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Chapter

Electrochemical Detection of Heavy Metals Based on Nanostructured, or Film-Modified Paper Electrodes

Alberto Sánchez Calvo and María del Carmen Blanco Lopez

Abstract

Heavy metals have a huge impact on the environment due to their toxicity and bioaccumulation capacity. A great variety of methods can be used to the determination. The electrochemical methods are one of the best options due to their sensitivity, selectivity, and rapidness. They are based on the use of electrochemical cells made of different materials depending on the analyte to determine. An eco-friendly cheap option that has earned big importance is paper-based electrodes, which are formed by a cellulose matrix modified with conductive inks. Carbon ink is the most used, and it can be modified with nanoparticles to increase sensitivity. Alternatively, metallic surfaces or “films” such as mercury or bismuth can improve the determination of heavy metals because of their interactions with the film. This chapter focuses on the methods to determination of heavy metals based on their affinity with different nanomaterials or films on low-cost electrode substrates.

Keywords: paper-based, heavy metals, nanomaterials, films, bismuth

1. Introduction

Heavy metals group are a group of metals, semimetals, or even non-metals, which can be related because of their density or molecular weight [1, 2]. They all have in common high toxicity and nonbiodegradable nature. Each one of them has a wide range of uses (pesticides, paints, fertilizers, batteries, or industrial manufacturing). However, their toxicity and bioaccumulation capacity are too dangerous not only for the environment but also for human health. The heavy metals usually being analyzed to test new monitoring methods are mercury, lead, cadmium, and arsenic.

Mercury is possibly one of the most studied heavy metal. Its toxicity in elemental or inorganic form can affect dangerously human health, damaging brain, kidney, and lungs, and its bioaccumulation capacity in methylmercury form makes it mandatory to be controlled in the environment (soil, water). Europe legislation limits the use of mercury in products and the exportation of it to other countries for mercury and mercury compounds [3]. In the case of mercury in drinking waters, the

Environmental protection agency (EPA) in 1991 has set a maximum concentration of Hg^{2+} of 2 ppb, while the Commission Regulation (EU) 2022/617 has set limits of 0.50 mg/kg in fish [4].

Lead has an impact on human health, interfering with enzymes of the cells in the brain, kidneys, heart, acting as a carcinogen, and causing cardiovascular and brain damage. The European Commission Regulation (EU) 2021/1317 has set limits of 0.10 mg/kg in cases of bovine and pig meat. Moreover, lead can also develop neurotoxicity in young children, and consequently, a limit of 0.02 mg/kg has been set for raw and 0.01 mg/kg for infant milk [5].

Cadmium toxicity is related to lungs, liver, and kidneys, generating chronic poisoning because of its slow release from the body. Cadmium can be present in water, soil, and food with limits of 0.005 mg/L in water and values between 0.02 and 0.2 mg/kg for different types of foods [5, 6]. There are also regulations of cadmium in the case of fertilizers [7].

Arsenic in inorganic form is highly toxic affecting skin, lungs, and livers causing seizures, and in high levels coma and death. Limits for arsenic (inorganic) in rice have been settled to 0.20 mg/kg and 0.10 in the case of food for young children [8].

There are a huge variety of analytical techniques for the determination of heavy metals, such as atomic fluorescence spectrometry, inductively coupled plasma with mass spectrometry (ICP-MS), or electrochemical analysis. All of them have high sensitivity and selectivity. However, electrochemical methods have also advantages, such as portability to make *in situ* analysis, and miniaturization, needing less volume of reagents to work, becoming therefore a cheaper and sustainable alternative.

Electrochemical methods are based on the use of a working electrode, which is a conductive transducer in which the heavy metal can be oxidized or reduced. Mercury was the first material used in a dropping mercury electrode. It has a renewable electrode surface with a broad cathodic potential window and a good affinity for metals, such as lead or cadmium, which increases their sensitivity, but its high toxicity has triggered the search for safer and more eco-friendly alternatives. Nowadays, carbon is usually the most used material for electrochemical sensors [9] but there are other alternatives, such as gold, silver, or platinum. One of the main advantages of carbon is the possibility of easy modification with different types of materials or polymers, depending on the objectives [10, 11]. It can be modified with nanomaterials to increase their conductivity and sensitivity, or in other cases, with films of materials such as bismuth to increase the selectivity and sensitivity of the analyte based on a strong interaction with it.

Different techniques can be applied depending on the range of concentrations needed or the selectivity required. Potentiometry is considered highly selective because it relies on the use of ion-selective electrodes (ISEs), which are composed of a membrane with a high affinity for the analyte. The interaction of the membrane with the sample and an inner solution of the ion generates a potential. This can be measured and related to the concentration by Nikolsky equation (Eq. (1)).

$$E = L + \beta \left(\frac{0.05916}{z_i} \right) \log \left[a_i + \sum_j \left(k_{i,j}^{pot} \cdot a_j^{z_i/z_j} \right) \right] \quad (1)$$

where E is the potential, L and β are constants, a_i is the activity of the ion to determine and a_j is the activity of an interference; z_i is the charge of the ion, and $k_{i,j}^{pot}$ is the potentiometric selective coefficient for the ion analyte and the interference.

Anodic stripping voltammetry is also used in the determination of heavy metals. With this technique, a preconcentration step is done previously to an oxidation step, in order to increase the sensitivity [12]. The stripping voltammetry can be done in linear sweep voltammetry (LSV), cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV). Different equations are used depending on the technique. For example, in linear and cyclic voltammetry, a linear potential sweep is applied to the electrode, and Randles-Ševčík equation (Eq. (2)) is used, where A is the electroactive area, C is the concentration of the analyte, v is the scan rate, n is the number of electrons, and D is the diffusion coefficient.

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D d^{\frac{1}{2}} C v^{\frac{1}{2}} \quad (2)$$

At DPV and SWV, different modulations are used in order to apply the potential to the electrode (see **Figure 1**): small pulses of fractions of a second at DPV, and a square function combining pulses of oxidation and reduction at SWV. The latter is especially favorable for reversible processes. In all cases, the peak intensity is also proportional to the area of the electrode and the concentration. By preconcentrating the analyte on the area of the electrode, an increase in the concentration is observed, which makes an increase in the intensity studied.

The new trends in the electrochemical determination of heavy metals are aligned with the Sustainable Development Goals, especially with the 6th (clean water and sanitation) and 15th (life on land), to develop new fast analysis methods to control the waste in the environment. Thus, one of the objectives for the development of new electrochemical transducers is their miniaturization, in order to save reagents. Initially, electrochemical cells were composed of three macroscopic electrodes with volumes of mL. However, in the last years, electrochemical cells with microliters volumes have become widely popular.

Apart from miniaturization, there is an interest in green and cheaper alternatives as it is being described in Sustainable Development Goal 12 (Responsible consumption and production). This would be attractive to extend the use of electrochemical sensors in under developed countries, but also in developed countries. Electrodes made of cellulose or paper-based electrodes have earned a significant relevance [13]. Paper is a cheap and abundant material, composed mainly of cellulose fibers or nitrocellulose, whose porosity allows hydrophilic samples to diffuse along the matrix by capillarity. Besides, paper can be modified with materials such as wax to create hydrophobically barriers and circuits, where samples diffuse and react with reagents previously immobilized within the cellulose matrix can be designed [14]. As a result, cheap and easy-to-use platforms with a rapid response for different applications, such as point-of-care-testing, can be obtained. Optical paper-based sensors are usually the most used, especially those with colorimetric detection. However, electrochemical paper-based sensors are becoming an improved alternative. Paper can be modified not only with biomarkers or wax but also with conductivity inks to form an electrochemical transducer. The resulting platform will have the capacity to determine analytes electrochemically active, such as heavy metals. Moreover, conductive markers can be used in voltammetric or amperometric biosensors, increasing the sensitivity in comparison with colorimetric biosensors [15].

Paper electrodes can be modified in the same way as commercial screen-printed electrodes. Nanomaterials are one of the most common options. Their optical properties make them be used as an indicator for colorimetric analysis, while their conductive properties help to increase the sensitivity in electrochemical paper-based

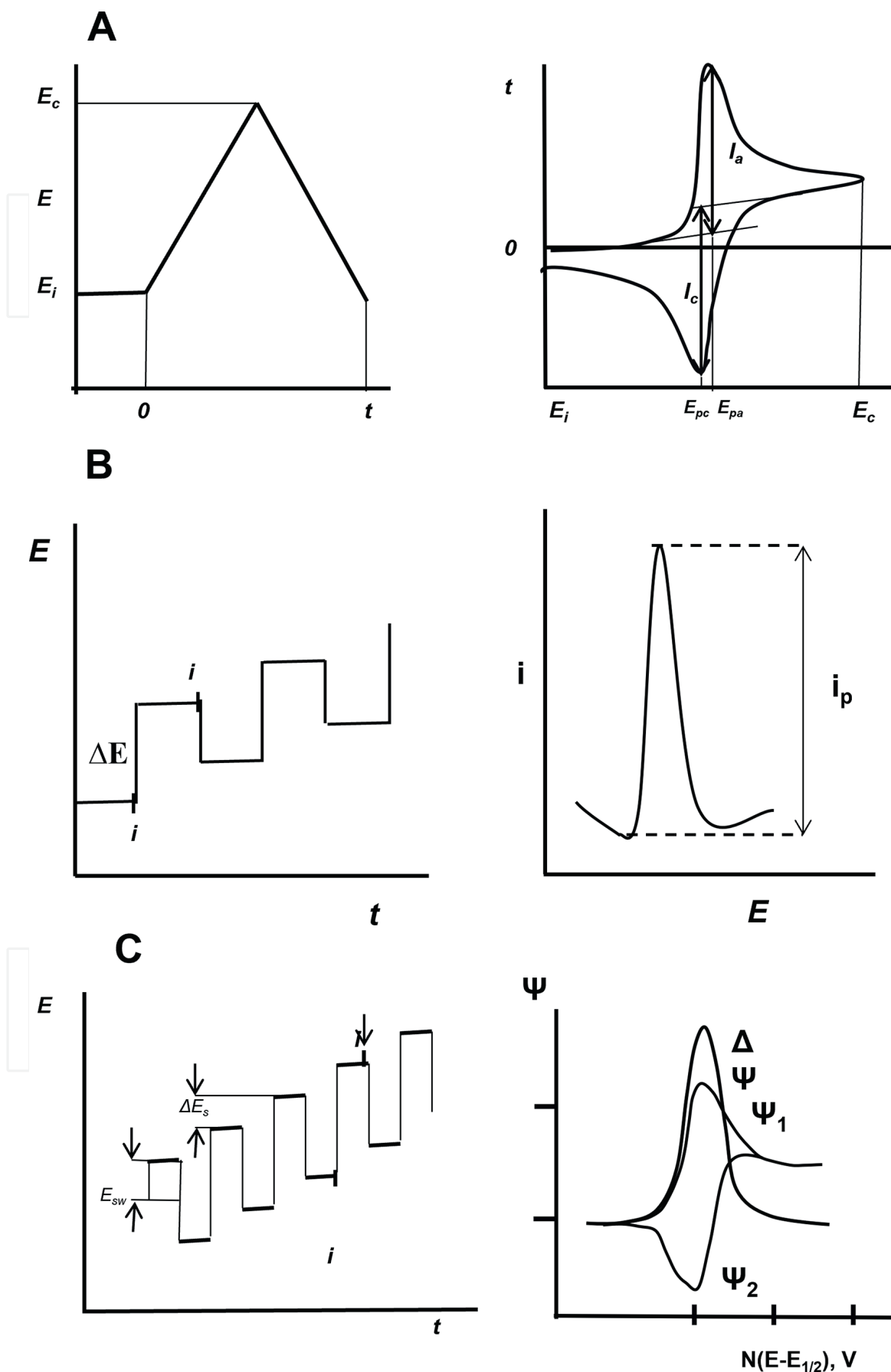


Figure 1. Modulations applied and voltamperograms obtained respectively in (A) cyclic voltammetry, (B) differential pulse voltammetry, (C) square wave voltammetry.

electrodes [16–18]. This is due to their capacity to increase the signal-to-area ratio. Finally, their compatibility with bioreagents allows them to be functionalized with antigens, antibodies, or proteins. Nanomaterials can be directly deposited into the matrix cellulose or electrogenerated on the working paper electrode. On the other hand, paper electrodes can be modified by metallic surfaces or “films” by electrodeposition. Films can be made from different materials, such as mercury or bismuth, which improve the sensitivity and selectivity of heavy metals based on their affinity with the metal film.

In this chapter, we focus on paper-based electrodes used to measure heavy metals and the different modifications were done to improve the sensitivity or selectivity, such as the modification with nanomaterials (graphene and gold nanoparticles) or the electrodeposition of metallic films.

2. Heavy metals determination by paper-based electrochemical cells

Electrochemical cells based on paper can be entirely designed manually, or just a part and they can be coupled to commercial platform. Different configurations can be found in the literature for the final device, depending on the analytes of interest, the detection procedure, the portability capacity, or the easy-to-use requirements.

Two different approaches can be followed: partial or total paper-based platforms.

2.1 Partially electrochemical paper-based platforms

The first part of this chapter focuses on paper devices with a function and an attachment to a commercial platform. There are sustainable interests to choose a paper substrate as a transducer: in this case, the supporting cell can be reused without any contamination, applying cleaning steps after the measurement, and saving reagents and time. In addition, paper working electrodes could be used to test how viable is the protocol before designing a full paper-based platform.

Reports with different protocols and analytes can be found in the literature. For instance, Kingkan Pungjunun designed a paper-based analytical device by an origami method coupled to a boron-doped diamond electrode (BDD) [19]. The BDD was used as a working electrode, whereas the paper-based device was placed on top to form a disposable electrochemical cell. Their main objective was the determination of total arsenic (As (III) + As (V)). Using a wax printer, the paper matrix was modified with wax, which was melted to create hydrophobic zones. After that, conductive inks (silver and carbon) were added to form reference and counter-electrodes. In the end, a paper device with three different chambers was created, each one with a purpose. First, there is the working electrode zone coupled to the BDD, the modification zone, and the detection zone. These last two zones consisted of an auxiliary and reference electrode, so they can form an electrochemical cell with the BDD. With these designs, the working electrode could be modified with nanoparticles and the sample could be analyzed just by unfolding and refolding the different zones. This way, *ex situ* steps that can complicate the measure were excluded. The electrodeposition of gold nanoparticles on the BDD with the modification chamber generated a more conductive transducer with higher selectivity for arsenic, which was then measured in the determination zone by square wave voltammetry with limits of detections of 0.02 µg/mL. Commercial rice samples were measured, and their results compared by an ICP-OES analysis showed no significant difference between both methods,

confirming the accuracy. An interferences study was also done, and copper was identified as a possible interference. However, it could be corrected by adding ferricyanide, obtaining a low-cost paper-based device with high sensitivity for arsenic determination.

Paper electrodes can also be modified with metal layers instead of nanomaterials. Rochelle Silva et al. designed a potentiometric sensor on a glassy carbon electrode coupled to a paper substrate, with the aim of using its filtering properties for the complex matrix of environmental samples. This way they protected the ion-selective membrane of the electrode [20]. However, the negative charges of cellulose can interact with the metallic ions obtaining a super-Nernstian response in the potentiometric analysis. In order to correct the response, paper substrates were modified with gold layers as a spacer between heavy metals and cellulose fibers. Palladium and platinum were also tested showing similar improvements in comparison with unmodified paper-based electrodes.

These last reports were based on a paper electrochemical cell coupled to a commercial working electrode or a selective membrane electrode. However, there are research works based on the opposite: paper working electrodes coupled to a commercial cell. E. Nunez-Bajo et al. designed a paper-based working electrode to be used on a commercial screen-printed electrode. Wax printing and carbon inks were also used, but in this case, a disposable working paper electrode was created [21]. The paper electrode was coupled to the screen-printed transducer by means of an adhesive, so the electrochemical cell was constructed by using its auxiliary and pseudo-reference electrodes. After the measurements, the paper electrode can be disposed of without altering the screen-printed electrode, and therefore, it can be reused again. The conductivity of the carbon paper electrode was improved by the electrodeposition of gold nanoparticles by chronoamperometry and cyclic voltammetry. After the electrodeposition, the paper electrodes were washed and peeled off from the screen-printed platform. Subsequently, they were placed on another clean screen-printed electrode to confirm the presence of nanoparticles in cellulose fibers instead of the working electrode of the previously used screen-printed working electrode.

In this case, total arsenic and arsenic (III) were measured by chronoamperometry by preconcentrating first arsenic (III) in a reduction step to arsenic (0), and then reoxidating it. The limit of detection obtained for total arsenic was (LOD) 2.4 $\mu\text{g/L}$ and 2.2 $\mu\text{g/L}$ for As (III). Real wine samples were measured and the results were validated by comparison with those of an ICP-MS method. No significant differences between them were found, and the viability of this quicker, cheaper, and easy-to-use method that consumes less reagents than the reference ICP-MS method. The paper working electrode coupling avoids the contamination of the screen-printed platform and can be easily disposed of away without any further treatment.

These two mentioned reports for arsenic determination with gold nanoparticles showed that different devices can be adapted to the same principle with good results, demonstrating the versatility of paper electrodes [19, 21]. Paper electrodes are not only limited to a single analysis but they can also be modified in different ways for multiplexed determinations.

The design described above was also used in other reports. A. Sánchez-Calvo et al. investigated the modification properties with carbon nanomaterials (graphene oxide and nanofibers) and compared the results with those of the nanostructuring of paper electrodes with gold nanoparticles (AuNPs), in order to develop a method for mercury determination in river water samples [22]. Different combinations of nanomaterials were tested. The best option was the use of carbon nanomaterials as

a conductive matrix combined with gold nanoparticles, as a selective transducer for mercury. Anodic stripping voltammetry was used. Mercury was preconcentrated on the surface on the basis of its high affinity for gold nanoparticles, and then it was redissolved. Three different oxidation peaks were observed, which could be assigned to the interaction of mercury with gold nanoparticle, gold nanoparticle nearly covered, or mercury without any interaction with gold nanoparticle, respectively [23]. The limits of detection obtained were 30 nM and spiked river samples could be analyzed with recoveries of 91%.

In this study, not only gold nanoparticles and carbon nanomaterials were tested. Cellulose fibers were also modified with metals like mercury or bismuth to form a conductive “film” with applications for the determination of heavy metals [24]. Solutions of bismuth (III) and mercury (II) were used to form a film by electrodeposition and compare their affinity for Cd (II), Pb (II), In (III), and Cu (II). The results show that mercury has higher sensitivity than bismuth films. Moreover, a bismuth oxidation peak overlapped the copper signal, impeding its determination. Water samples were spiked with Cd (II), Pb (II), and Zn (II) salts to avoid the formation of intermetallic compounds. Recoveries obtained on mercury and bismuth films were around 99 and 88%, respectively, confirming the better sensitivity of mercury films. Nevertheless, the use of bismuth films could be more attractive since they have not been found toxic to the environment. With this option, the lineal range of concentrations for heavy metal determination is around mg/L or “ppm.” This limitation on the sensitivity would mean that those sensors would not be useful for trace-level analysis without a preconcentration treatment.

2.2 Full made paper-based platforms

There are different techniques to create entire paper-based platforms. Screen printing is the most frequently used for electrochemical cells. M. Medina-Sánchez *et al.* developed a lateral flow paper-based sensor with a flow channel in which the sample diffuses and gets in contact with a screen-printed electrode. This was formed by a graphite area acting as a working and counter electrode, with a silver/silver chloride as a reference electrode [25]. This design benefits from the capillarity of the cellulose acting as a filter of solid particles in water samples and increases the sensitivity because of the continuous flow of the sample along the electrodes during the deposition step.

In this case, the sensor must be disposed of after the measurement, because a successful cleaning step could not be developed. However, this work is still interesting as a source of inspiration for low-cost paper-based sensor technology. Cadmium (II) and lead (II) were determined with limits of detection of 11 and 7 ppb, respectively. Solutions with both metals showed changes in potential probably due to the formation of intermetallic species or alloys, but sensitivity was not affected. Samples of complex matrixes like mud or seawater were analyzed in order to test the filtering capacity, confirming that the protocol was efficient and there was no need for a pretreatment step. Therefore, this disposable quick sensor was valid as a single-use device. In another report, Yue-Hong Pang *et al.* designed a portable sample cell made of 1 mm thick double-sided adhesive tape, which was 8 mm punched and aligned with a platinum sheet with an 8 mm hole. On the bottom layer of the portable cell, an auxiliary electrode (carbon) and a reference electrode (Ag/AgCl) were integrated [26]. Apart from the cell another layer formed by a carbon paper acting as a working electrode was modified by gold nanoparticles (AuNPs) by electrodeposition

followed by addition of a metal-organic framework (Co-MOF-NH₂) material. After the modification procedure, the two parts were combined in a sensor and optimized to quantify Cd (II) and Pb (II). The limits of detection (LOD) found were 0.07 ng/mL and 0.011 ng/mL, respectively, and these metals could be successfully determined in real food samples (grain, juice, and vegetables). The reusability was found acceptable, with no high deviation for repeated measurements.

Full paper platforms were also used by Huang et al. [27]. These authors designed a paper-based electrochemiluminescence biosensor adapted to the determination of Ni (II) and Hg (II) [27]. The biosensor had two different channels, each one adapted to the determination of an analyte. In this case, silver nanoparticles (AgNPs) and cubic Cu₂O were added to increase the conductivity and as a catalyst for hydrogen peroxide in each case. The origami design has the possibility of an auto-cleaning procedure, lowering the number of steps needed and reducing the measurement time. The limits of detection found for Ni (II) and Hg (II) were 3.1 nM and 3.9 pM, respectively. Real river samples were spiked and analyzed with recovery values from 96 to 104% confirming the reliability of the platform. The different channels prepared confirmed the good features of the cellulose matrix and the suitability of the capillarity as a driving force for testing different analytes in different procedures with the same sensor at the same time.

Qiu-Mei Feng et al. designed a disposable electrode to determine heavy metals by anodic stripping voltammetry [28]. The electrode was composed of conductive carbon tape on an indium tin oxide (ITO) glass as a way to enhance the conductivity. The carbon working electrode was modified with bismuth by electrodeposition, in order to increase the stripping analysis with successful measurements of Zn, Cd, and Pb ions. Apart from the good sensitivity and capacity to distinguish among heavy ions, the low-cost and low volumes are also important highlights to consider. Another full paper-based electrode modified with bismuth film was developed by D. Soulis. In this report, the channels for fluid flow were marked by a pen instead of melted wax and combined with a graphite screen-printed electrochemical cell for the determination of Pb (II) and Cd (II) [29]. Here, instead of forming the bismuth film in a procedure apart from measuring the sample or what it can be called in a “*ex situ*” way, bismuth and heavy metals were stored in the same solution. By applying a reduction potential, the three elements were simultaneously reduced together, forming metal alloys that were subsequently oxidized. The limits of detection obtained were 2.4 µg/L for Cd (II) and 4.2 for Pb (II), which are lower than the limits for drinking water in the EU and USA. This method has the advantage of saving time and reagents because all the requirements for preconcentration are included in a single step.

Paper-based sensors are usually coupled to a single detection system. However, their versatility and flexibility are suitable for the design of multiple detection systems. Habdias A. Silva-Neto et al. designed a paper-based plug-and-play platform with both colorimetric and electrochemical sensors for the detection of metals [30]. The sensor consists of two different paper platforms, each one with one detection method and a polymer substrate. The polymer was prepared by die cutting, so it could be connected with the colorimetric and the electrochemical sensor on each extreme of the template. The colorimetric paper platform was designed in a tree shape containing three channels with three different zones (pretreatment, colorimetric, and waste zone), whereas the electrochemical zone is formed by a self-made screen-printed paper-electrode composed of graphite ink containing multi-walled carbon nanotubes (MWCNT). Those platforms can be reversibly assembled using a plug-and-play mechanism and using the same drop of sample. In conclusion, both detection

measurements can be done at the same time. This way not only heavy metals, such as Cd (II), Pb (II), Zn (II), and Ni (II) can be determined, but also other metals, such as Fe (II) and Cu (II). The analysis of river samples was validated by comparison with results obtained by atomic absorption spectrometry. This method combined the flexibility of using paper platforms with their modification properties to detect multiple analytes by different principles. Miniaturization is also an important advantage, allowing to use lower volumes than the reference method.

Platform	Type	Analytes	Linear range	Limit of detection (LoD)
AuNPs paper filter/ boron-doped diamond electrode	Partially electrochemical paper-based platform	Total As	0.1–1.5 µg/mL	20 ng/mL
AuNPs + Working paper electrode /SPCE commercial		As (III)	2–50 µg/L	2.2 µg/L
		Total As	2–50 µg/L	2.4 µg/L
AuNPs paper filter/ion membrane electrode		Pb (II)	10 ⁻⁵ –10 ^{-2.2} M	10 ⁻⁵ M
Carbon nanomaterial + AuNPs working paper electrode /SPCE commercial		Hg (II)	0.1–1.2 µM	30 nM
Mercury or bismuth films working paper/SPCE commercial		Cd (II)	0.5–10 /2.5–10 µg/mL	0.4/1 µg/mL
		Pb (II)	0.5–10/1–10 µg/mL	0.1/0.7 µg/mL
		In (III)	0.1–5/1–4 µg/mL	0.04/0.6 µg/mL
		Cu (II)	0.25–6.35/X µg/mL	0.2/X µg/mL
Full paper electrode	Full made paper-based platform	Pb (II)	10–100 µg/L	7 µg/L
		Cd (II)	10–100 µg/L	11 µg/L
Co-MOF-NH ₂ /AuNPs full paper electrode		Pb (II)	0.5–20 ng/mL	0.011 ng/mL
		Cd (II)	0.75–35 ng/mL	0.07 ng/mL
AgNPs + Cu ₂ O-Au Full paper electrode		Ni (II)	10 nm–0.2 mM	3.1 nM
		Hg (II)	1 pm–1 µM	3.8 pM
Bismuth film Full paper electrode		Pb (II)	0–500 µg/L	2 µg/L
Bismuth film Full paper electrode		Pb (II)	10–1000 µg/L	2.4 µg/L
		Cd (II)	5–800 µg/L	4.2 µg/L
Tin working electrode Full paper electrode		Cd (II)	5–40 µg/L	0.9 µg/L
		Zn (II)	5–40 µg/L	1.1 µg/L
MWCNT Full paper electrode		Zn (II)	100–1400 µg/L	10.5 µg/L
		Cd (II)	10–1400 µg/L	1.3 µg/L
		Pb (II)	10–1400 µg/L	0.9 µg/L

Table 1. Comparison of results of electrochemical analysis on paper-based platforms.

Most of paper electrodes are made of carbon, but there are alternatives. C. Kokkinos et al. designed a microfluidic paper electrode with a working electrode composed of a sputtered film of tin (Sn) to determine Cd (II) and Zn (II) at trace levels with limits of detection of 0.9 and 1.1 $\mu\text{g/L}$, respectively [31]. The tin working electrode and the auxiliary and reference electrode were made by sputtering over the paper substrate. A microfluidic channel was printed on reverse paper. This helps to diffuse the samples, taking advantage of the capillarity. Volumes as low as 10 μL could be used.

All mentioned reports show a variety of options for designing paper electrochemical cells for heavy metal determination. **Table 1** resumes all the results previously commented. All of them contribute to the goal of low-cost, sustainable, easy-to-use, and green analytical platforms. This is especially attractive for use in underdevelopment countries or in places in which portability and rapidity are the main requirements.

3. Conclusions

Heavy metal determination by electrochemical methods has evolved over time, following the analytical trends of miniaturization and, more recently, sustainable and eco-friendly processes. Paper-based platforms are the next alternative to low-cost and easy-to-use electrodes. In this chapter, the main designs reported in the literature have been critically analyzed. The modification with nanomaterials or metal films in order to increase their conductivity properties was found successful strategy. This confirms that cellulose-based platforms are the foundations of a new generation of versatile and low-cost electrochemical sensors.

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Conflict of interest

The authors declare no conflict of interest.

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