWASV	River water	Hg is plated ex situ from an acetate buffer solution containing mercury acetate salt. Semicontinuous monitoring	[33, 34]
Cd ²⁺	0.22	60	SWASV	River water	Hg is plated ex situ from an acetate buffer solution containing mercury nitrate salt. Screen-printed electrode modified by a 200 μL microwell	[35]
Cd ²⁺	1.3	300	SWASV	River water	Hg is plated ex situ from an acetate buffer solution containing mercury nitrate salt. Array electrodes combining screen-printing and fem to second laser ablation technologies	[36]
Pb ²⁺ , Zn ²⁺ , Cd ²⁺ , Cu ²⁺	–	300	DPASV	–	Hg is plated in situ. The formation of CuZn intermetallic complex makes the calibration of Cu and Zn difficult. Gallium addition solves the problem	[37, 38]
Pb ²⁺ , Cd ²⁺ , Cu ²⁺	1, 2, 5	120	SWASV	–	Hg film formed in situ	[39]
Pb ²⁺ , Cd ²⁺ , Cu ²⁺	–	120	LSASV	Lake water	Screen-printed with phenol resin-based carbon ink containing fine particles of mercuric oxide as a built-in mercury precursor	[40]
Pb ²⁺ , Cd ²⁺ , Cu ²⁺	0.3, 1, 1.5	240	SWASV	Azonal collar mining soil and sediment samples	Electrode is modified with a cellulose-derivative mercury coating	[41]
Pb ²⁺ , Zn ²⁺ , Cd ²⁺ , Cu ²⁺	1.4, 4.2, 0.6, 1.3	315	SWASV	Water samples and sediments	Electrode is modified with a cellulose-derivative mercury coating. Automated determination by Sequential Injection Analysis (SIA)	[42]
Pb ²⁺ , Cd ²⁺	1.66, 0.67	120	LSASV	River water	Screen-printed electrode modified by a crown-ether based membrane	[43]
Pb ²⁺ , Cd ²⁺	1.66, 0.67	120	LSASV	Tap water	Screen-printed electrode modified by a crown-ether based membrane. Semicontinuous analysis. Membrane is stable during 42 h	[44]
Pb ²⁺ , Cd ²⁺ , Cu ²⁺	4.77, 1.35, 1.27	300	SWASV	River water	Electrodes are coated with a mixture of multi-walled carbon nanotubes and chitosan followed by adsorption of mercury (nanodroplets)	[45]

SWASV square wave anodic stripping voltammetry, DPASV differential pulse anodic stripping voltammetry, PSA potentiometric stripping analysis, LSASV linear sweep anodic stripping voltammetry, L.O.D. limit of detection

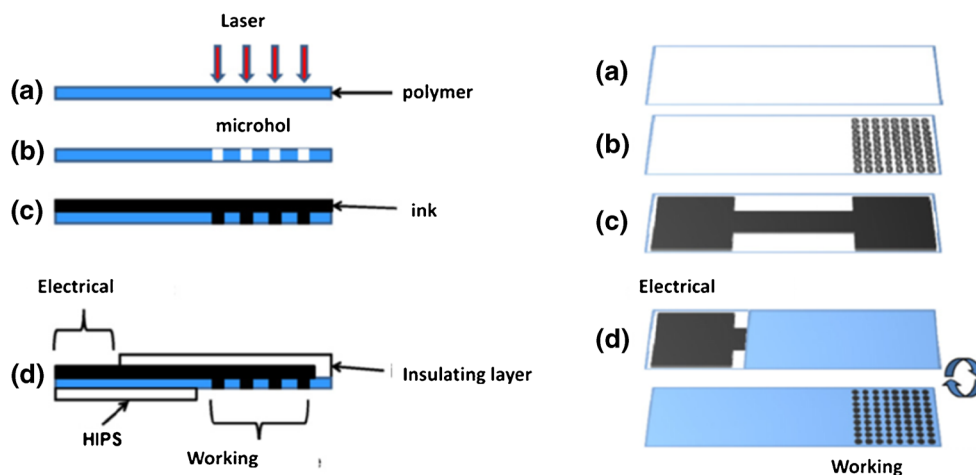


Fig. 4 Side and top views of different steps for microelectrode array fabrication **a** membrane of mylar **b** membrane after laser ablation, **c** ablated membrane after screen-printing, **d** side of screen-printed membrane after insulation showing the electrical contact and the other side of screen-printed membrane after insulation, showing the working surface. Reprinted from *Sensors and Actuators B: Chemical*, Volume 143, Issue 1,

[28, 46] became a good alternative since these electrodes maintain the advantages of mercury coated electrodes and, at the same time, are environmentally friendly. In this sense, a comparative study of the simultaneous determination of HMI in highly saline samples by ASV using both mercury and bismuth film electrodes as working electrodes was carried out [46].

From the year 2000 when Wang et al. published the first bismuth coated electrodes (glassy and carbon fibers) [47], a great number of articles have been published using these kind of electrodes. Several reviews have been published where the applications of these electrodes are discussed [48–50].

In Table 2 a collection of applications of bismuth-coated SPEs to detection of metals in waters is shown. There are two widely used methods for the preparation of the bismuth film: in situ plating and ex situ plating. In the first method, bismuth ions are introduced to the sample solution prior to the analytical procedure and bismuth films are simultaneously plated on the electrode surfaces with the accumulation of analytes [51–53]. This method has serious limitations due to the pH sensitivity of the sample solution, and the influence of interfering species. In the second method, a pre-plated bismuth film electrode is employed as the working electrode [54, 55]. However, a complicated bismuth plating process is required and insufficient adhesion of the film causes degradation of the electrode.

Another option is the bulk method where the modification with bismuth takes place during SPE production and lies in the preparation of a mix between the graphite ink and a determined amount of a bismuth precursor (i.e., bismuth oxide, bismuth aluminate, etc.) before the printing procedure. Bismuth precursor is later electrochemically reduced to metallic bismuth at a selected potential [56–62].

C. Cugnet, O. Zaouak, A. René, C. Pécheyan, M. Potin-Gautier, L. Authier. A novel microelectrode array combining screen-printing and femtosecond laser ablation technologies: Development, characterization and application to cadmium detection, pp. 158–163, Copyright (2009), with permission from Elsevier [36]

In other cases, the electrode surface is modified with bismuth nanoparticles [63]. On the other hand, the use of sputtered bismuth SPEs avoids the use of bismuth plating solutions or bismuth precursors mixed with conductive inks [64].

As in the case of mercury-coated SPEs, the most used electrochemical technique is square wave voltammetry, despite the bismuth-coated electrodes are not sensible to the presence of oxygen in the medium, which would allow the use of other wave formats that do not discriminate the oxygen wave.

The wide use of these bismuth-coated electrodes for metal detection are readily applicable for measurements of electrolytically deposited elements with standard potentials more negative than bismuth. But the quantification of copper, antimony, and bismuth itself (among the metals commonly measured at mercury electrodes) are hampered.

Gold-coated SPEs

Other materials like gold electrodes or gold-coated electrodes have been used as transducers for the detection of HMI. Table 3 summarizes examples of the applications of different gold-coated electrodes. Apart from the detection of lead and cadmium, other metals as mercury, arsenic [65] and antimony [66] can be detected using gold sensors. Moreover, metals such as mercury, arsenic and lead present a process called under potential deposition (UPD). UPD is a fundamental electrochemical process and has attracted a long-standing interest. It happens by the strong interaction between the metal and the gold electrode after the reduction of ionic metal, resulting in the formation of an adlayer. In the case of mercury, this process is of particular importance due to its special electrochemical properties and the amalgam formation. Thus, mercury has

Table 2 Applications of bismuth-coated SPEs to detection of HMI

Metals	L.O.D. ($\mu\text{g L}^{-1}$)	Preconcentration time/s	Electrochemical technique	Sample	Comments	Reference
Pb^{2+} , Cd^{2+} , Zn^{2+}	–	120	SWASV	Tap and waste water	Bi film is plated in situ on the electrode surface	[51]
Pb^{2+}	2	120	SWASV	Surface waters-	Bi film deposited in situ from a Whatman paper disk that is impregnated in Bi and Zn solution. Zn is used as internal standard	[52, 53]
Cd^{2+}	1.3	120	SWASV	River water	Bi film deposited ex situ on microbands SPEs	[54]
Pb^{2+} , Cd^{2+} , Zn^{2+}	–	60	DPASV	–	Bi film is deposited ex situ	[55]
Tl^+	0.03	600	SWASV	–	Bimano powder modified electrode. The interferences of Pb and Cd are solved by adding of EDTA	[56]
Pb^{2+} , Cd^{2+}	8, 16	120	CCSCP	Soil and water samples	Bismuth oxide (Bi_2O_3), 2 % was mixed with graphite-carbon ink to obtain the modified electrode	[57]
Pb^{2+} , Cd^{2+} , Zn^{2+}	10, 5, 30	120	SWASV	River waters	Bismuth oxide (Bi_2O_3), 2 % was mixed with graphite-carbon ink to obtain the modified electrode	[58]
Zn^{2+}	33	180	SWASV	Seawater	Bismuth oxide (Bi_2O_3), 2 % was mixed with graphite-carbon ink to obtain the modified electrode	[59]
Pb^{2+} , Cd^{2+}	2.3, 1.5	300	SWASV	River water-	Bismuth oxide (Bi_2O_3), paste (25 %) modified electrode. The interference of copper is blocked with the addition of ferrocyanide	[60]
Hg^{2+}	0.09	180	SWASV	Tap water and human hair	Bi powder and multivalled carbon nanotubes mixed with graphite-carbon ink and printed on polyethylene terephthalate substrate	[61]
Tl^+	1	120	DPASV	Lake water	Different Bi precursor compounds (bismuth oxide, bismuth alumimates, bismuth zirconate)	[62]
Pb^{2+} , Cd^{2+} , Zn^{2+}	0.9, 1.3, 2.6	120	SWASV	Drinking and waste water	Bi nanoparticles adsorbed on screen-printed electrodes. Use of convective and flow cells. Lower L.O.D. with latter cells.	[63]
Pb^{2+} , Cd^{2+}	0.18, 0.10	360	DPASV	Groundwater	Sputtered Bi SPEs	[64]

SWASV square wave anodic stripping voltammetry, DPASV differential pulse anodic stripping voltammetry, PSA potentiometric stripping analysis, LSASV linear sweep anodic stripping voltammetry, CCSCP constant current stripping chronopotentiometric, L.O.D. limit of detection

Table 3 Applications of gold-coated SPEs to detection of HMI

Metals	L.O.D. ($\mu\text{g L}^{-1}$)	Preconcentration time/s	Electrochemical technique	Sample	Electrode material and comments	Reference
As ³⁺	0.09	130	DPASV	Groundwater	Poly-L-lactide stabilized gold nanoparticles modified screen-printed carbon electrodes. Drop-casting a mixture of Ploy-L-lactide and gold nanoparticles on electrode surface	[65]
Pb ²⁺ , Cd ²⁺ , Cu ²⁺ , Hg ²⁺	0.5, 1.4, 2, 0.9	120	SWASV	River waters	Gold SPE	[67]
Pb ²⁺	2	240	SWASV	Soil and sediments extracts	Gold SPE	[68]
Hg ²⁺	1.1	60	SWASV	Rain waters	Gold SPEs	[69]
Pb ²⁺ , Hg ²⁺	0.6, 0.5	240	PSA	–	Gold coated SPEs. Gold is plating at -0.4 V during 20 min	[70, 71]
Pb ²⁺ , Hg ²⁺	0.5, 1.5	120	SWASV	Tap water	Gold film screen-printed carbon electrodes fabricated by electrodeposition. Thiol magnetic beads are used to separate and preconcentrate the metals.	[72]
Hg ²⁺	0.8	180	SWASV	River and waste waters	Gold nanofilm deposited by vacuum vaporation method on carbon electrode printed on polyethylene terephthalate substrate	[73]
Hg ²⁺	0.22	110	SWASV	Seawater	Gold film deposited in situ on screen-printed carbon electrode. Sequential injection system.	[74]
Pb ²⁺	0.8	120	SWASV	Drinking and tap waters	On line exchange method to diminish chlorides ions effect	[75]
Hg ²⁺	0.2	120	SWASV	Tap and river waters	Gold-sputtered SPEs (50 nm layer). Flow injection analysis.	[76]
Sb ³⁺	0.12	200	DPASV	Seawater	Nanohybrid MWCNT/gold nanoparticles modified screen-printed carbon electrodes	[77]
Cd ²⁺	2.6	100	DPASV	River and tap water	Gold nanoparticles modified screen-printed carbon electrodes obtained by electrodeposition	[78]
Pb ²⁺	0.09	90	SWASV	Water and blood	Gold nanoparticles amalgam modified screen-printed carbon electrodes. The electrodes are modified in two steps. First one for electrodeposition of gold nanoparticles and second for mercury electrodeposition by electrodeposition at constant current	[79]
Pb ²⁺ , Cd ²⁺	0.23, 0.35	240	DPASV	Real waters	Graphene sheet-Nafion-gold nanoparticles nanocomposite film modified screen-printed carbon electrodes	[80]
Cu ²⁺	1.3	120	SWASV	Marine waters	Gold deposited on carbon electrode screen-printed on neoprene. A wearable sensor in marine garments	[81]

SWASV square wave anodic stripping voltammetry, DPASV differential pulse anodic stripping voltammetry, MWCNT multiwalled carbon nanotubes, L.O.D. limit of detection

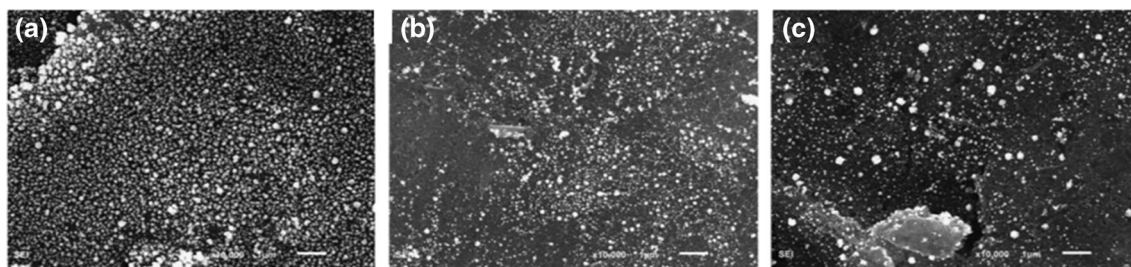


Fig. 5 SEM images of **a** gold nanostructured; **b** gold CNT hybrids SPEs; **c** gold-graphene hybrids SPEs. Magnification factor: 1×10^4

been detected using electrodes such as gold SPEs [67–69] and gold film SPEs electrodes [70–74], gold sputtered [75] as well as hybrid carbon nanomaterials/gold nanoparticles modified electrodes [76] (Fig. 5).

SPEs can be easily modified with different nanomaterials so that after the modification, the resolution of new analytical problems is possible. The unique electronic, chemical, thermal and mechanical properties of nanostructured materials make them extremely attractive for heavy metal electrochemical sensors in comparison to conventional materials. Sensing using nanostructures takes advantage of the increased electrode surface area and fast electron transfer rate, catalytic activity and enhancement of the analytical signal due to its high volume–surface relation compared to electrodes based on bulk materials.

Modification of SPEs with gold nanoparticles can be performed using different methodologies. Thus, screen-printed carbon electrodes have been modified by drop-casting of a gold nanoparticle solution stabilized with Poly-L-lactide on the electrode surface to detect As [65], or by electro-deposition at a fixed potential [77, 78] or at constant current [79].

The use of hybrid nanomaterials have also been applied for metals detection. Thus, the above mentioned sensor device [76] consists of carbon nanotubes modified SPEs, followed by gold nanoparticles electro-deposition at constant current. Another approach where nanomaterials hybrids are used as transducers is that developed by Feng et al. [80] that modifies a screen-printed carbon electrode with a mixture of graphene

sheets/nafion/gold nanoparticles to detect lead and cadmium in real waters with good limits of detection, (0.23 and $0.35 \mu\text{g L}^{-1}$, respectively).

An interesting device based on gold-films deposited on graphite electrodes screen-printed on neoprene has been developed by Malzahn et al. [81]. This wearable sensor is able to determine the presence of copper in marine environments. The device is connected to a miniaturized potentiostat directly on the underwater garment.

Finally, some authors [72, 82, 83] presented the use of magnetic particles to preconcentrate the metals and after to perform the detection using gold film electrodes [72]. This strategy is very interesting because it allows separation and/or preconcentration of the metals before their detection when the samples are very complex or the level of the metals are very low.

Chemically modified and unmodified carbon SPEs

There are very few works related to the use of unmodified and chemically modified screen printed carbon electrodes (SPCEs) in the determination of metals. Graphite materials are preferred due to their simple technological processing and low-cost.

Honeychurch et al. have used screen printed carbon electrodes (SPCEs) to detect lead [84] in pond waters and copper [85] in serum and waters using DPASV. The limits of detection obtained were $2.5 \mu\text{g L}^{-1}$ and $8.2 \mu\text{g L}^{-1}$, respectively. Guell et al. [86] determined simultaneously lead and cadmium



Fig. 6 **a** PDV 6000 plus from Modern Water [102] **b** Heavy Metals HM-3000P from Skyray Instruments [103] **c** Nanotek2000 from Labsun Co [104] **d** Metalyser HM1000 from Trace2o [105]

Table 4 Comparison of portable heavy metal analysers

Analyser	Working electrode	Heavy metal ions	Detection limit	Analysis time
PDV6000 ^a	C or Au	As (III), As (total), Cd, Pb, Cu, Zn, Hg, Cr, Ni, Zn	5 ppb	5–10 min
HM3000P ^b	C or Au	Cu, Cd, Pb, Zn, Hg, As, Cr, Ni, Mn, Tl, Fe, Co, Ni	1 ppb	5 min
Nanotek2000 ^c	C	Cu, Zn, As, Hg, Cd and Pb	0.5 ppb	5 min
HM1000 ^d	C or Au	As (III), As (total), Cd, Pb, Cu, Zn, Hg, Cr, Ni, Zn	5 ppb	5–10 min

^a Modern Water^b Skyray Instruments^c Labsun Co^d Trace2o

in seawater using SPCEs. In this case the limits of detection achieved using SWASV were 1.8 and 2.9 $\mu\text{g L}^{-1}$ for an accumulation time of 2 min. Aragay et al. [87] studied the effect of temperature upon the electrochemical stripping performance of a heavy metal sensor based on carbon nanoparticles. The multi-detection of cadmium, lead, copper and mercury ions is more effective because of the greater surface area available for the metals deposition and the electron transfer enhancement due to the increase of edge-like planes. Another cause can be a faster deposition of the metals because at higher temperatures the ions' mobility increases.

With respect of chemically modified SPCEs, a variety of compounds (from complexes to polymers) have been used to modify the SCPEs with the goal of pre-concentrating the metals before their detection or in order to improve the selectivity of the method. Thus cation exchange resin modified SPEs have been used to determine copper [88] with a limit of detection of 0.5 $\mu\text{g L}^{-1}$ for an accumulation time of 10 min.

Sommers et al. have used polyaniline (PANI), polyaniline-poly(2,2'-dithiodianiline) (PANI-PDTDA) or PANI-methylene blue [89–91] to detect metals (mercury, lead, cadmium and nickel) obtaining a limit of detection in the case of mercury of 56 $\mu\text{g L}^{-1}$ for 120 s and DPASV as electrochemical techniques.

Chitosan, poly-[μ -1-4]-2-amino-2-deoxy-d-glucopyranose (CTS), can form stable chelates with many transition-metal ions through hydroxyl and amino groups. CTS and its derivatives have been used for the electrochemical determination of metal ions SPCEs for the simultaneous determination of lead, copper, cadmium and mercury with pre-concentration time of only 30 s [92]. The stability of this sensor was tested for 6 months. This chitosan modified sensor retains simultaneously the chlorocomplexes of lead, copper, cadmium and mercury achieving limits of detection of 3.4, 5, 5 and 2 $\mu\text{g L}^{-1}$.

Finally, Arduini et al. [93] have developed a carbon black and thiocholine modified SPE to detect mercury. Thiocholine is an electroactive compound but when it forms a complex with mercury, it loses its electroactivity, decreasing the signal. The limit of detection obtained in this case was 1 $\mu\text{g L}^{-1}$.

Enzyme inhibition-based biosensors SPEs

Biosensors based on the principle of enzyme inhibition have been applied for a wide range of significant analytes such as organophosphorous and organochlorine pesticides, derivatives of insecticides, HMI and glycoalkaloids in a wide range of samples [94]. In general, the development of these biosensing systems relies on a quantitative measurement of the enzyme activity before and after exposure to a target analyte.

Although several enzymes have been used to fabricate the inhibition-based biosensors to detect HMI, the most popular is urease [95–99]. Rodríguez et al. [95, 96] have developed amperometric urease-glutamic dehydrogenase based sensors for detection of copper and mercury. The sensor for the monitoring of urease activity was made feasible by coupling the urea breakdown reaction catalysed by urease to the reductive amination of ketoglutarate catalysed by glutamidedehydrogenase (GLDH). The ammonia provided by the urea conversion is required for the conversion of ketoglutarate to glutamate with the concomitant oxidation of the NADH cofactor. When copper or mercury is presented in the sample, the urease is inhibited and the ammonia production is reduced, and thus NADH oxidation occurs at a lower rate. There is a detection limit of 7.2 $\mu\text{g L}^{-1}$ and 8.5 $\mu\text{g L}^{-1}$ for mercury and copper, respectively, whereas other metals such as cadmium or zinc produce enzyme inhibition in the range 1–30 mg L^{-1} , with limits of detection of 0.3 mg L^{-1} for cadmium and 0.2 mg L^{-1} for Zn. The total analysis time is 15 min including the inhibition time.

Another amperometric urease-based sensor has been developed by Domínguez-Renedo et al. [99]. The sensor is fabricated using gold nanoparticles modified SPEs and urease. The presence of mercury ions provokes the inhibition of the urease due to their binding to thiol groups of protein aminoacids habitually forming the active centre of the enzyme. In this case the limit of detection obtained for mercury is 11 $\mu\text{g L}^{-1}$.

Other urease-sensors [97, 98] have been developed but based on potentiometric measurements. In these cases the sensors are modified with ruthenium oxide that is sensitive to pH

changes. The inhibition of the urease by silver or copper provokes a decrease of ammonium and consequently a pH change. The main drawback of these sensors is the long analysis time because the inhibition time alone is about 30 min.

Other examples of enzyme inhibition-based biosensors that have been developed were a glucose sensor to detect mercury, silver, copper and nickel [100] in a flow system or an acetylcholinesterase-sensor [101] that was used to detect arsenic in tap water.

Despite the considerable research activity devoted to the development of biosensors based on enzyme inhibition, analytical applications are still limited since these sensor technologies are not usually able to discriminate various toxic compounds in the same sample. In particular, the simultaneous presence of HMI and pesticides in contaminated samples provides a challenge for their use for purely regulatory purposes where a specific analyte must be determined with a prescribed accuracy. However these devices can be used as alarm systems or as indicators of total contamination of a particular sample.

Commercial electrochemical portable heavy metal analysers

Limits on HMI in waste water and drinking water are often stated in parts per billion (ppb) and are heading in only one direction: down. Current techniques for detection of HMI in the low ppb range, such as inductively coupled plasma – mass spectrometry (ICP–MS), are expensive, requiring a great investment. These instruments are operated by a trained scientist and remain stationary once installed. Extensive sample preparation may be required and a single mislabelled sample can result in excessive downtime. These workhorse instruments excel at metals analysis, however a method simpler in implementation is advantageous.

A portable alternative would allow for in situ analysis in real time without expensive sample transportation and preparation. Contaminants could be monitored on a regular basis and high contaminant concentrations can be detected before harm is done. Such metal test kits are currently available. Most of them are based on voltammetry technology but there are also analysers based on colorimetric principles.

Addition of multiple reagents may be necessary, the test procedure for each metal is different, and the detection limits are usually not single ppb level. The USEPA's (US Environmental Protection Agency) Maximum Contaminant Limits for Lead and Mercury (inorganic) are currently 15 ppb and 2 ppb, respectively. Many colorimetric test kits fail to test below these levels.

Figure 6 shows some of the portable heavy metal analyser devices currently available on the market based on Anodic Stripping Voltammetry (ASV), while Table 4 lists some of

their characteristics. Each of these devices offer portability, multi analyte detection, (relatively) fast detection time, ease of use, GUI's and ability to store data and transfer results to a PC.

Conclusion

Screen printed bare electrodes or modified ones with mercury, bismuth or gold materials are used for the detection of HMI in environmental water samples. The small size of screen printed electrodes, low cost and no need of cleaning procedures make them an ideal candidate for the development of in situ heavy metal analysis. Anodic Stripping Voltammetry by using Square Wave Voltammetry or Potentiometric Stripping Analysis are the electroanalytical techniques most used in heavy metal detection methodologies providing sensitivities in the low ppb level as requested by Environmental regulations. Although SPEs are well suited for these applications, there is not any heavy metal portable analyser in the market based on these electrodes. Conventional glassy carbon or gold solid electrodes are still preferred in commercially available equipment.

Since lead, mercury, cadmium, zinc and copper have been identified as hazardous substances of priority concern for the European marine environment by the Water Framework Directive and are included in Descriptor 8 of the Marine Strategy Framework Directive, more work is ongoing to adapt heavy metal portable analysers to sea water based matrixes. Screen printed based devices are expected to play a key role within this topic.

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