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sensing platforms



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Recent advances in portable heavy metal electrochemical sensing platforms

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In 2020, the new European Drinking Water Directive will be updated to include new drinking-water safety parameters. These will introduce reduced thresholds for the presence of heavy metals, pesticides and other contaminants in domestic drinking water. The aim of these reduced thresholds is to impose a higher level of consumer protection as well as provide guidance for effective monitoring, planning and water management. An example of a newly proposed threshold is the concentration of lead ions (Pb^{2+}) within drinking water, which has been reduced from 10 to 5 parts per billion (ppb). The strict timeframe for water suppliers to meet the new thresholds has created an impetus to develop *in situ* detection techniques to quantify the levels of chemical contamination on-site in drinking water, allowing them to make prompt interventions. This review explores and discusses the current advances related to electrochemical methods, electrode materials and modifications that have the potential to be the foundations of a new generation of portable electrochemical sensors towards trace-level ion *in situ* heavy metal sensors.

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Water impact

The 2020 Drinking Water Directive (DWD) has legislated new lower thresholds for the heavy metal (HM) contamination within consumable/tap water. This has created an impetus for novel *in situ* HM sensors to be developed. This review highlights the new DWD HM detection limits and describes the parameters that have to be considered in order to build a suitable *in situ* electrochemical sensor.

1. Introduction

As the global population is increasingly found within urban conurbations, there is an ever-growing demand to resource these population centres with safe drinkable water. However, the aging/inadequate water infrastructure present within many cities results in severe problems, arising from contaminants (particularly heavy metals) entering the domestic water supply.¹ These heavy metal contaminants not only occur due to leaching from the existing water infrastructure but are also a result of anthropogenic, agricultural, mining and industrial activities, which have drastically increased the levels of such metals within the environment.^{2,3} Heavy metals (HM) that commonly occur as contaminants within domestic water supplies are Hg^{2+} , Pb^{2+} , Cu^{2+} and Cd^{2+} , although copper for example is considered nutritionally essential for human beings,⁴ heavy metals are toxic at high concentrations.

This toxicity of these heavy metals arises from their ability to bind with protein sites, displacing the original essential metals, bio-accumulating and ultimately becoming harmful. The detrimental effects that occur (post biological safe concentrations) typically affect the nervous system, kidney/liver function and on hard tissue such as bones and teeth.^{5–9} According to EU water quality reports, the main sources of heavy metal presence in drinking water are: its natural presence, pollution, waste water treatment and water distribution systems.¹⁰ HMs present in the water will enter small organisms and bio-accumulate within the food chain; in the case of humans there is also risk due to direct exposure/intake of HM.

The first attempt to limit the negative effect of HM water contamination was with water quality standards. These were introduced by the EU in 1980 when the Water Framework Directive (WFD) was established to ensure the protection of rivers, lakes, ground-waters, bathing waters, environmental organisations, nature and water-using sectors.¹¹ In 1998, the Drinking Water Directive (DWD)¹² was enacted to regulate the quality of water intended for human consumption. The DWD was amended in 2015 to include monitoring programs, parameters and sampling methods.¹³ As a result of the

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popular 'Right2Water' campaign, which gathered 1.8 million citizens' signatures, in 2020 the EU is renewing the DWD, aiming to update and control 48 parameters that must be monitored by water suppliers and regulators.¹⁴ These parameters include chemicals, such as heavy metals, pesticides, acrylamides *etc.* and microbiologicals (*i.e.* *Clostridium perfringens* spores, *E. coli*, somatic coliphages *etc.*).¹⁴ Table 1 provides a comparison of heavy metal presence in drinking water between the current US Environmental Protection Agency (EPA)¹⁵ and European Union (EU)¹⁶ limits and the newly updated EU limits.¹⁴ Note that the permissible concentration of lead (Pb²⁺) and chromium (Cr³⁺) in drinking water, is set to be lowered from 10 down to 5 µg L⁻¹ (ppb) and from 50 to 25 PPB respectively. These values are to be met no longer than 10 years after the initiation of this directive.¹⁴

In order for countries to comply with the newly proposed contaminant thresholds, there is a requirement to employ the latest scientific methods/knowledge to create technological solutions that are able to reduce costs, preparation/analysis time and to improve the performance of *in situ* contaminants monitoring. As an example of HM drinking water contamination, copper (Cu²⁺) is an important parameter to monitor as it can leach from copper pipes due to the corrosive action of the oxygen present in the water. This can vary greatly depending on the pH, hardness and Cu²⁺ availability in the water distribution system,¹⁷ meaning that there is a need to identify areas, which are particularly at risk. High Cu²⁺ concentrations can lead to overt signs of contamination such as stains on sanitary appliances at levels above 1 parts per million (ppm), and a bitter taste to water at 5 ppm or higher.¹⁷

Lead (Pb²⁺), is recognised as an exceptional case because it arises in drinking water from the plumbing system. In the UK, the ubiquitous use of lead solder¹⁸ and fittings¹⁹ in properties built before 1970 (after which it was banned) presents a considerable challenge as the replacement and re-fitting of the systems would be cost/time prohibitive (the total lead fitting replacement was estimated to be around £7 billion only for UK properties²⁰). The presence of Pb²⁺ in drinking water also depends on the pH, alkalinity and concentration of orthophosphates in the sample,^{21,22} reaffirming the need to quickly identify areas that are most at risk of high exposure (*i.e.* schools and hospitals) using affordable, mass-producible, *in situ* and accurate methods.

Typically, in order to accurately assess the levels of HM contamination with drinking water, large, sophisticated and expensive lab-based techniques such as atomic absorption spectrometry (AAS),^{23,24} mass spectrometry (MS),²⁵ inductively coupled plasma MS (ICP-MS),²⁵ atomic emission spectrometry (AES), X-ray fluorescence (XRF)²⁶ and optical²⁷ techniques are required in order to perform trace metal analysis. These techniques might also apply preconcentration and separation techniques (such as solid-phase micro- and normal extraction, dispersive liquid-liquid microextraction or cloud point extraction²⁸), for the highly qualified technician, to be able to run the sample. Unfortunately, chemical, biological and physical reactions can occur during transportation, handling, pre-treatment and analysis of the water samples, which can affect the sample's composition and potentially result in inaccurate results.²⁹ The development of new state-of-the-art *in situ* sensors is needed to reduce the time, cost and sampling of

Table 1 Comparison of current EPA, EU, and newly approved EU drinking water guidelines for selected parameters

Parameter	EPA limit ¹⁵	EU limit ¹⁶	New EU limit 2020 (ref. 14)	Unit	Note
Antimony	6	5	5	µg L ⁻¹	
Arsenic	10	10	10	µg L ⁻¹	
Cadmium	5	5	5	µg L ⁻¹	
Chromium	100	50	25	µg L ⁻¹	The value shall be met, at the latest, by [10 years after the entry into force of this directive]. The parametric value for chromium until that date is 50 µg L ⁻¹
Copper	1.3	2	2	mg L ⁻¹	
Lead	15	10	5	µg L ⁻¹	The value shall be met at the latest by [10 years after the entry into force of this directive]. The parametric value for lead until that date is 10 µg L ⁻¹ After the transitional period, the value of 5 µg L ⁻¹ shall be met at least at the point of supply to the domestic distribution system
Mercury	2	1	1	µg L ⁻¹	For inorganic mercury
Nickel	100	20	20	µg L ⁻¹	
Selenium	50	40	10	µg L ⁻¹	Parametric value of 30 µg L ⁻¹ shall be applied for regions where geological conditions may lead to high levels in ground water
Uranium	30	30	30	µg L ⁻¹	



such monitoring studies in order to mitigate the problems highlighted above.²⁷ Currently commercially available HM detection kits offer high sensitivities, but require image analysis (colorimetric analysis using microfluidic paper-based devices³⁰) or the use of molecular recognition probes.³¹ The complexity and price of these commercial kits makes them impractical for large scale real time *in situ* environmental monitoring. Electrochemical methods on the other hand, can be considered one of the most suitable methods for *in situ* analysis of HM,^{32–34} mainly due to the small size of equipment, easy installation, low cost, simple sample preparation and the ability to perform multi-elemental detection. As shown in Fig. 1A, electrochemical detection uses a transducer to generate a measurable current, potential, charge, phase or frequency changes made by the electrochemical reaction taking place at the working electrode (WE)–electrolyte interface. Fig. 1B depicts a classic electrochemical cell comprised by the working, reference and counter electrodes (WE, RE and CE), respectively, where an electrochemical process called anodic stripping voltammetry is shown (Fig. 1B). Pad-printing, roll-to-roll and screen-printing electrode circuit fabrication methods have been applied to electrode manufacturing as a response to classic solid electrodes, by offering a reduction in manufacturing costs and the ability of performing laboratory-in-field experiments.^{35–38} In Fig. 2, one can observe the main differences between classic electrode platforms against those of screen-printed electrodes (SPEs), where the latter can be used as single-shot, disposable, reproducible and ready to use electrode. On the other hand, classic (solid) electrodes such as glassy carbon (GC), edge plane and basal plane pyrolytic graphite (EPPG and BPPG respectively) or highly ordered pyrolytic graphite (HOPG) (and others) need to be rigorously polished and cleaned before undertaking every measurement and require the presence of external RE and CE. Through offering a disposable, low-cost, reproducible and yet easily modified platform^{39,40} SPEs are one of the

most used platforms for *in situ* electrochemical methods due to their versatility and can be applied towards a multitude of sensing devices towards a variety of targets such as gases,^{41,42} food quality,^{43,44} biomolecules⁴⁵ or drugs of abuse,⁴⁶ to name a few. SPEs have previously been played a pivotal role within the multi-billion dollar industry of the biological glucose sensing where they are used vital components of point-of-care devices. Their disposable nature allows them to be cheaply used on a daily basis enabling individuals with diabetes to accurately check their blood glucose levels without having to visit a clinic, hospital or pharmacy.^{35,47}

2. Portable devices

There are several essential electronic components required to manufacture portable sensors, which thanks to the advances in computing power, electronics energy efficiency and manufacturing techniques have been able to be manufactured at a low-cost and within a small/portable package; thus making widespread small, fast and easy to use point-of-care (POC) testing more viable. A potentiostat is the most common electronic hardware used to control and measure electroanalytical experiments (adjusting/monitoring the signal, electrical current, voltage, resistance, *etc.*). Portable potentiostats are now widely available commercially as small, portable and low-cost devices that are applicable to *in situ*/on-line/point-of-care analysis. Open-source format technology has also reached electrochemists in the form of electric circuits, components, circuit boards, micro-controllers, software *etc.*^{48–52} In recent years, there has been a lot of development the miniaturization and increased portability of potentiostat devices. Researchers such as Moussy *et al.*⁵³ have designed an implantable and dynamically configurable potentiostat for remote monitoring. Ainala *et al.*⁴⁸ have recently simplified potentiostats, designing an of open-source universal battery powered and bluetooth connected potentiostat (UWED)⁴⁸ capable of offering enough

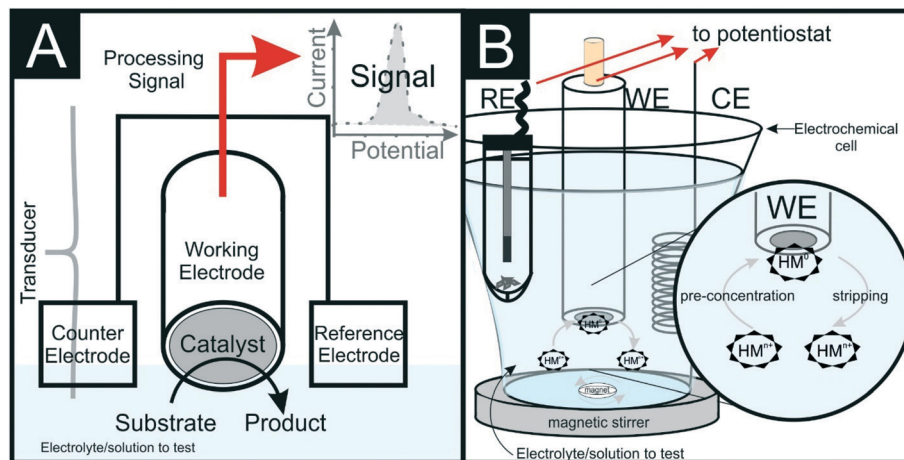


Fig. 1 Schematic representation of electrochemical sensing (A) and a classic electrochemical cell/stripping voltammetric method (B).



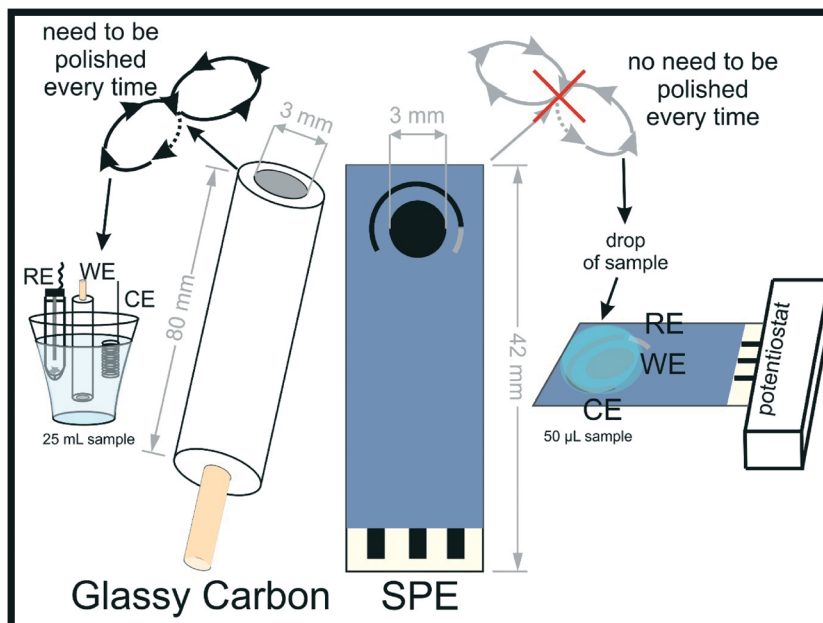


Fig. 2 Schematic overview comparing a classic electrochemical cell vs. a screen-printed electrode platform performing the analysis within a single drop of analyte.

potential ranges for most electrochemical analysis in aqueous solutions.

3. Electroanalytical methods towards the detection of heavy metals in drinking water

Electroanalytical methods study the relationship between chemistry and electricity by measuring the resultant signal outputs (current, potential, charge, phase, frequency *etc.*) associated with a chemical reaction.⁵⁴ The use of electrochemistry for analytical purposes includes quality control,⁵⁵ environmental,^{56,57} food^{43,58} and biomedical^{45,59} applications to name a few. These are typically dynamic processes that occur at the electrode–electrolyte interface.^{60,61}

Potentiostatic and potentiometric are the main two types of electroanalytical methods.

Potentiostatic methods study the transfer of charge at the electrode–electrolyte interface by measuring oxidation/reduction of species through the analysis of the observable current. This is undertaken by changing the potential between WE and RE electrodes, respectively. The main advantages of potentiostatic measurements over other detection techniques are high sensitivities, selectivity, microliter-size sample volumes, low limit of detections (LODs) and wide linear ranges.^{60,61} A widely used potentiostatic approach for HM ions determination is the use of stripping voltammetry.^{5,54,62} Stripping voltammetry can be mainly divided into anodic, cathodic or adsorptive stripping voltammetry (ASV, CSV or AdSV respectively).⁶¹ As shown in Fig. 3A, stripping analysis is based on a pre-concentration step on the surface of the WE followed by a stripping step,

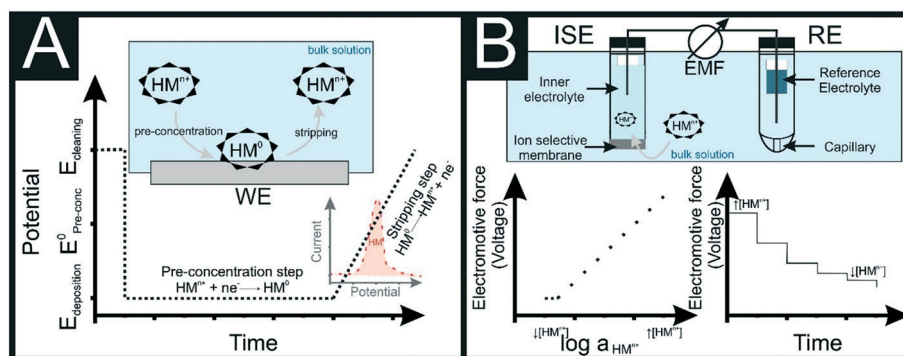


Fig. 3 Schematic diagram of a potentiostatic (anodic stripping voltammetry; A) and a potentiometric (ion-selective electrode (ISE); B) method respectively.



inducing Faradaic loss of the accumulated HM from the electrode (the HM ions go back into solution).⁶¹ Lastly, it measures the associated current, which is directly proportional to its concentration and pre-concentration time which can be generally expressed by the following equation:⁶²

$$i = K C t_{\text{pre-concentration}}$$

where the term K , is a constant that includes the electrode (geometric) area (A), scan rate (v), diffusion coefficient (D), number of electrons transferred in the electrochemical process (n) and convection rate (usually applied using the deposition step). Electrochemical stripping metal detection offers low limits of detection within the ppb-range, multi-element determination, an associated low-cost and the ability to perform HM on-site/*in situ* determination.⁶² Stripping voltammetry generally detects the concentration of free HMs at the pH of the sample, unlike many other detection techniques, such as ICP-MS, which require to be strongly acidified to force all the HM ions into free state.⁶³ It is also essential to note that an adequate WE is required for effective accumulation step and a favourable redox reaction of the target HM. Ideally the WE should be highly reproducible, display low background currents and have wide potential ranges.⁶²

Potentiometric methods are also an applicable methods, they are zero-current techniques in which the recorded response is the voltage across a membrane (electromotive force) that is directly related to the sample composition.⁵⁴ In this case, different types of membranes, depending on their ion recognition capabilities have been commonly applied towards the detection of ionic species such as H^+ , Ca^{2+} , F^- and K^+ ions in complex matrixes.^{54,64,65} Fig. 3B shows a typical schematic of an ion-selective electrode (ISE) performing a potentiometric method. ISEs are placed between two aqueous phases (sample and an inner electrolyte), a reference electrode (RE) as well as a salt bridge.⁶⁶ ISEs offer rapid selective measurements, low energy consumption and low-cost, although LODs and multielement detection remain a challenge.⁶⁷ The membrane, which can be polymeric, polycrystalline or made from glass,⁶⁸ is the most fundamental part of the sensor and depending on the chosen membrane's properties, the sensor will have specific selectivity and performance. However, they exhibit ion interference and potential drift over time plus they need delicate handling, pre-measurement calibration.⁶⁸ Pretsch *et al.*⁶⁹ reported direct potentiometry at trace levels, a method capable of sub-femtomole LODs for Ca^{2+} , Pb^{2+} and Ag^{2+} , however its application to real samples with unknown composition remains a challenge, due to the difficulties in predicting the optimal applied current required.⁷⁰ Cui *et al.*⁷¹ recently reported a μISE , that by taking advantage of microfabrication techniques, cleverly fabricating a multiplexed micro array comprised of different ionophores targeting Pb^{2+} , Cd^{2+} , Hg^{2+} and AsO_2^- capable of reaching ppb levels in drinking water.

4. Electrode materials

The electroanalytical output of the electrode is critically associated with the material of which the WE is comprised/made. The selection of an appropriate WE for a given analyte is therefore vital. Typically for electrochemical sensors one would choose a WE that has: an efficient electron transporter, high surface-to-volume-ratio, wide potential window, low background current, chemical stability and (electrochemically) interference-free.^{72,73} Historically speaking, hanging mercury drop electrodes (HMDE) were the most widely used WE material from the mid-20th century.⁶² HMDEs were followed by precious metals (such as polycrystalline Au, Ag and Pt) and carbon electrodes in the last three decades due to their low background current, wide potential range and chemical inertness.^{74,75}

4.1 Metallic electrodes

Platinum (Pt) and gold (Au) are traditional electrode materials and have been utilised in a plethora of electrochemical reactions due to their excellent stability over a wide range of potentials and electrolytes whilst offering very favourable electron transfer kinetics.^{54,76} Au electrodes, display wide anodic polarization ranges⁷⁷ and have conventionally been the optimal choice for mercury and arsenic determination.^{78,79} Copper (Cu), nickel (Ni) or silver (Ag) have also been used as electrode materials for sensing applications, however they are less applicable than Au in many electrochemical detection methodologies due to them forming high-valence oxy-hydroxide species acting as redox mediators.^{54,80,81} Cu is easily oxidised and offers poor long-term stability,⁸² therefore is not typically used as an WE. Cu is however low cost and widely used within industrial manufacturing and micro-fabrication methods, thereby making it application to niche applications.⁸³ Last, bismuth film electrodes (BiFE) have been presented as a "green" alternative to mercury (Hg) films at the beginning of the century due to their similar performance to Hg but lower toxicity. BiFE and other metal film electrodes (PbFE, SnFE and SbFE) introduction to electrochemical detection was considered a landmark in the research of "green" electrode materials for stripping analysis towards sensing Cd^{2+} , Pb^{2+} , Tl^{2+} , Cu^{2+} and Zn^{2+} ,⁸⁴ although they need polishing and surface renewal steps prior to its use, which makes them highly dependent on the experimentalist.^{85,86} Banks *et al.*⁵⁷ deposited Bi, Sb, Sn films on SPEs as well as classic electrode platforms (BDD and GC) and tested the platforms towards the detection of Cd^{2+} and Pb^{2+} . Interestingly, they found that unmodified SPEs are capable of detecting both analytes at WHO levels, without any electrode pre-treatment (prior use, polishing and/or electrochemical treatment/surface- or bulk-modification).

4.2 Graphitic electrodes

Graphite, GC, nano-graphite, carbon black as well as a plethora of other graphitic materials have been widely reported as electrode materials for electrochemical



applications.^{87–93} They offer excellent electrical conductivity, chemical stability, structural versatility, broad potential windows, abundant surface groups and robust carbon-to-carbon bonds (both internally and externally).⁹⁴ In order to move away from large immobile testing equipment, research has focused on developing miniaturised, simple and low-cost electrodes. SPEs can be modified with chosen catalysts to make them applicable for niche applications.⁹⁵ SPEs allow for increased portability, decentralised analysis and a reduction in the cost of sensors. They can also be easily modified with selected additives enabling them to display the beneficial properties of other materials. Graphitic materials such as carbon nanotubes (CNTs), graphene, graphene oxide (GO), carbon nanofibers (CNFs) and carbon nano-powders (CNPs) all have been successfully applied to SPEs, as modifications and/or inks for HM analysis in drinking water,^{96–101} river-waters^{102–105} and also food.^{106–108} However, as suggested by Ping *et al.*, the synthesis and application of some 2D-nanomaterials to large-scale production might be sometimes impractical.¹⁰⁹

4.3 Electrode modifications

The electrochemical sensitivity of some WE's can be enhanced not only by using 2D nanomaterials with enhanced properties, but also by using surface modifications to take advantage of the previously described beneficial properties of different materials. There are four typical categories of surface modifications, these being: adsorption, covalent bonding, electrochemical polymerization and electrochemical deposition.^{34,110} Adsorption methods consist of a non-covalent bond between the surface and the modified suspension, and can be sub-divided into: coatings, chemical adsorption and self-assembled monolayers. The most common adsorption method used is coating (*i.e.* drop-casting,¹¹¹ spin-coating¹¹² and dip-coating¹¹³), consists in covering the bare/unmodified WE's surface with a solvent-modifier mixture, the solvent then evaporates leaving a coat on the surface.³⁴ Electro-polymerisation and deposition methods consist of passing a voltage through the WE and the electrolyte, which contains the chosen modifier, to create stable polymers¹¹⁴ or metal¹¹⁵ films onto the WE's surface. Bulk modification of the SPE's ink with the same materials as described above, is a convenient mass-producible approach that is commonly explored within the literature to overcome the limitation of surface modification, such as poor cycling stability and uneven distribution by adding the chosen modification to the WE's ink. Mass-producible ink modification of SPE's has been widely reported towards sensing Cu²⁺,¹¹⁶ Pb²⁺,^{56,117} Cd²⁺,⁵⁶ and Zinc²⁺,⁵⁶ to name a few.

Molecular imprinted polymers (MIPs), or plastic antibodies, are bio-mimetic receptors based on cross-linking and functional monomers that are co-polymerised in the presence of the target analyte (the imprint molecule), acting as a template.^{118,119} Molecular imprinted polymers (IPs), as shown in Fig. 4, can be synthesised by a combination of

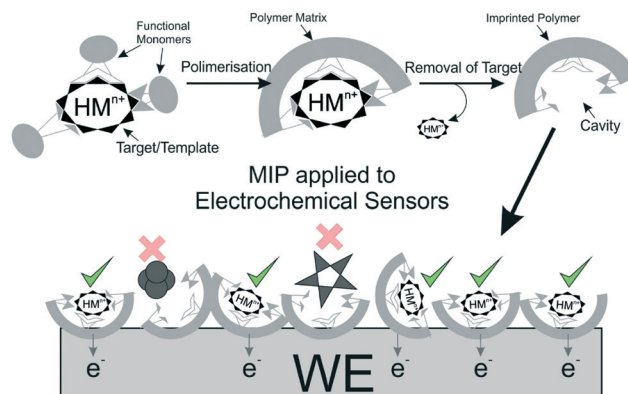


Fig. 4 Schematic representing MIPs applied to electrochemical sensor platforms.

monomers, cross-linkers, initiators and solvents, where the monomers polymerise around the target/imprint molecule with a high cross-link polymeric structure.¹²⁰ Next, the removal of the imprint molecule reveals the scaffolds with exclusive non-covalent binding sites (molecular memory) to the target analyte.¹²¹ Imprinted polymer's main advantages are simple and low-cost preparation, high stability, affinity, selectivity, versatility of template/target molecule and ease of application as transducer in assays/sensors.¹²² They are currently applied to HM sensors,¹²³ enzyme mimics,¹²⁴ solid phase extractions,¹²⁵ antibody mimics,^{126,127} biomarkers *etc.*¹²⁸ Those MIPs that can specifically recognise and remove ions are called ion imprinted polymers (IIPs), these benefit from being broadly applicable, highly selective and water-compatible.¹²⁹ IIP-based electrochemical sensors have been reported towards Co²⁺,¹³⁰ Cd²⁺,^{131,132} and others¹³³ exhibiting ultra-trace levels in water samples.

Metal dopants/modifications (in the form of nanoparticles, films *etc.*) upon the surface of SPEs have also been widely studied concerning their application as sensors. Bismuth film electrodes (Bi-modified) SPEs has been reported to offer a simple, portable, mass-produce and yet sensitive and with multi-element detection capabilities of HM such as Cd²⁺ and Pb²⁺.^{56,57,134} Bastos-Arrieta *et al.*¹³⁵ recently reported that the main factor to enhance SPE's electrocatalytic performance is the shape of the nanoparticles, rather than the mere incorporation of them, when detecting Cd²⁺ or Pb²⁺ with Ag-NP SPEs. Barton *et al.*²⁷ elegantly reviewed the use of Au-coated SPEs to detect HM, showing the determination of Pb²⁺, Cd²⁺, Hg²⁺, As²⁺, Cu²⁺ and Sb²⁺ in a variety of modifications such as Au bulk-modified inks, Au-coated, Au-sputters and nano-deposited, towards matrixes such as ground-,¹³⁶ river-,^{137–139} rain-,¹⁴⁰ waste-,¹³⁸ sea-waters^{141–143} and soil extracts.¹⁴⁴ Gold nanoparticles (AuNPs) modified graphitic SPEs have shown to be excellent alternatives to mercury electrodes as they exhibit high sensitivity and selectivity towards the simultaneous detection of Hg and Pb.¹⁴⁵ For example Bernalte *et al.*¹⁴⁶ reported LODs of 2.2, 1.5 and 1.3 ppb for the simultaneous determination of Pb²⁺, Cu²⁺ and Hg²⁺



respectively in *in situ* Amazonian waters by using bulk-film modified Au-SPEs. Cu-SPEs have also been demonstrated as point-of-care (POC) disposable sensors for Pb^{2+} , Cd^{2+} and Zn^{2+} ,⁸³ however the sensor cannot detect metals such as As and Ag due potential oxidation of Cu.⁸³

The functionalization of an electrodes surface using ether crowns is also widely reported within the literature for Cu^{2+} (ref. 147) and Pb^{2+} (ref. 148–150) and other HMs^{151–153} sensing applications. Crown ethers are cyclic compounds with remarkable ability to form selective strong complexes with metal and organic cations.^{154,155} Del Valle *et al.*¹⁵⁶ reported the simultaneous use of CB-15-crown-5 and CB-18-crown-6 for the Cd^{2+} , Pb^{2+} and Cu^{2+} multi-elemental determination exhibiting ultra-trace sensing in environmental samples, when combined with chemometric tools to deconvolute the signals.

With the recent interest in applications for 2D materials, numerous studies have explored the utilisation of hybrid layered transition metal dichalcogenides (LTMDs) (such as MoS_2 , MoSe_2 , WS_2 *etc.*) with graphene/graphitic nanomaterials towards HM sensing applications.^{157,158} The combination of 2D materials with LTMDs allows the construction of heterojunctions that can be adjusted by changing the energy band of each semiconductor, which offers strong adsorption and fast electron transfer.^{158,159} Fig. 5 shows the electrochemical steps that occur when TMDs are used within an electrochemical sensor. The HM ions (HM^{n+}) freely flow in solution (A); a chosen deposition potential is applied (B) the HM pre-accumulates onto the highly adsorption sites (as HM^0) of the TMDs (C); the stripping step applies a voltage re-dissolving (as HM^{n+}) and the stripping signal will be recorded. Chen *et al.*¹⁵⁸ recently reported a tailored 3D Ni/NiO/ MoO_3 /chitosan heterojunction

for the direct electrochemical detection of Cu^{2+} . In this NiO and MoO_2 both offer large band gaps and the chitosan (CS) exhibits exceptional Cu^{2+} adsorption capacity due to its abundance of hydroxyl and carboxyl reactive functional groups.^{160,161} The reported technique is a promising solution for the direct selective detection of HM in real water samples as the application of an interfacial barrier filters the solution and improves the electrochemical signal output. Another interesting study was performed by Huang *et al.*¹⁶² who reported an electrochemical sensitivity of $133.90 \mu\text{A} \mu\text{M}^{-1}$ when detecting Pb^{2+} using a Mn- MoS_2 modified GC. This technique takes advantage of the interaction between Pb^{2+} and S atoms caused by tailored phases and defects at the nanosheet to offer high conductivity. Huang *et al.*¹⁶² reported that Pb-S bonding occurs due to the stimulated activity of S atoms, facilitating the electron transfer and promoting the *in situ* Pb reduction/re-oxidation at the Mn- MoS_2 nanosheet.

4.4 Screen-printed electrode (SPEs) designs

The capability to shape an electrode's design has strong electrochemical performance implications. As represented in Fig. 6, changing the design from a macro- to a micro-electrode can change the profile of the diffusion regime for basic electron transfer (from hemi-spherical to planar and/or from non- to over-lapping), which can increase current densities, reduce ohmic drops and improve the ratio of faradaic-capacitive currents.^{35,40,163} Micro-electrode array sensors have been reported to exhibit lower LODs and greater sensitivities in comparison to macro-electrodes with equivalent geometrical areas, when single micro-electrodes are placed in a parallel configuration.^{35,164} This is due to the creation of diffusional independent voltammetric

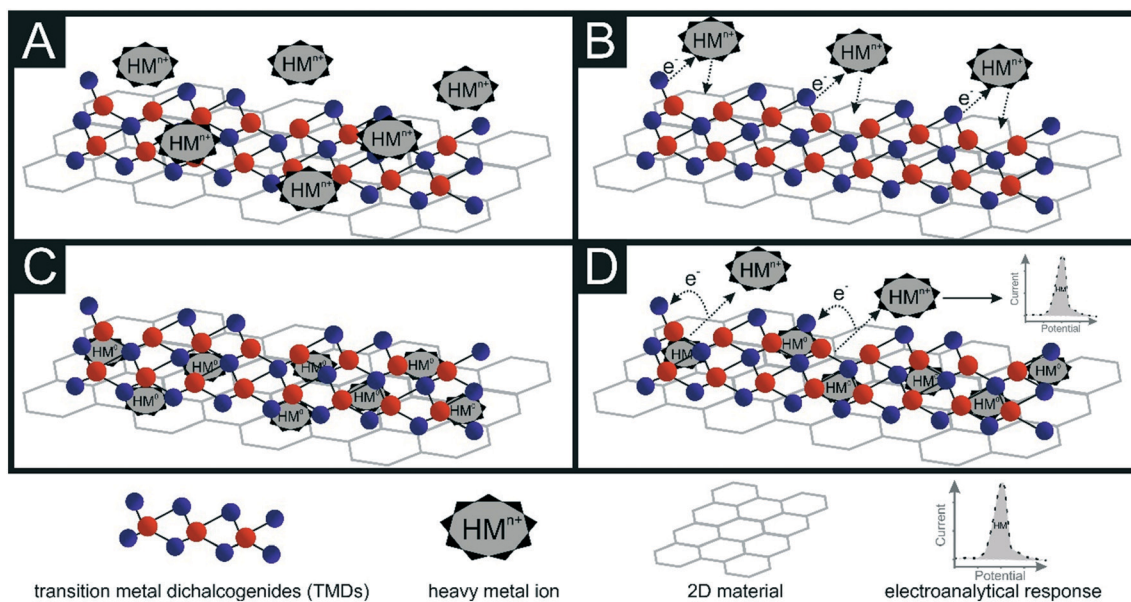


Fig. 5 Schematic representing the electrochemical steps when TMDs are used within an electrochemical sensor: pre-measurement (A), deposition potential application (B), pre-accumulation step (C) and stripping step (D).





Fig. 6 Schematic representing the categories of diffusion profiles at different micro-electrode array configurations. Planar diffusion layers at macro-electrodes (A), individual non-planar diffusion layers at micro-electrodes (B), non-overlapping diffusion layers at micro-electrodes (C) and planar overlapping diffusion layers at micro-electrodes (D).

responses.¹⁶³ The configuration of multiple single electrodes in parallel to each other takes advantage of radial diffusion dominating the mass transport, which results in a larger combined diffusional area than a single macro-electrode yielding improved electroanalytical sensing.¹⁶⁵ Using multiple distinct also allows for simultaneous determination of analytes by using different electrode modifications on each

WE, which can also save time and money in the case of critical situations.^{166–168} An elegant application of this was made by Rusling,¹⁶⁹ who by modifying each electrode differently (different antibodies immobilised on each WE of the array) has reported the performance enhancement of microfluidic immuno-sensors,^{169,170} widening the application of these SPE platforms to a plethora of different target



Fig. 7 Schematic representation of possible options for tailoring screen-printed electrochemical sensing platforms.



analytes at the same time; such an approach has the potential to be applied to HMs.

Micro-electrode arrays and designs can be obtained *via* a wide range of processes such as sono-chemical/laser ablation, which can encounter challenges to seal the patterned material leading to leakages.⁴⁰ Other methods include screen-printing technologies using small defined geometries.¹⁶³ Further approaches include the fabrication of co-planar,¹⁷¹ micro-band electrodes,¹⁷² flexible micro-electrodes,¹⁷³ ultra-micro-electrodes (UME)^{174,175} and micro-tubes¹⁷⁶ to name a few. Zufelt *et al.*¹⁷⁷ reported the fabrication of a photolithography fabricated array, which consisted of 18 WE's each with a geometric area of 0.0025 mm². This array was ideal for ion sensing in aqueous solutions as it had the ability of multi-elemental monitoring conducting different electrochemical measurements in each single WE. The geometry and configuration of the WE plays an important role in sensors. Macro-electrode array/multiplexed designs have also been explored in the literature, offering the possibility of modifying each WE in a different way to detect different target analytes.^{178–183} The presence of multiple WEs using the same SPE also brings new challenges, such as an increase in internal circuit's resistance. This has been reported to contribute to frequency and severity of imprecisions and errors when electrode designs are not symmetrical.¹⁸⁴ Fig. 7 highlights the essential aspects that need to be considered when producing a sensor for a specific role such as heavy metal sensing in water. The plethora of modifications include the alteration and/or inclusion of active materials, catalyst, bulk modified recognition systems (added into screen-printing ink), plus the electrode/sensor design, and substrate of the electrochemical sensing platform. Considering the discussed research, we can conclude that SPE platforms offer a simple, customisable, cheap and highly sensitive approach to detect HMs. However, they still require improvements in terms of their reproducibility and interference avoidance from other metal, organic or inorganic soluble molecules present in the electrolyte at the same time.

5. Conclusions

In situ monitoring of water quality at the source point of human consumption is vital in order to comply with the new lower permissible contaminant levels imposed by European directives. This review comprehensively introduces the parameters that one has to consider when developing HM electrochemical sensors capable of meeting the newly imposed LODs. The majority of the studies described within this manuscript offer sensing platforms capable of meeting these LODs. However, they typically require expensive electrode materials that can only be used within a lab, need reagents/chemicals and suffer from multi-elemental interferences. There are a limited number of studies that demonstrate a realistic approach of meeting the new EU regulations in a cost effective manner. It is therefore essential

that research focuses on the development of portable/cost effective HM detection technologies in order to allow for facile, cheap and rapid in-field HM detection devices. The combination of electrochemical techniques, made possible by miniaturised and portable potentiostats, with cheap, calibration-less and tailorable screen-printed electrodes are promising candidates to support this transition. Further work is required regarding determination methods, composition/design of WE *etc.*, in order to produce *in situ* sensor devices capable of meeting the new EU regulation requirements, quality targets and effectively monitor a wide variety of global health parameters that affect us all.

Conflicts of interest

The authors declare no competing financial and/or non-financial interests in relation to the work described herein.

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References

- 1 R. I. McDonald, K. Weber, J. Padowski, M. Flörke, C. Schneider and P. A. Green, *et al.*, Water on an urban planet: Urbanization and the reach of urban water infrastructure, *Glob. Environ. Change*, 2014, **27**, 96–105.
- 2 H. Kim, G. Jang and Y. Yoon, Specific heavy metal/metalloid sensors: current state and perspectives, *Appl. Microbiol. Biotechnol.*, 2020, **104**(3), 907–914.
- 3 P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla and D. J. Sutton, Heavy metal toxicity and the environment, *Exper. Suppl.*, 2012, **101**, 133–164.
- 4 E. J. Underwood, Factors influencing trace element needs and tolerances in man, *Mar. Pollut. Bull.*, 1974, **5**(6), 86–88.
- 5 G. Aragay, J. Pons and A. Merkoçi, Recent Trends in Macro-, Micro-, and Nanomaterial-Based Tools and Strategies for Heavy-Metal Detection, *Chem. Rev.*, 2011, **111**(5), 3433–3458.
- 6 J. W. Hamilton, R. C. Kaltreider, O. V. Bajenova, M. A. Ihnat, J. McCaffrey and B. W. Turpie, *et al.*, Molecular basis for effects of carcinogenic heavy metals on inducible gene expression, *Environ. Health Perspect.*, 1998, **106**(Suppl 4), 1005–1015.
- 7 B. L. Vallee and D. D. Ulmer, Biochemical effects of mercury, cadmium, and lead, *Annu. Rev. Biochem.*, 1972, **41**(10), 91–128.
- 8 T. Partanen, P. Heikkilä, S. Hernberg, T. Kauppinen, G. Moneta and A. Ojajarvi, Renal cell cancer and occupational exposure to chemical agents, *Scand. J. Work, Environ. Health*, 1991, **17**(4), 231–239.
- 9 M. Jaishankar, T. Tseten, N. Anbalagan, B. B. Mathew and K. N. Beeregowda, Toxicity, mechanism and health effects of some heavy metals, *Interdiscip. Toxicol.*, 2014, **7**(2), 60–72.



- 10 Commission E., Proposal for a Directive of the European Parliament and of the Council on the quality of water intended for human consumption, in *Environment D-Gf*, 2018, p. 134, <https://eur-lex.europa.eu>.
- 11 *Exploitation and marketing of natural mineral waters*, 80/777/EEC, 1980.
- 12 *Quality of water intended for human consumption*, 98/83/EC, 1998.
- 13 *Annexes on the quality of water intended for human consumption*, 2015/1787, 2015.
- 14 ECI, *ECI. Right2Water*, 2020, Available from: <https://www.right2water.eu/>.
- 15 *Drinking Water Standards and Regulations*, EPA 822-F-18-001.
- 16 COUNCIL, *DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption*, 1998.
- 17 Organization WHO, in *Guidelines for drinking-water quality*, ed. W. Press, World Health Organization, 4th edn, 2011, p. 564.
- 18 T. D. B. Lyon and J. M. A. Lenihan, Corrosion in Solder Jointed Copper Tubes Resulting in Lead Contamination of Drinking Water, *Br. Corros. J.*, 1977, **12**(1), 41–45.
- 19 M. Zabochnicka-Świątek, *Best Practice Guide on the Control of Lead in Drinking Water*, 2010.
- 20 S. Potter, in *Lead in Drinking Water*, ed. Section SaE, House of Commons Library, 1997.
- 21 G. Korshin, J. Ferguson and A. Lancaster, Influence of natural organic matter on the corrosion of leaded brass in potable water, *Corros. Sci.*, 2000, **42**, 53–66.
- 22 E. J. Kim, J. E. Herrera, D. Huggins, J. Braam and S. Koshowski, Effect of pH on the concentrations of lead and trace contaminants in drinking water: a combined batch, pipe loop and sentinel home study, *Water Res.*, 2011, **45**(9), 2763–2774.
- 23 P. Pohl, Determination of metal content in honey by atomic absorption and emission spectrometries, *TrAC, Trends Anal. Chem.*, 2009, **28**, 117–128.
- 24 J. Gasparik, D. Vladarova, M. Capcarova, P. Smehyl, J. Slamecka and P. Garaj, *et al.*, Concentration of lead, cadmium, mercury and arsenic in leg skeletal muscles of three species of wild birds, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2010, **45**(7), 818–823.
- 25 R. Flamini and A. Panighel, Mass spectrometry in grape and wine chemistry. Part II: The consumer protection, *Mass Spectrom. Rev.*, 2006, **25**(5), 741–774.
- 26 F. E. Mcneil and J. M. O'meara, *The In Viva Measurement of Trace Heavy Metals by K X-Ray Fluorescence*, 1999.
- 27 J. Barton, M. B. G. García, D. H. Santos, P. Fanjul-Bolado, A. Ribotti and M. McCaul, *et al.*, Screen-printed electrodes for environmental monitoring of heavy metal ions: a review, *Microchim. Acta*, 2016, **183**(2), 503–517.
- 28 G. Peng, Q. He, G. Zhou, Y. Li, X. Su and M. Liu, *et al.*, Determination of heavy metals in water samples using dual-cloud point extraction coupled with inductively coupled plasma mass spectrometry, *Anal. Methods*, 2015, **7**(16), 6732–6739.
- 29 Z. Zou, A. Jang, E. T. MacKnight, P. Wu, J. Do and J. S. Shim, *et al.*, An On-Site Heavy Metal Analyzer With Polymer Lab-on-a-Chips for Continuous Sampling and Monitoring, *IEEE Sens. J.*, 2009, **9**(5), 586–594.
- 30 G. G. Morbioli, T. Mazzu-Nascimento, A. M. Stockton and E. Carrilho, Technical aspects and challenges of colorimetric detection with microfluidic paper-based analytical devices (μ PADs) – A review, *Anal. Chim. Acta*, 2017, **970**, 1–22.
- 31 N. Ullah, M. Mansha, I. Khan and A. Qurashi, Nanomaterial-based optical chemical sensors for the detection of heavy metals in water: Recent advances and challenges, *TrAC, Trends Anal. Chem.*, 2018, **100**, 155–166.
- 32 O. J. Guerra, J. Eichman, J. Kurtz and B.-M. Hodge, Cost Competitiveness of Electrolytic Hydrogen, *Joule*, 2019, **3**(10), 2425–2443.
- 33 G. E. Batley, Electroanalytical techniques for the determination of heavy metals in seawater, *Mar. Chem.*, 1983, **12**(2), 107–117.
- 34 Y. Lu, X. Liang, C. Niyungeko, J. Zhou, J. Xu and G. Tian, A review of the identification and detection of heavy metal ions in the environment by voltammetry, *Talanta*, 2018, **178**, 324–338.
- 35 C. Banks, C. Foster and R. Kadara, *Screen-Printing Electrochemical Architectures*, 2016.
- 36 J. Willmann, D. Stocker and E. Dörsam, Characteristics and evaluation criteria of substrate-based manufacturing. Is roll-to-roll the best solution for printed electronics?, *Org. Electron.*, 2014, **15**(7), 1631–1640.
- 37 S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park and Y. Zheng, *et al.*, Roll-to-roll production of 30-inch graphene films for transparent electrodes, *Nat. Nanotechnol.*, 2010, **5**(8), 574–578.
- 38 M. Hösel, R. R. Søndergaard, D. Angmo and F. C. Krebs, Comparison of Fast Roll-to-Roll Flexographic, Inkjet, Flatbed, and Rotary Screen Printing of Metal Back Electrodes for Polymer Solar Cells, *Adv. Eng. Mater.*, 2013, **15**(10), 995–1001.
- 39 A. García-Miranda Ferrari, C. W. Foster, P. Kelly, D. C. Brownson and C. E. Banks, Determination of the Electrochemical Area of Screen-Printed Electrochemical Sensing Platforms, *Biosensors*, 2018, **8**(2), 53.
- 40 J. P. Metters, R. Kadara and C. Banks, New directions in screen printed electroanalytical sensors: An overview of recent developments, *Analyst*, 2011, **136**, 1067–1076.
- 41 A. Morata, J. P. Viricelle, A. Tarancón, G. Dezanneau, C. Pijolat and F. Peiro, *et al.*, Development and characterisation of a screen-printed mixed potential gas sensor, *Sens. Actuators, B*, 2008, **130**(1), 561–566.
- 42 J. Lee, G. Hussain, C. Banks and D. Silvester, Screen-Printed Graphite Electrodes as Low-Cost Devices for Oxygen Gas Detection in Room-Temperature Ionic Liquids, *Sensors*, 2017, **17**(12), 2734.
- 43 K. Ngamchuea, P. Hurst, C. Batchelor-McAuley and R. G. Compton, Handheld electrochemical device for the



- determination of the strength of garlic, *Sens. Actuators, B*, 2016, **232**, 138–142.
- 44 R. Kachosangi, G. G. Wildgoose and G. R. Compton, Carbon Nanotube-Based Electrochemical Sensors for Quantifying the ‘heat’ of Chilli Peppers: The Adsorptive Stripping Voltammetric Determination of Capsaicin, *Analyst*, 2008, **133**, 888–895.
- 45 N. Hernández-Ibáñez, L. García-Cruz, V. Montiel, C. W. Foster, C. E. Banks and J. Iniesta, Electrochemical lactate biosensor based upon chitosan/carbon nanotubes modified screen-printed graphite electrodes for the determination of lactate in embryonic cell cultures, *Biosens. Bioelectron.*, 2016, **77**, 1168–1174.
- 46 H. M. Elbardisy, A. García-Miranda Ferarri, C. W. Foster, O. B. Sutcliffe, D. A. C. Brownson and T. S. Belal, *et al.* Forensic Electrochemistry: The Electroanalytical Sensing of Mephedrone Metabolites, *ACS Omega*, 2019, **4**(1), 1947–1954.
- 47 A. Heller and B. Feldman, Electrochemical Glucose Sensors and Their Applications in Diabetes Management, *Chem. Rev.*, 2008, **108**(7), 2482–2505.
- 48 A. Ainla, M. P. S. Mousavi, M.-N. Tsaloglou, J. Redston, J. G. Bell and M. T. Fernández-Abedul, *et al.*, Open-Source Potentiostat for Wireless Electrochemical Detection with Smartphones, *Anal. Chem.*, 2018, **90**(10), 6240–6246.
- 49 M. D. M. Dryden and A. R. Wheeler, DStat: A Versatile, Open-Source Potentiostat for Electroanalysis and Integration, *PLoS One*, 2015, **10**(10), e0140349.
- 50 A. A. Rowe, A. J. Bonham, R. J. White, M. P. Zimmer, R. J. Yadgar and T. M. Hobza, *et al.*, CheapStat: An Open-Source, “Do-It-Yourself” Potentiostat for Analytical and Educational Applications, *PLoS One*, 2011, **6**(9), e23783.
- 51 T. Dobbelaere, P. M. Vereecken and C. Detavernier, A USB-controlled potentiostat/galvanostat for thin-film battery characterization, *HardwareX*, 2017, **2**, 34–49.
- 52 P. Lopin and K. V. Lopin, PSoC-Stat: A single chip open source potentiostat based on a Programmable System on a Chip, *PLoS One*, 2018, **13**(7), e0201353.
- 53 R. Beach, R. Conlan, M. Godwin and F. Moussy, Towards a Miniature Implantable In Vivo Telemetry Monitoring System Dynamically Configurable as a Potentiostat or Galvanostat for Two- and Three-Electrode Biosensors, *IEEE Trans. Instrum. Meas.*, 2005, **54**, 61–72.
- 54 J. Wang, *Analytical electrochemistry*, 2006.
- 55 R. Pemberton, A. Amine and J. Hart, Voltammetric Behavior of Chlorophyll a at a Screen-Printed Carbon Electrode and Its Potential Role as a Biomarker for Monitoring Fecal Contamination, *Anal. Lett.*, 2007, **37**, 1625–1643.
- 56 R. O. Kadara, N. Jenkinson and C. E. Banks, Disposable Bismuth Oxide Screen Printed Electrodes for the High Throughput Screening of Heavy Metals, *Electroanalysis*, 2009, **21**(22), 2410–2414.
- 57 C. W. Foster, A. P. de Souza, J. P. Metters, M. Bertotti and C. E. Banks, Metallic modified (bismuth, antimony, tin and combinations thereof) film carbon electrodes, *Analyst*, 2015, **140**(22), 7598–7612.
- 58 E. P. Randviir, J. P. Metters, J. Stainton and C. E. Banks, Electrochemical impedance spectroscopy versus cyclic voltammetry for the electroanalytical sensing of capsaicin utilising screen printed carbon nanotube electrodes, *Analyst*, 2013, **138**(10), 2970–2981.
- 59 N. Hernández-Ibáñez, I. Sanjuán, M. Á. Montiel, C. W. Foster, C. E. Banks and J. Iniesta, l-Cysteine determination in embryo cell culture media using Co (II)-phthalocyanine modified disposable screen-printed electrodes, *J. Electroanal. Chem.*, 2016, **780**, 303–310.
- 60 A. Bard and L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, Inc, 2001.
- 61 R. G. Compton and C. E. Banks, *Understanding Voltammetry*, Imperial College Press, 2nd edn, 2010.
- 62 J. Wang, Stripping Analysis, *Encyclopedia of Electrochemistry*, 2007.
- 63 A. J. Borrill, N. E. Reily and J. V. Macpherson, Addressing the practicalities of anodic stripping voltammetry for heavy metal detection: a tutorial review, *Analyst*, 2019, **144**(23), 6834–6849.
- 64 C. De Stefano, D. Milea, N. Porcino and S. Sammartano, Speciation of Phytate Ion in Aqueous Solution. Sequestering Ability toward Mercury(II) Cation in NaClaq at Different Ionic Strengths, *J. Agric. Food Chem.*, 2006, **54**(4), 1459–1466.
- 65 R. W. Cattrall, C. G. Gregorio, R. D. Webster, A. M. Bond and K. B. Oldham, Interaction between Silver and Other Heavy Metal Ions and the Ionophore S,S-Dipropyl Pyridine-2,6-dicarbothioate, *Anal. Chem.*, 1997, **69**(16), 3353–3359.
- 66 S. Makarychev-Mikhailov, A. Shvarev and E. Bakker, New trends in ion-selective electrodes, in *Electrochemical Sensors, Biosensors and their Biomedical Applications*, ed. X. Zhang, H. Ju and J. Wang, Academic Press, San Diego, 2008, ch. 4, pp. 71–114.
- 67 E. Malinowska, Z. Brzózka, K. Kasiura, R. J. M. Egberink and D. N. Reinhoudt, Lead selective electrodes based on thioamide functionalized calix[4]arenes as ionophores, *Anal. Chim. Acta*, 1994, **298**(2), 253–258.
- 68 X. Tang, P.-Y. Wang and G. Buchter, Ion-Selective Electrodes for Detection of Lead (II) in Drinking Water: A Mini-Review, *Environments*, 2018, **5**(9), 95.
- 69 A. Malon, T. Vigassy, E. Bakker and E. Pretsch, Potentiometry at Trace Levels in Confined Samples: Ion-Selective Electrodes with Subfemtomole Detection Limits, *J. Am. Chem. Soc.*, 2006, **128**(25), 8154–8155.
- 70 L. Höfler, I. Bedlechowicz, T. Vigassy, R. E. Gyurcsányi, E. Bakker and E. Pretsch, Limitations of Current Polarization for Lowering the Detection Limit of Potentiometric Polymeric Membrane Sensors, *Anal. Chem.*, 2009, **81**(9), 3592–3599.
- 71 R. You, P. Li, G. Jing and T. Cui, Ultrasensitive micro ion selective sensor arrays for multiplex heavy metal ions detection, *Microsyst. Technol.*, 2019, **25**(3), 845–849.
- 72 U. Yogeswaran and S.-M. Chen, A Review on the Electrochemical Sensors and Biosensors Composed of



- Nanowires as Sensing Material, *Sensors*, 2008, **8**(1), 290–313.
- 73 I. Moldoveanu, R.-I. van Stefan-Staden and J. F. van Staden, Electrochemical Sensors Based on Nanostructured Materials, in *Handbook of Nanoelectrochemistry: Electrochemical Synthesis Methods, Properties and Characterization Techniques*, ed. M. Aliofkhaezai and A. S. H. Makhlof, Springer International Publishing, Cham, 2016, pp. 1–15.
- 74 A. Hayat and J. L. Marty, Disposable Screen Printed Electrochemical Sensors: Tools for Environmental Monitoring, *Sensors*, 2014, **14**(6), 10432–10453.
- 75 R. W. Murray, A. G. Ewing and R. A. Durst, Chemically modified electrodes. Molecular design for electroanalysis, *Anal. Chem.*, 1987, **59**(5), 379A–390A.
- 76 V. S. Bagotsky, *Fundamentals of Electrochemistry*, Wiley, 2005.
- 77 A. Economou, Screen-Printed Electrodes Modified with "Green" Metals for Electrochemical Stripping Analysis of Toxic Elements, *Sensors*, 2018, **18**(4), 1032.
- 78 D. Martín-Yerga, M. B. González-García and A. Costa-García, Electrochemical determination of mercury: A review, *Talanta*, 2013, **116**, 1091–1104.
- 79 D. E. Mays and A. Hussam, Voltammetric methods for determination and speciation of inorganic arsenic in the environment—a review, *Anal. Chim. Acta*, 2009, **646**(1–2), 6–16.
- 80 L. A. Colon, R. Dadoo and R. N. Zare, Determination of carbohydrates by capillary zone electrophoresis with amperometric detection at a copper microelectrode, *Anal. Chem.*, 1993, **65**(4), 476–481.
- 81 I. G. Casella, T. R. I. Cataldi, A. M. Salvi and E. Desimoni, Electrocatalytic oxidation and liquid chromatographic detection of aliphatic alcohols at a nickel-based glassy carbon modified electrode, *Anal. Chem.*, 1993, **65**(21), 3143–3150.
- 82 A. J. de Bethune, Reference electrodes: Theory and practice, *J. Chem. Educ.*, 1962, **39**(2), A134.
- 83 X. Pei, W. Kang, W. Yue, A. Bange, W. R. Heineman and I. Papautsky, Disposable Copper-Based Electrochemical Sensor for Anodic Stripping Voltammetry, *Anal. Chem.*, 2014, **86**(10), 4893–4900.
- 84 J. Wang, J. Lu, S. B. Hocevar, P. A. M. Farias and B. Ogorevc, Bismuth-Coated Carbon Electrodes for Anodic Stripping Voltammetry, *Anal. Chem.*, 2000, **72**(14), 3218–3222.
- 85 K. Bedin, E. Mitsuyasu, A. Ronix, A. L. Cazetta, O. Pezoti and V. Almeida, Inexpensive Bismuth-Film Electrode Supported on Pencil-Lead Graphite for Determination of Pb(II) and Cd(II) Ions by Anodic Stripping Voltammetry, *Int. J. Anal. Chem.*, 2018, **2018**, 1–9.
- 86 A. Króllicka and A. Bobrowski, Bismuth film electrode for adsorptive stripping voltammetry - Electrochemical and microscopic study, *Electrochem. Commun.*, 2004, 99–104.
- 87 D. A. C. Brownson, D. K. Kampouris and C. E. Banks, An overview of graphene in energy production and storage applications, *J. Power Sources*, 2011, **196**(11), 4873–4885.
- 88 D. A. C. Brownson and C. E. Banks, Graphene electrochemistry: an overview of potential applications, *Analyst*, 2010, **135**(11), 2768–2778.
- 89 M. Pumera, Electrochemistry of graphene: new horizons for sensing and energy storage, *Chem. Rec.*, 2009, **9**(4), 211–223.
- 90 D. A. C. Brownson, P. J. Kelly and C. E. Banks, In situ electrochemical characterisation of graphene and various carbon-based electrode materials: an internal standard approach, *RSC Adv.*, 2015, **5**(47), 37281–37286.
- 91 K. Zeng and D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, *Prog. Energy Combust. Sci.*, 2010, **36**(3), 307–326.
- 92 W. M. Singh, T. Baine, S. Kudo, S. Tian, X. A. N. Ma and H. Zhou, *et al.*, Electrocatalytic and Photocatalytic Hydrogen Production in Aqueous Solution by a Molecular Cobalt Complex, *Angew. Chem., Int. Ed.*, 2012, **51**(24), 5941–5944.
- 93 S. Srinivasan and F. J. Salzano, Prospects for hydrogen production by water electrolysis to be competitive with conventional methods, *Int. J. Hydrogen Energy*, 1977, **2**(1), 53–59.
- 94 R. L. McCreery, Advanced Carbon Electrode Materials for Molecular Electrochemistry, *Chem. Rev.*, 2008, **108**(7), 2646–2687.
- 95 A. García-Miranda Ferrari, O. Amor-Gutiérrez, E. Costa-Rama and M. T. Fernández-Abedul, Batch injection electroanalysis with stainless-steel pins as electrodes in single and multiplexed configurations, *Sens. Actuators, B*, 2017, **253**, 1207–1213.
- 96 L. Fu, X. Li, J. Yu and J. Ye, Facile and Simultaneous Stripping Determination of Zinc, Cadmium and Lead on Disposable Multiwalled Carbon Nanotubes Modified Screen-Printed Electrode, *Electroanalysis*, 2013, **25**(2), 567–572.
- 97 S. Chaiyo, E. Mehmeti, K. Žagar, W. Siangproh, O. Chailapakul and K. Kalcher, Electrochemical sensors for the simultaneous determination of zinc, cadmium and lead using a Nafion/ionic liquid/graphene composite modified screen-printed carbon electrode, *Anal. Chim. Acta*, 2016, **918**, 26–34.
- 98 C. Huangfu, L. Fu, Y. Li, X. Li, H. Du and J. Ye, Sensitive Stripping Determination of Cadmium(II) and Lead(II) on Disposable Graphene Modified Screen-Printed Electrode, *Electroanalysis*, 2013, **25**(9), 2238–2243.
- 99 S.-M. Choi, D.-M. Kim, O.-S. Jung and Y.-B. Shim, A disposable chronocoulometric sensor for heavy metal ions using a diaminothiophene-modified electrode doped with graphene oxide, *Anal. Chim. Acta*, 2015, **892**, 77–84.
- 100 C. Pérez-Ràfols, N. Serrano, J. M. Díaz-Cruz, C. Ariño and M. Esteban, Simultaneous determination of Tl(I) and In(III) using a voltammetric sensor array, *Sens. Actuators, B*, 2017, **245**, 18–24.
- 101 C. Pérez-Ràfols, N. Serrano, J. M. Díaz-Cruz, C. Ariño and M. Esteban, A screen-printed voltammetric electronic tongue for the analysis of complex mixtures of metal ions, *Sens. Actuators, B*, 2017, **250**, 393–401.



- 131 K. Huang, Y. Chen, F. Zhou, X. Zhao, J. Liu and S. Mei, *et al.*, Integrated ion imprinted polymers-paper composites for selective and sensitive detection of Cd(II) ions, *J. Hazard. Mater.*, 2017, **333**, 137–143.
- 132 S. A. Rezvani Ivary, A. Darroudi, M. H. Arbab Zavar, G. Zohuri and N. Ashraf, Ion imprinted polymer based potentiometric sensor for the trace determination of Cadmium (II) ions, *Arabian J. Chem.*, 2017, **10**, S864–S869.
- 133 S. Hu, X. Xiong, S. Huang and X. Lai, Preparation of Pb(II) Ion Imprinted Polymer and Its Application as the Interface of an Electrochemical Sensor for Trace Lead Determination, *Anal. Sci.*, 2016, **32**(9), 975–980.
- 134 H. Wang, G. Zhao, Y. Yin, Z. Wang and G. Liu, Screen-Printed Electrode Modified by Bismuth/Fe₃O₄ Nanoparticle/Ionic Liquid Composite Using Internal Standard Normalization for Accurate Determination of Cd(II) in Soil, *Sensors*, 2018, **18**(1), 6.
- 135 K. Torres-Rivero, L. Torralba-Cadena, A. Espriu-Gascon, I. Casas, J. Bastos-Arrieta and A. Florido, Strategies for Surface Modification with Ag-Shaped Nanoparticles: Electrocatalytic Enhancement of Screen-Printed Electrodes for the Detection of Heavy Metals, *Sensors*, 2019, **19**(19), 4249.
- 136 Y.-S. Song, G. Muthuraman, Y.-Z. Chen, C.-C. Lin and J.-M. Zen, Screen Printed Carbon Electrode Modified with Poly(L-Lactide) Stabilized Gold Nanoparticles for Sensitive As(III) Detection, *Electroanalysis*, 2006, **18**(18), 1763–1770.
- 137 S. Laschi, I. Palchetti and M. Mascini, Gold-based screen-printed sensor for detection of trace lead, *Sens. Actuators, B*, 2006, **114**(1), 460–465.
- 138 X. Niu, C. Chen, Y. Teng, H. Zhao and M. Lan, Novel Screen-Printed Gold Nano Film Electrode for Trace Mercury(II) Determination Using Anodic Stripping Voltammetry, *Anal. Lett.*, 2012, **45**(7), 764–773.
- 139 L. Zhang, D. Li, W. Song, L. Shi, Y. Li and Y. Long, High Sensitive On-Site Cadmium Sensor Based on AuNPs Amalgam Modified Screen-Printed Carbon Electrodes, *IEEE Sens. J.*, 2010, **10**(10), 1583–1588.
- 140 E. Bernalte, C. M. Sánchez and E. P. Gil, Determination of mercury in ambient water samples by anodic stripping voltammetry on screen-printed gold electrodes, *Anal. Chim. Acta*, 2011, **689**(1), 60–64.
- 141 E. Punrat, S. Chuanuwatanakul, T. Kaneta, S. Motomizu and O. Chailapakul, Method development for the determination of mercury(II) by sequential injection/anodic stripping voltammetry using an in situ gold-film screen-printed carbon electrode, *J. Electroanal. Chem.*, 2014, **727**, 78–83.
- 142 O. Domínguez Renedo and M. J. Arcos Martínez, Anodic stripping voltammetry of antimony using gold nanoparticle-modified carbon screen-printed electrodes, *Anal. Chim. Acta*, 2007, **589**(2), 255–260.
- 143 K. Malzahn, J. R. Windmiller, G. Valdés-Ramírez, M. J. Schöning and J. Wang, Wearable electrochemical sensors for in situ analysis in marine environments, *Analyst*, 2011, **136**(14), 2912–2917.
- 144 M. F. Noh and I. E. Tothill, Development and characterisation of disposable gold electrodes, and their use for lead(II) analysis, *Anal. Bioanal. Chem.*, 2006, **386**(7–8), 2095–2106.
- 145 I. Ait Tayeb and K. Razak, Development of Gold Nanoparticles Modified Electrodes for the Detection of Heavy Metal Ions, *J. Phys.: Conf. Ser.*, 2018, **1083**, 012044.
- 146 E. Bernalte, S. Arévalo, J. Pérez-Taborda, J. Wenk, P. Estrela and A. Avila, *et al.*, Rapid and on-site simultaneous electrochemical detection of copper, lead and mercury in the Amazon river, *Sens. Actuators, B*, 2020, **307**, 127620.
- 147 V. S. Ijery and A. K. Srivastava, Voltammetric determination of copper at chemically modified electrodes based on crown ethers, *Fresenius' J. Anal. Chem.*, 2000, **367**(4), 373–377.
- 148 V. S. Ijery and A. K. Srivastava, Voltammetric Determination of Lead at Chemically Modified Electrodes Based on Crown Ethers, *Anal. Sci.*, 2001, **17**(5), 605–608.
- 149 S. V. Prabhu, R. P. Baldwin and L. Kryger, Preconcentration and determination of lead(II) at crown ether and cryptand containing chemically modified electrodes, *Electroanalysis*, 1989, **1**(1), 13–21.
- 150 I.-M. Simionca, A. Arvinte and M. Pinteala, Crown ether-based structures for sensitive electrochemical detection, *High Perform. Polym.*, 2015, **27**(5), 669–675.
- 151 G. Zhiqiang, L. Peibiao and Z. Zaofan, Anodic stripping voltammetric determination of traces of mercury with a chemically modified electrode, *Microchem. J.*, 1991, **43**(2), 121–132.
- 152 M. V. Tsybmal, I. Y. Tuijan, Z. A. Temerdashev and K. Z. Brainina, Crown ethers in stripping voltammetry of palladium, *Electroanalysis*, 1994, **6**(2), 113–117.
- 153 S. Tanaka and H. Yoshida, Stripping voltammetry of silver(I) with a carbon-paste electrode modified with thiocrown compounds, *Talanta*, 1989, **36**(10), 1044–1046.
- 154 Z. Huang and S. Chang, Synthesis of Unique Ionophores of penta-Crown Ethers, *Synlett*, 2005, **2005**, 2257–2259.
- 155 H. An, J. S. Bradshaw, R. M. Izatt and Z. Yan, Bis- and Oligo(benzocrown ether)s, *Chem. Rev.*, 1994, **94**(4), 939–991.
- 156 N. Serrano, A. González-Calabuig and M. del Valle, Crown ether-modified electrodes for the simultaneous stripping voltammetric determination of Cd(II), Pb(II) and Cu(II), *Talanta*, 2015, **138**, 130–137.
- 157 Y.-F. Sun, J.-H. Sun, J. Wang, Z.-X. Pi, L.-C. Wang and M. Yang, *et al.*, Sensitive and anti-interference stripping voltammetry analysis of Pb(II) in water using flower-like MoS₂/rGO composite with ultra-thin nanosheets, *Anal. Chim. Acta*, 2019, **1063**, 64–74.
- 158 J. Shang, M. Zhao, H. Qu, H. Li, R. Gao and S. Chen, New application of p-n junction in electrochemical detection: The detection of heavy metal ions, *J. Electroanal. Chem.*, 2019, **855**, 113624.
- 159 N. Baghban, E. Yilmaz and M. Soylak, A magnetic MoS₂-Fe₃O₄ nanocomposite as an effective adsorbent for dispersive solid-phase microextraction of lead(II) and



- copper(II) prior to their determination by FAAS, *Microchim. Acta*, 2017, **184**(10), 3969–3976.
- 160 B. Wang, Z. Bai, H. Jiang, P. Prinsen, R. Luque and S. Zhao, *et al.*, Selective heavy metal removal and water purification by microfluidically-generated chitosan microspheres: Characteristics, modeling and application, *J. Hazard. Mater.*, 2019, **364**, 192–205.
- 161 Y. Fu, L. Qin, D. Huang, G. Zeng, C. Lai and B. Li, *et al.*, Chitosan functionalized activated coke for Au nanoparticles anchoring: Green synthesis and catalytic activities in hydrogenation of nitrophenols and azo dyes, *Appl. Catal., B*, 2019, **255**, 117740.
- 162 W.-Y. Zhou, S.-S. Li, X.-Y. Xiao, S.-H. Chen, J.-H. Liu and X.-J. Huang, Defect- and phase-engineering of Mn-mediated MoS₂ nanosheets for ultrahigh electrochemical sensing of heavy metal ions: chemical interaction-driven in situ catalytic redox reactions, *Chem. Commun.*, 2018, **54**(67), 9329–9332.
- 163 R. O. Kadara, N. Jenkinson and C. E. Banks, Screen printed recessed microelectrode arrays, *Sens. Actuators, B*, 2009, **142**(1), 342–346.
- 164 T. J. Davies, S. Ward-Jones, C. E. Banks, J. del Campo, R. Mas and F. X. Muñoz, *et al.* The cyclic and linear sweep voltammetry of regular arrays of microdisc electrodes: Fitting of experimental data, *J. Electroanal. Chem.*, 2005, **585**(1), 51–62.
- 165 P. N. Bartlett and S. L. Taylor, An accurate microdisc simulation model for recessed microdisc electrodes, *J. Electroanal. Chem.*, 1998, **453**(1), 49–60.
- 166 D. Ortiz-Aguayo, M. Bonet-San-Emeterio and M. del Valle, Simultaneous Voltammetric Determination of Acetaminophen, Ascorbic Acid and Uric Acid by Use of Integrated Array of Screen-Printed Electrodes and Chemometric Tools, *Sensors*, 2019, **19**(15), 3286.
- 167 V. Ruiz-Valdepenas Montiel, E. Povedano, S. Benede, L. Mata, P. Galan-Malo and M. Gamella, *et al.*, Disposable Amperometric Immunosensor for the Detection of Adulteration in Milk through Single or Multiplexed Determination of Bovine, Ovine, or Caprine Immunoglobulins G, *Anal. Chem.*, 2019, **91**(17), 11266–11274.
- 168 E. C. Rama and A. Costa-García, Screen-printed Electrochemical Immunosensors for the Detection of Cancer and Cardiovascular Biomarkers, *Electroanalysis*, 2016, **28**(8), 1700–1715.
- 169 M. Sharafeldin, K. McCaffrey and J. F. Rusling, Influence of antibody immobilization strategy on carbon electrode immunoarrays, *Analyst*, 2019, **144**(17), 5108–5116.
- 170 F. Crespilho, *Nanobioelectrochemistry*, 2013.
- 171 J. P. Metters, R. O. Kadara and C. E. Banks, Fabrication of co-planar screen printed microband electrodes, *Analyst*, 2013, **138**(9), 2516–2521.
- 172 D. H. Craston, C. P. Jones, D. E. Williams and N. El Murr, Microband electrodes fabricated by screen printing processes: Applications in electroanalysis, *Talanta*, 1991, **38**(1), 17–26.
- 173 R. O. Kadara, N. Jenkinson and C. E. Banks, Characterization and fabrication of disposable screen printed microelectrodes, *Electrochem. Commun.*, 2009, **11**(7), 1377–1380.
- 174 W. C. Chen, Y. L. Hsu, S. Venkatesan and J. M. Zen, Disposable Screen-Printed Edge Band Ultramicroelectrodes for Use as Nitric Oxide Gas Sensor in Designing an Easily Applicable Method for Real Sample Analysis of Nitrite with Superior Selectivity and Sensitivity, *Electroanalysis*, 2014, **26**, 565–572.
- 175 J. Wang, J. Lu, B. Tian and C. Yarnitzky, Screen-printed ultramicroelectrode arrays for on-site stripping measurements of trace metals, *J. Electroanal. Chem.*, 1993, **361**(1), 77–83.
- 176 N. G. Karousos, R. Carrington, S. J. Wilkins, C. Livingstone and J. Davis, Molecular sieving of anti-oxidants at a copper-carbon laminate assembly, *Electrochem. Commun.*, 2005, **7**(5), 500–504.
- 177 R. D. Gardner, A. Zhou and N. A. Zufelt, Development of a Microelectrode Array Sensing Platform for Combination Electrochemical and Spectrochemical Aqueous Ion Testing, *Sens. Actuators, B*, 2009, **136**(1), 177–185.
- 178 E. Sánchez-Tirado, C. Salvo, A. González-Cortés, P. Yáñez-Sedeño, F. Langa and J. M. Pingarrón, Electrochemical immunosensor for simultaneous determination of interleukin-1 beta and tumor necrosis factor alpha in serum and saliva using dual screen printed electrodes modified with functionalized double-walled carbon nanotubes, *Anal. Chim. Acta*, 2017, **959**, 66–73.
- 179 V. Escamilla-Gómez, D. Hernández-Santos, M. B. González-García, J. M. Pingarrón-Carrazón and A. Costa-García, Simultaneous detection of free and total prostate specific antigen on a screen-printed electrochemical dual sensor, *Biosens. Bioelectron.*, 2009, **24**(8), 2678–2683.
- 180 F. Conzuelo, S. Campuzano, M. Gamella, D. G. Pinacho, A. J. Reviejo and M. P. Marco, *et al.*, Integrated disposable electrochemical immunosensors for the simultaneous determination of sulfonamide and tetracycline antibiotics residues in milk, *Biosens. Bioelectron.*, 2013, **50**, 100–105.
- 181 J. Pilas, T. Selmer, M. Keusgen and M. J. Schöning, Screen-Printed Carbon Electrodes Modified with Graphene Oxide for the Design of a Reagent-Free NAD⁺-Dependent Biosensor Array, *Anal. Chem.*, 2019, **91**(23), 15293–15299.
- 182 S. K. Tuteja, C. Ormsby and S. Neethirajan, Noninvasive Label-Free Detection of Cortisol and Lactate Using Graphene Embedded Screen-Printed Electrode, *Nano-Micro Lett.*, 2018, **10**(3), 41.
- 183 D. Xie, C. Li, L. Shangguan, H. Qi, D. Xue and Q. Gao, *et al.*, Click chemistry-assisted self-assembly of DNA aptamer on gold nanoparticles-modified screen-printed carbon electrodes for label-free electrochemical aptasensor, *Sens. Actuators, B*, 2014, **192**, 558–564.
- 184 R. García-González, A. Costa-García and M. T. Fernández-Abedul, Dual screen-printed electrodes with elliptic working electrodes arranged in parallel or perpendicular to the strip, *Sens. Actuators, B*, 2014, **198**, 302–308.

