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Recent advances in portable heavy metal electrochemical sensing platforms

Alejandro García-Miranda Ferrari, [a] Paul Carrington,[b] Samuel J. Rowley-Neale *[a] and Craig E. Banks *[a]

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

[a] *Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK. E-mail: s.rowley-neale@mmu.ac.uk, c.banks@mmu.ac.uk; Fax: +44(0)1612476831; Tel: +44(0)1612471196*
[b] *Aquacheck Engineering Ltd, Royle Barn Road, Castleton, Rochdale, Lancashire, OL11 3DT, UK*

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 (Pb^{2+}) and chromium (Cr^{3+}) 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 (Cu^{2+}) 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 Cu^{2+} availability in the water distribution system,[17] meaning that there is a need to identify areas, which are particularly at risk. High Cu^{2+} 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 (Pb^{2+}), is recognised as an exceptional case because it arises in drinking water from the plumbing system. In the UK, the ubiquitous use of lead solder[18] and fittings[19] 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 properties[20]). The presence of Pb^{2+} 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 optical[27] 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 extraction[28]), 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 devices[30]) 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] biomolecules[45] 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. There 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. Ainla *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

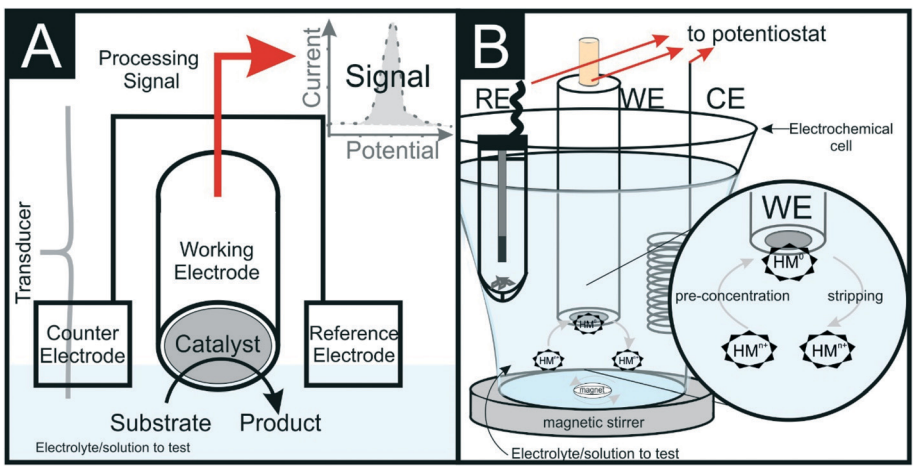

Fig. 1 Schematic representation of electrochemical sensing (A) and a classic electrochemical cell/stripping voltammetric method (B).

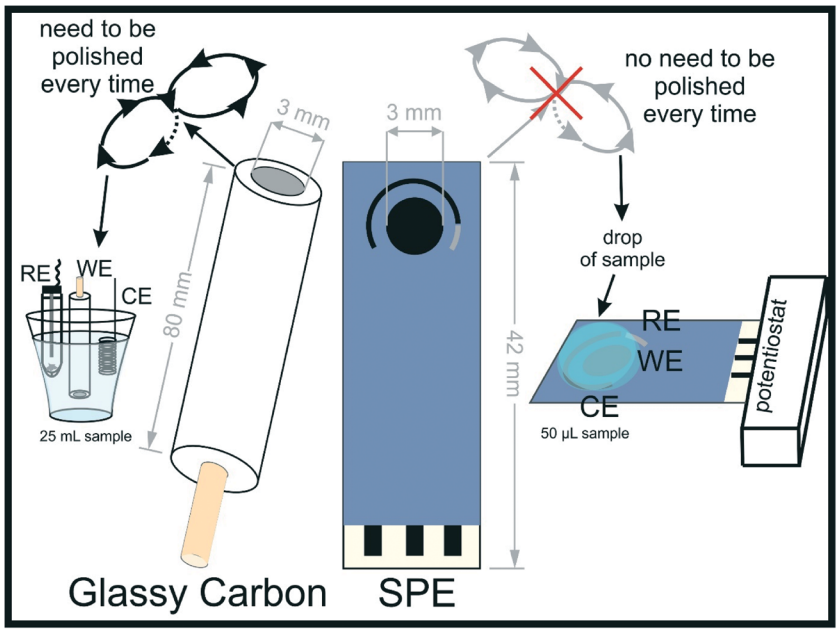

Fig. 2 Schematic overview comparing a classic electrochemical cell *vs.* a screen-printed electrode platform performing the analysis within a single drop of analyte.

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 use 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,

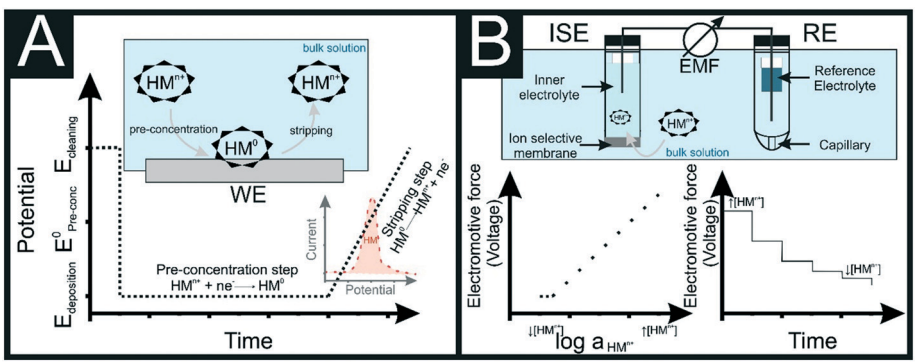

Fig. 3 Schematic diagram of a potentiostatic (anodic stripping voltammetry; A) and a potentiometric (ion-selective electrode (ISE); B) method respectively.

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]

$$i = KCt_{\text{pre-concentration}}$$

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 ranges[77] 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-coating[112] and dip-coating[113]), 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 thought the WE and the electrolyte, which contains the chosen modifier, to create stable polymers[114] or metal[115] 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 Cu^{2+},[116] Pb^{2+} [56,117] Cd^{2+},[56] and $Zinc^{2+}$ [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

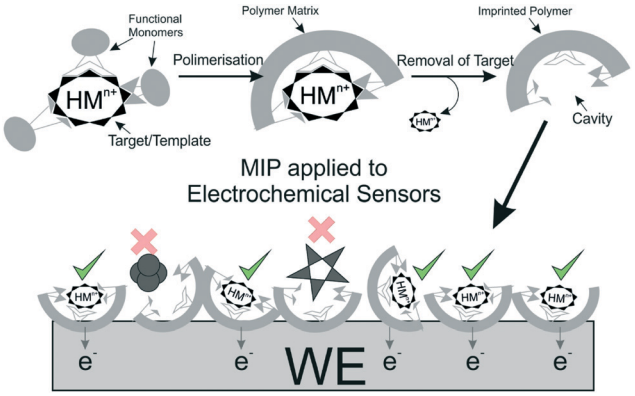

Fig. 4 Schematic representing MIPs applied to electrochemical sensor platforms.

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 Co^{2+},[130] Cd^{2+} [131,132] and others[133] 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 and multi-element detection capabilities of HM such as Cd^{2+} and Pb^{2+}.[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 Cd^{2+} or Pb^{2+} with Ag-NP SPEs. Barton *et al.*[27] elegantly reviewed the use of Au-coated SPEs to detect HM, showing the determination of Pb^{2+}, Cd^{2+}, Hg^{2+}, As^{2+}, Cu^{2+} and Sb^{2+} 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 Pb^{2+}, Cu^{2+} and Hg^{2+}

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 μA μM^{-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

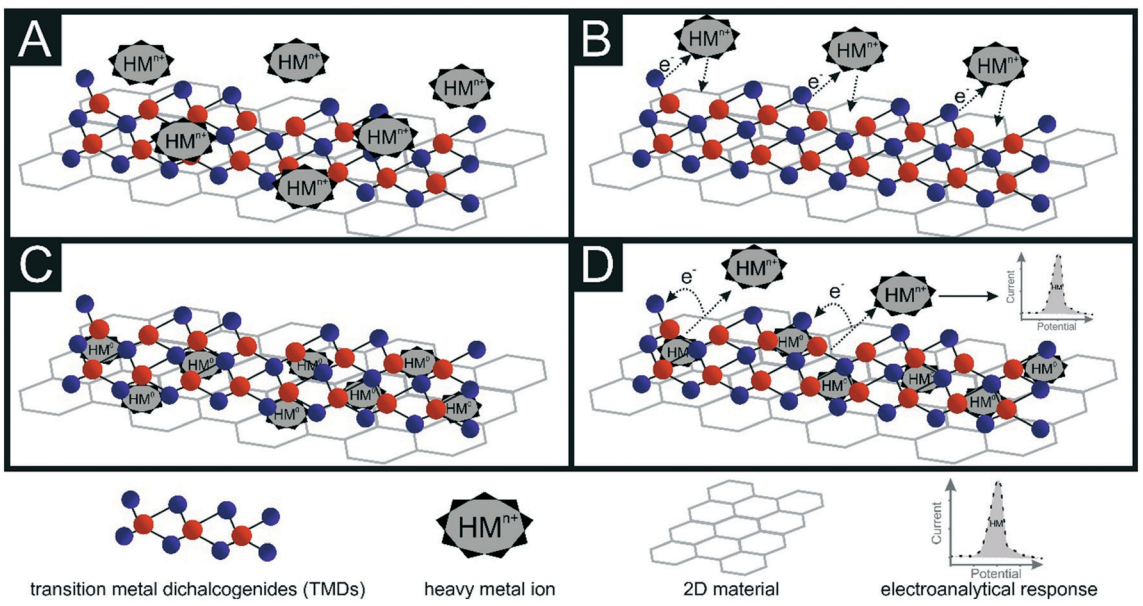

Fig. 5 Schematic representing the electrochemical steps when TMDS are used within an electrochemical sensor: pre-measurement (A), deposition potential application (B), pre-accumulation step (C) and stripping step (D).

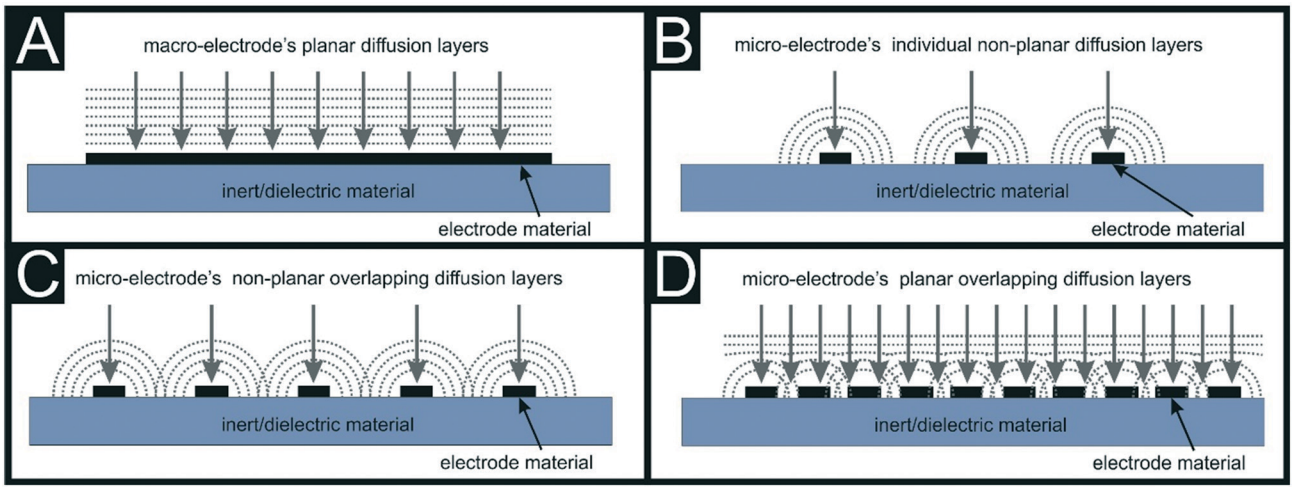

Fig. 6 Schematic represensing the catergories of diffusion profiles at different micro-electrode array configurations. Planar diffusion layers at macro-electrodes (A), individual non-planar diffusion layers at micro-electrodes (B), non-overlapping diffusion layers at micro-electrodes (C) and planar overlapping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

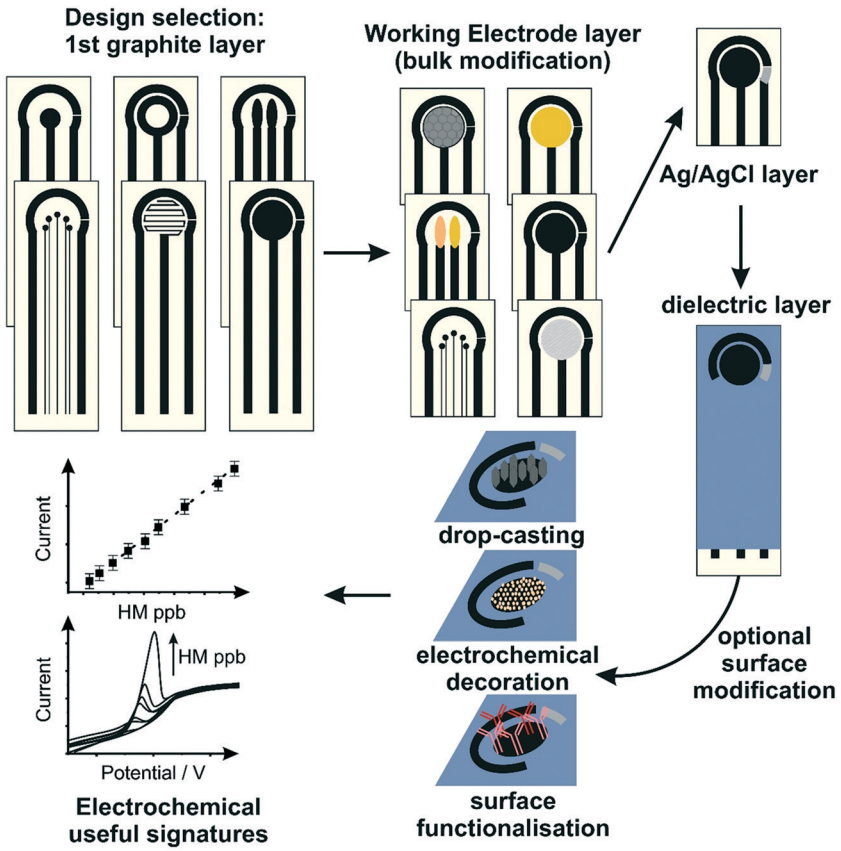

Fig. 7 Schematic representation of possible options for tailoring screen-printed electrochemical sensing platforms.

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-tubes[176] 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 mm^2. 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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