

CHAPTER 1

Advances in Stripping Analysis of Metals

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1.1 Introduction

Electrochemical stripping analysis (SA) has been established as a successful trace analysis technique for more than three decades. Stripping analysis is a general term that encompasses a wide family of electroanalytical techniques that make use of a “preconcentration” step of the analyte on the surface of the working electrode. In SA, the preconcentration step is followed by the detection step in which the accumulated analyte is detected and quantified by means of a voltammetric or chronopotentiometric scan. While in solution-phase electrochemical detection the redox signal is determined by the rate of mass transport of the electroactive analyte to the electrode surface, in SA the redox signal is determined by the amount of the accumulated analyte. Therefore, the accumulation step is responsible for the high sensitivity of SA whereas the different potential methods of accumulation of the analyte on the working electrode (discussed in Section 1.2) and the multi-parametric nature of SA provide versatility, wide applicability and enhanced selectivity. Typical metals and semi-metals that can be determined with SA are listed in Table 1.1. The theory and practice of SA are described in specialized monographs^{1,2} and general review articles.^{3–5}

Table 1.1 Metals and semi-metals that can be determined by SA (in *italics* are the species that are normally determined only after electrolytic accumulation, underlined are the species that are normally determined after non-electrolytic accumulation and in **bold** are the species that can be determined after either electrolytic or non-electrolytic accumulation).

												<u>Al</u>						
	<u>Sc</u>	<u>Ti</u>	<u>V</u>	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	Cu	Zn	<u>Ga</u>	<i>Ge</i>	<i>As</i>	<i>Se</i>				
	<u>Y</u>	<u>Zr</u>		<u>Mo</u>	<u>Tc</u>			<u>Pd</u>	Ag	Cd	In	Sn	Sb					
	<u>La</u>	<u>Hf</u>						<u>Pt</u>	Au	Hg	<i>Tl</i>	<i>Pb</i>	<i>Bi</i>					
<u>Ce</u>	<u>Pr</u>					<u>Eu</u>				<u>Dy</u>	<u>Ho</u>				<u>Yb</u>	<u>Lu</u>		
<u>Th</u>		<u>U</u>																

A brief account of the birth and gradual evolution of SA is provided in earlier work.^{1,5,6} SA was first conceptualized and applied in 1931 by Zbinden to determine low concentrations of copper at a platinum electrode.⁷ However, not until the 1950s was SA revisited when the hanging mercury drop electrode was developed by Kemula. In the same decade, the remarkable sensitivity of SA was stressed by many workers and new types of thin mercury-film electrodes were introduced. In the 1960s, the theory for SA and pulsed potential-time waveforms was developed. The commercial availability of low cost multi-purpose apparatus and the expanding use of SA to many new analytical applications took place in the 1970s. The development of non-electrolytic preconcentration approaches and of automated flow-through manifolds, together with the introduction of microelectrodes for SA, dominated the 1980s and 1990s. Recent advances in SA are concentrated on research on new eco-friendly electrode materials, the extended use of microfabrication technologies and miniaturization and the development of integrated devices for on-site monitoring. Therefore, this chapter will not focus on specific applications but will try to highlight developments in sensor types, fabrication and materials.

1.2 The Principle of Stripping Analysis

The distinctive feature of SA in comparison to other electroanalytical techniques is the accumulation/preconcentration step. In most applications involving analysis of metals, preconcentration is carried out with electrolysis of the target metal cations to the respective metals (and some special cases to metal oxides) and deposition on the surface of the working electrode^{1,2} (Figure 1.1A). Following accumulation, the accumulated metals are oxidized (or the metal oxides reduced) to the respective cations and stripped back into the solution. Depending on the nature of the working electrode surface, the

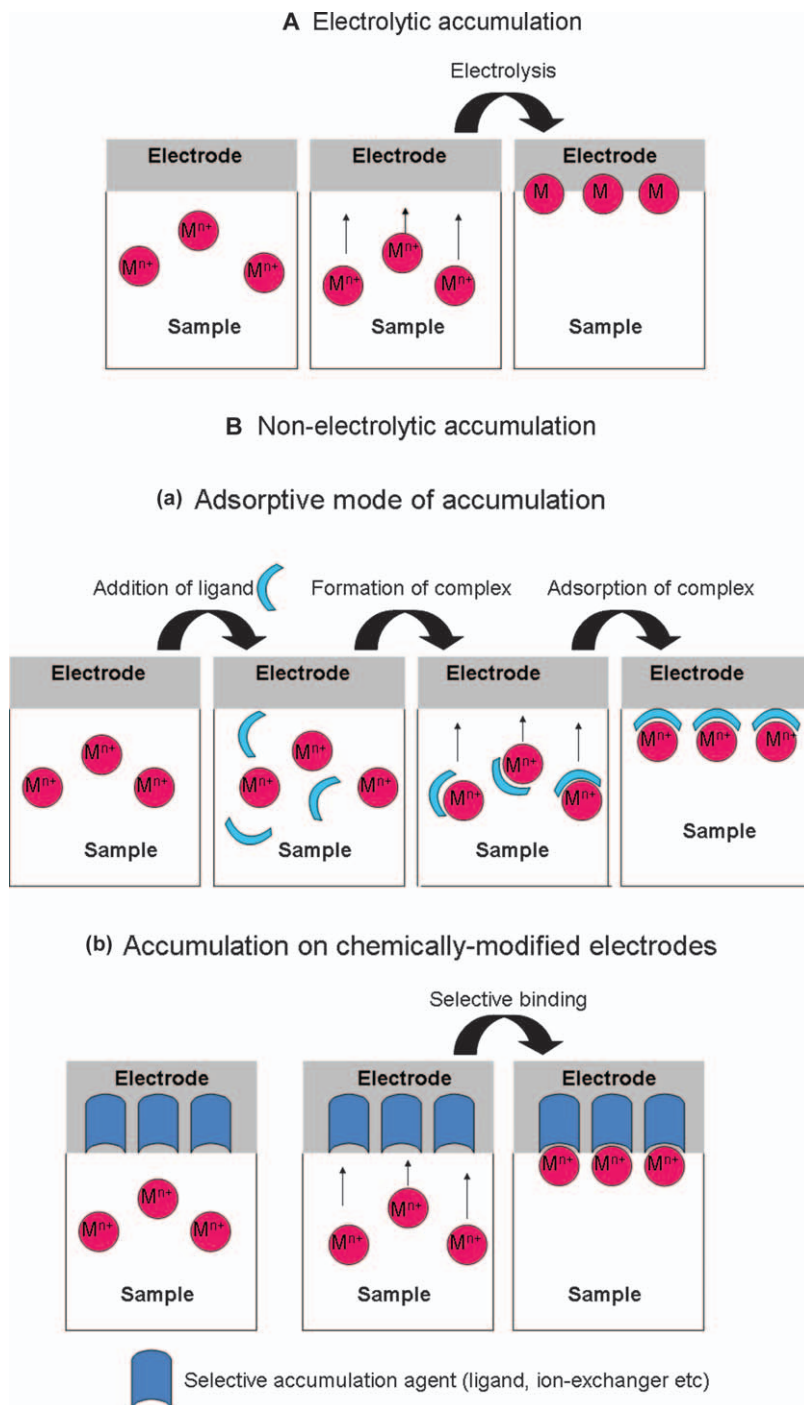


Figure 1.1 Modes of accumulation in SA of metals.

deposited metal can form a thin film, an amalgam or an alloy with the electrode. Reduction of metals on inert electrodes (such as carbon, platinum or boron-doped diamond) proceeds *via* the formation of a monolayer of the target metal (underpotential deposition, UPD) followed by the deposition of the bulk-phase metal. Although simple and potentially useful, electrolytic preconcentration on inert solid electrodes is characterized by multiple stripping peaks that are hard to interpret.^{8,9} This is due to the easy formation of intermetallic compounds on the electrode surface and to the different oxidation (stripping) potentials associated with the different states of the metal deposits. Amalgams are typically generated when heavy metals deposit on mercury electrodes or during the deposition of mercury on gold electrodes. Finally, alloys are formed when bismuth, tin or antimony electrodes are used for electrolytic accumulation of alloy-forming metals. Amalgamation and alloying facilitate the electrolytic deposition and stripping of metals and lead to stripping signals that are easier to interpret. Following electrolytic accumulation, the stripping step can be performed by an anodic voltammetric scan, a constant oxidation current or by a chemical oxidizing agent.^{1,2}

Non-electrolytic accumulation can be alternatively employed for metals that are not amenable to electrolytic deposition, are not readily oxidized during the stripping step or produce overlapping oxidation stripping peaks with other target or interfering species when accumulated by electrolysis.¹⁰ The adsorptive mode of accumulation involves addition of a selective complexing ligand (such as dimethylglyoxime, catechol, 8-hydroxyquinoline) with surface-active properties in the sample¹⁰⁻¹³ (Figure 1.1B-a). The metal cations form a complex with the ligand and the complex is then physisorbed on the electrode surface. The stripping step is usually based on the reduction of the metal cation in the accumulated complex but the reduction of the ligand or catalytic effects can be also exploited.^{13,14} A second strategy is based on the utilization of chemically-modified electrodes.^{10,15,16} In this case, the working electrode is bulk- or surface-modified with a suitable agent that can selectively bind the target metal cation. In the context of SA of metals, accumulation at chemically-modified electrodes can proceed by electrostatic interactions (with a clay or ion-exchanger modifier) or complexation (with a complexing ligand as the modifier). When the electrode is immersed in the sample, the modifier on the electrode interacts and binds with the target metal cations, which are accumulated on the electrode surface in their native oxidation state (Figure 1.1B-b). In the simplest scenario, the stripping step can be a reductive scan in which the accumulated metal cations are reduced.⁹ A more complex protocol involves potentiostatic reduction of the accumulated metal cations followed by an anodic stripping step in which the target metals are oxidized.⁹ Again, stripping can be performed by either a voltammetric scan or a (reductive or oxidizing) constant current.

The nomenclature in SA is not standardized and usually more or less established empirical abbreviations define a technique by reference to the

accumulation mode, the stripping step or both. To avoid the confusion caused by this practice, the guidelines proposed earlier are adopted here.¹⁷ When voltammetry is used in the stripping step, the terms anodic stripping voltammetry (ASV, anodic scan) and cathodic stripping voltammetry (CSV, cathodic scan) are used. In ASV and CSV, the peak-shaped current–potential (i – E) response is recorded and the oxidation peak current is measured and related to the respective metal concentration in the sample. The voltammetric scan is normally performed in the differential-pulse (DP) or the square-wave (SW) mode, which offer better rejection of the background current and lower limits of detection.¹ When the stripping step is performed by an oxidant in solution or a constant current (irrespective of its polarity), the term stripping chronopotentiometry (SCP) is used. In SCP, the potential of the working electrode is recorded with respect to time as the target analytes are oxidized (by the application of current or chemically) and the residence time (time during which the potential of the working electrode remains stable) is related to the respective metal concentration in the sample. In modern instruments, the response is converted into a peak-shape by plotting the differential dt/dE with respect to potential. The relative strengths of the potentiometric and voltammetric stripping modes have been reviewed.¹⁸ In both cases, the mode of accumulation of the target analyte(s) should be explicitly defined as electrolytic or non-electrolytic.¹⁷

Some more specialized variations of SA, particularly useful for metal speciation, include the “competitive ligand equilibration–adsorptive cathodic stripping voltammetry” and the “absence of gradients and Nernstian equilibrium stripping (ANGES)” approaches.¹⁹ Abrasive SA is widely used for the elemental analysis of solid samples of archeological²⁰ or forensic²¹ interest.

In SA, the sensitivity critically depends on the amount of the analyte accumulated onto the surface of the electrode during the preconcentration step and, therefore, on the rate of mass transport. Efficient mass transfer of the analyte to the surface of the working electrodes during the preconcentration step is normally carried out under conditions of forced convection by mechanical stirring of the solution or rotation of the electrode. However, in addition to these conventional methods of enhancing the mass transport efficiency, some unconventional techniques to enhance mass transfer (ultrasound, microwaves or heating of the working electrode) have been developed. The principles, enhancing mechanisms, instrumentation and applications of these approaches have been reviewed.²² In “sonoelectrochemistry”, ultrasound is applied with frequencies between 20 and 100 kHz and power densities from *ca.* 8 to 500 W cm⁻². The high energy density transferred by the sound wave promotes turbulent solution flow and cavitation effects that lead to reduction of the diffusion layer thickness and *in situ* cleaning/activation of the electrode. Heating of electrodes causes heat to stream out of the heated surface and warm up the solution near the electrode. Density gradients between hot and cold regions induce laminar flow. This “micro-stirring” effect is more efficient than mechanical stirring

and can be exploited during the accumulation step in SA. Electrode heating can be achieved by means of a high frequency AC current or microwave heating. Finally, application of constant or high-frequency magnetic fields have been reported for SA.

1.3 Advances in Electrodes, Sensors and Devices

1.3.1 Carbon Electrodes

Carbon still remains one of the most important and widely used electrode materials in SA. Applications of carbon-based electrodes in SA of metals have been reviewed previously.^{23,24} Glassy carbon, impregnated graphite, carbon paste, carbon fibres, carbon-containing composite materials, carbon nano-materials or screen-printed inks can be used; graphite ink screen-printed electrodes will be covered in Section 1.3.2.

Glassy carbon (GC) is still a widely used material in SA. Since the sensitivity of bare GC in the SA of metals is low, the GC surface is usually subject to preliminary (*ex situ*) surface modification and/or *in situ* modification to achieve the desired surface properties. Thin films of metals, conducting polymers, selective organic reagents, clay minerals and ion-exchangers have been reported for surface modification of GC.²³ Occasionally, more than one modifying layers is used. Metal films (mercury, bismuth, gold, antimony, copper) facilitate the accumulation of metal cations and the stripping procedure of deposited metals. Conducting polymers (polyaniline, cellulose acetate, Nafion) can provide selectivity against macromolecules in complex samples and may serve as cation exchangers, thus facilitating the accumulation of metals. Organic ligands such as crown ethers and EDTA (ethylenediaminetetraacetic acid) (sometimes immobilized in polymers) are used to fabricate chemically-modified electrodes suitable for non-electrolytic accumulation of metal cations.

Carbon paste electrodes (CPEs) are made by homogenizing graphite and a water-immiscible binding liquid (paraffin, silicon oil, tricresyl phosphate). These CPEs are suitable for *in situ* or *ex situ* surface modification with metal films (mercury, bismuth, antimony) or metal oxides (which are converted into the respective metals by reduction).^{23,25} CPEs are also very convenient for bulk modification by incorporating organic ligands (crown compounds, calixarenes), clays (vermiculite and montmorillonite) and ion exchangers (resins) within the paste material in order to facilitate metal preconcentration.^{23,25}

Carbon composite electrodes are made of graphite, carbon, glassy, carbon or diamond powders mixed with polymeric binders such as epoxy resins, methacrylate, silicon, styrene-acrylonitrile and polyester. Although there are some reports of unmodified composite electrodes in SA of metals, most applications involve bulk or surface modification of composite materials by metal films or organic ligands that lead to higher sensitivity and better selectivity.^{24,26}

Nanoscale carbon-based materials (single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), fullerenes and graphene) exhibit many characteristics that make them ideal as electrode materials. Due to their strong adsorption ability, nanoscale carbon-based materials can be used as sorbents for metal ions.²⁷ Therefore, there are many recent reports of the detection of multiple heavy metal ions by SA following a sorption/preconcentration step on nanoscale carbon-based electrodes either unmodified or modified with chelators, metal films or clays.^{28–36}

Boron-doped diamond (BDD) consists of a diamond lattice *p*-type doped with boron typically to 10^{20} cm^{-3} (which corresponds to approximately 1 boron atom per 1000 carbon atoms) ensuring good conductivity and electrochemical properties. Over the last 15 years diamond electrodes have been used for a wide range of electrochemical applications and one of the main areas on which research has focused is the use of unmodified or metal film-modified boron-doped diamond as a mercury-free alternative for analysis using SA.³⁷ Due to their inertness, BDD electrodes are compatible with ultrasound-, microwave-, heating- and laser-enhanced deposition in SA.

1.3.2 Screen-Printed Electrodes

The fabrication of screen-printed electrodes (SPEs) involves squeezing the printing material (an ink paste) through a screen mesh (which defines the electrode's geometrical pattern) onto an electrically insulating substrate. The advantages of screen printing as a method for electrode fabrication are the low cost (in terms of the capital cost of the printing apparatus and the cost of consumables), the flexibility in selecting and modifying the electrode material, the potential for miniaturization and the scope for mass production of disposable sensors. SPEs have been widely used in SA of metals and their fabrication and applications have been covered in comprehensive reviews.^{9,38,39} The printing material is normally some type of graphite-containing ink but gold, platinum and silver SPEs can be produced by using ink loaded with these metals. Additionally, screen-printed microelectrodes or microelectrode arrays with various configurations can also be prepared by different technologies.²⁴ Bare SPEs have been reported with some success but these are normally of limited utility due to the complicated voltammograms obtained. SPEs covered with mercury films and, more recently, with bismuth and antimony films are the most popular such sensors combined with electrolytic ASV and SCP.^{38,39} SPEs made by using gold-containing ink or coated with gold are also frequently used for the determination of mercury and arsenic while silver and platinum SPEs have been occasionally used. Numerous applications employing chemically-modified SPEs have been reported for non-electrolytic accumulation of metals.^{38,39} A chelating ligand can be incorporated on the surface of the SPE by drop-coating or into the bulk of the SPE by mixing in with the carbon ink prior to printing.

1.3.3 Solid Amalgam Electrodes

Recent research has indicated that solid amalgam electrodes can, in many cases, successfully substitute mercury electrodes in SA. Amalgam electrodes are essentially solid electrodes consisting of an amalgam of mercury with another metal (such as silver) or of an amalgam dispersed in a conductive polymer or pasting liquid. The classification, fabrication methods and analytical applications of amalgam electrodes in SA of metals have been extensively reviewed.⁴⁰ Amalgams are claimed to be non-toxic since the mercury contained in the amalgam is not readily released.⁴¹ The main challenges in developing solid amalgam electrodes approaching the performance of their mercury counterparts are: (a) to obtain a sufficiently wide cathodic potential window (since the presence of various metals in the amalgam normally causes a reduction of the cathodic overpotential of mercury) and (b) to achieve a reproducible and stable surface.⁴² In practical terms, silver amalgam electrodes in conjunction with ASV and electrolytic deposition are the most widely used for SA of metals.^{40,42}

1.3.4 “Green” Metal and Metal-film Electrodes

In 2000, a new type of “green” metallic electrode, the bismuth-film electrode (BiFE), was introduced, consisting of a thin layer of bismuth electroplated on a conductive substrate.⁴³ The BiFE was the bismuth counterpart of the existing mercury film electrode (MFE), itself widely used in SA of heavy metals.⁴⁴ This pioneering work initiated an intense research effort for the development of different types of eco-friendly electrodes for SA. Bismuth-based electrodes are the most promising “green” sensors for SA of heavy metals using both electrolytic and non-electrolytic accumulation as demonstrated in some earlier reviews.^{45–48} The attractions of these transducers are their low toxicity combined with the ability to form low-temperature alloys with many metals similar to the amalgams formed with mercury. In its simplest form, the electrode consists of a bismuth rod or bismuth-containing composite or carbon paste. BiFEs are the most popular bismuth electrodes and can be fabricated by *in situ* or *ex situ* electroplating of a thin bismuth film on a conductive substrate (noble metals, different forms of carbon) from a Bi(III) solution or by deposition on glass or silicon *via* thin-layer microelectronic techniques.^{49–51} The bismuth film can also be coated with polymeric materials (such as Nafion) to improve the selectivity and sensitivity. Recently, there is an increasing number of applications involving the use of carbon-based nanomaterials (nanotubes, graphene oxide) in conjunction with BiFEs.^{52,53} Another interesting possibility is to incorporate a bismuth precursor compound (bismuth oxide or an insoluble bismuth salt) in carbon paste or screen-printed graphite inks;^{54,55} when used for cathodic electrolytic accumulation, the bismuth precursor compound is converted into metallic bismuth that forms a film on the surface of the electrode.

Following the success of bismuth electrodes, antimony-film electrodes (SbFEs) were introduced in 2007.⁵⁶ Antimony is also a less toxic electrocatalytic material than mercury and has been shown to exhibit excellent performance in more acidic media.⁵⁷ The usual fabrication method of antimony (SbFEs) electrodes is again electroplating but microfabrication approaches have also been used.^{58,59} Finally, tin-film,^{60,61} lead-film,^{62,63} gallium-film,⁶⁴ selenium-film⁶⁵ and tantalum-film⁶⁶ electrodes have been reported as mercury-free sensors for SA of metals. The main drawback of all these alternative electrodes compared to mercury is their limited anodic range since these metals are oxidized at a more negative potential than mercury. The comparative performance of electroplated and precursor-modified bismuth, tin and antimony electrodes with the benchmark MFE for the detection of Cd(II) and Pb(II) by DPASV is illustrated in the Figure 1.2.

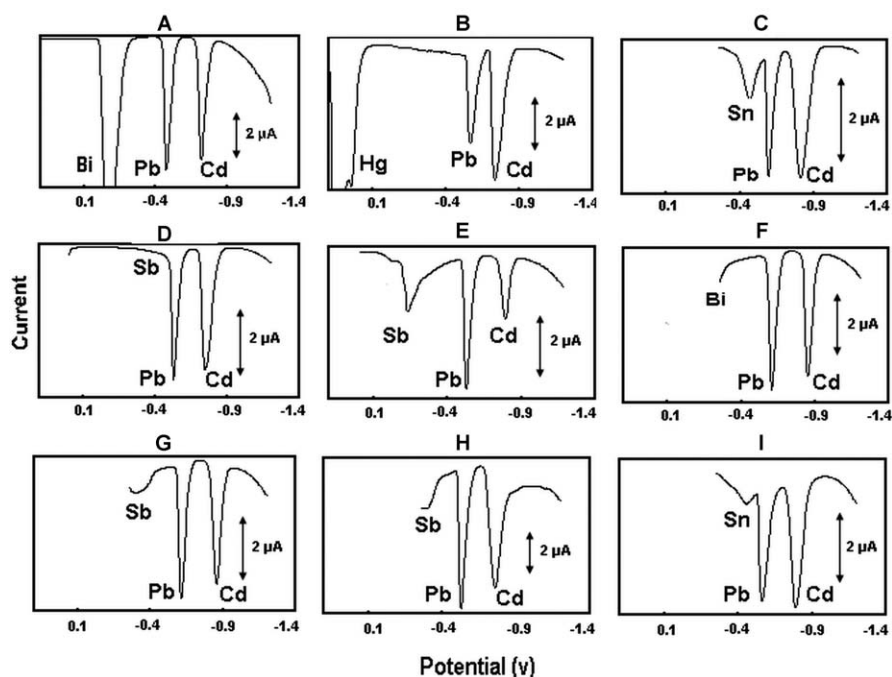


Figure 1.2 Comparative DPASV responses in a solution containing $25 \mu\text{g L}^{-1}$ Pb(II) and $50 \mu\text{g L}^{-1}$ Cd(II) at *in situ* electroplated screen-printed sensors: (A) BiFE, (B) MFE, (C) SnFE, (D) SbFE (in acetate buffer), (E) SbFE (in 0.01 mol L^{-1} HCl) and at screen-printed sensors modified with 4% (w/w): (F) bismuth oxide; (G) antimony oxide; (H) antimony oxalate hydroxide; (I) antimony tin oxide. Buffer, 0.1 mol L^{-1} acetate (pH 4.5) (except D); preconcentration time, 240 s; preconcentration potential, -1.4 V (except C) and (I), -1.5 V ; plating metal concentrations, 1 mg L^{-1} . (Reproduced with permission from ref. 60.)

Gold electrodes have been widely used mainly for the detection of mercury⁶⁷ and arsenic⁶⁸ and to a lesser extent for the detection of some other heavy metals. A drawback of bare gold electrodes is that the simultaneous determination of Cd(II) and Pb(II) is not possible.⁶⁹

1.3.5 Microelectrodes and Microelectrode Arrays

IUPAC defines as a microelectrode any electrode whose characteristic dimension is, under the given experimental conditions, comparable to or smaller than the diffusion layer thickness (δ)⁷⁰ (typically ranging from a few μm to 50 μm). Microelectrodes exist in different geometries and can be arranged as single microelectrodes or as arrays (ensembles) of microelectrodes. The most popular arrangements of single microelectrodes are those of disk, hemisphere, sphere-caps and cylinder while arrays (or ensembles) of microelectrodes can be configured as microdisks, microchemispheres, microbands and interdigitated structures.^{6,71} The first analytical applications of microelectrodes were recorded during the 1980s when advances in microelectronic technology made it possible to fabricate micron-sized structures in a reproducible manner.^{6,72} Several characteristic properties of microelectrodes make them attractive in combination with SA in comparison to conventional electrodes:^{6,71-73} high rates of mass transport, low ohmic drop, reduced charging current and enhanced signal-to-noise ratios. Moreover, due to their small dimensions, microelectrode systems are suitable for miniaturization, which makes possible the development of portable analytical instruments for on-site measurements of trace elements.^{72,73}

A drawback in the use of single microelectrodes is the extremely low currents that are obtained. A solution to this is the use of regular microelectrode arrays (MEAs) whereby multiple microelectrodes are arranged in a geometrical pattern and operated in parallel.^{6,71-73} In MEAs, the individual microelectrodes' critical dimension and the inter-electrode distances define the mass transport regime and are critical for the MEA performance.^{6,71-74} Under conditions of non-overlapping diffusion regimes, the electrochemical signal increases in proportion to the number of microelectrodes in the array.

The fabrication methods and analytical applications of microelectrodes and MEAs in SA of metals have been comprehensively reviewed.^{6,71-73} Construction of MEAs is usually based on thin-film microelectronic technologies as well as screen-printing. Single microelectrodes may consist of carbon fibres, carbon microdisks, platinum, gold, silver, iridium and alloy microdisks and microwires.^{6,71} MEAs can consist of carbon, platinum, gold, iridium, rhodium, indium tin oxide (ITO), BDD and alloy microelectrodes. These can be used directly in SA of metals using UPD but multi-element analysis is usually complicated by intermetallic compound formation, multiple stripping peaks and narrow cathodic potential range. More common is the modification of these substrates with mercury, bismuth and gold films as well as with antifouling coatings (such as agar and Nafion).^{6,71-73}

1.3.6 Microfabricated, Cell-on-a-chip, Paper-based and Wearable Devices

Advances in, and wider access to, microfabrication technologies have enabled the realization of different cell-on-a-chip and integrated miniaturized devices for SA of metals. Single “green” bismuth, antimony and tin sensors have been fabricated by thin layer microengineering approaches^{50,59,75} and this work was extended to complete cell-on-a-chip devices.^{76–78} A series of publications has reported the implementation of thin-film integrated three-electrode devices with working electrodes made of copper, palladium and bismuth and their application to SA of metals.^{79–81}

Microfluidic devices combine the advantages of microfabrication with convenient delivery of low volume of sample using flow in microchannels. The earliest example of such a device, consisting of a microchannel in glass with electrokinetic flow and a mercury-coated SPE electrode for Ni(II) detection by SA, was reported in 2000.⁸² Plastic fluidic chips with integrated electrodes made of carbon-loaded polystyrene have been fabricated and used for metal detection by SA.^{83–85} Several other designs of micromachined fluidic chips with varying degrees of complexity have been reported for trace metal detection using bismuth^{86–89} and gold or silver^{90–92} working electrodes. An integrated electronic tongue device with gold working electrode suitable for the detection of heavy metals by CSV and ASV in wastewater or seawater is illustrated in Figure 1.3. The monitor employs a gold electrode for Mn and As CSV detection (cell 1) and a mercury-covered silver electrode for Zn, Cd, Pb and Cu detection by ASV (cell 2).

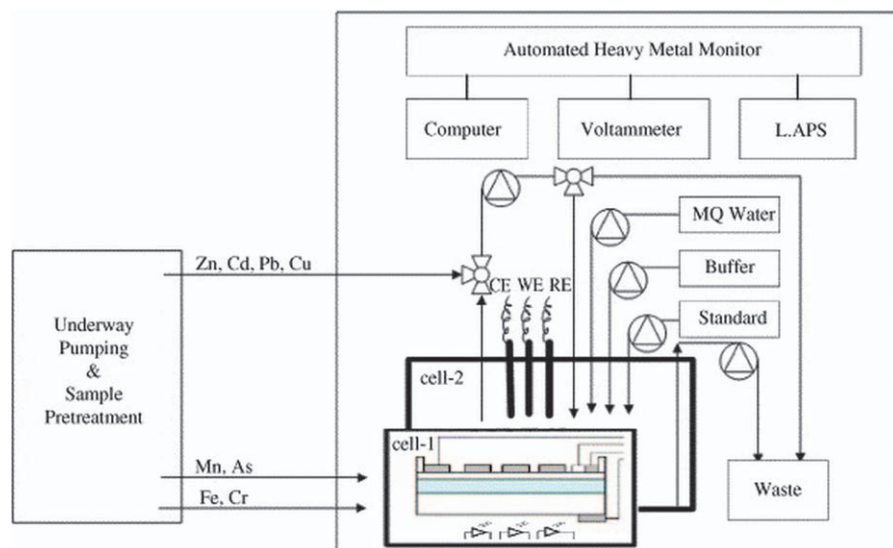


Figure 1.3 Scheme of the electronic tongue instrument system for detection of Mn and As by CSV and Zn, Cd, Cu and Pb by ASV. (Reproduced with permission from ref. 92.)

Paper-based devices (or μ PADs) constitute a new exciting field of research.^{93,94} In μ PADs, an hydrophilic paper substrate is patterned with hydrophobic areas using different technologies to manipulate sample flow. In the context of electrochemical detection, electrodes are printed on the paper layer enabling SA detection of different metals.^{95–99}

Finally, wearable sensors (integrated on either a textile material or directly on the epidermis) can be used for multi-analyte monitoring in the user's environment.¹⁰⁰ Wearable electrochemical sensors based on screen-printing have been used for heavy metals detection by ASV after electrolytic pre-concentration in marine environments¹⁰¹ or for the detection of gunshot residue by abrasive stripping voltammetry.¹⁰²

1.3.7 Flow Systems and Probes for Environmental and Personal Exposure Monitoring

Advantages of coupling SA to flow manifolds include better control of the preconcentration efficiency, the scope for increased automation, faster optimization, sample pretreatment, calibration and analysis, higher precision and accuracy and lower consumption of sample and reagents.¹⁰³ Flow injection analysis (FIA), sequential injection analysis (SIA) and multi-comutation manifolds combined with wall-jet, thin layer or tubular cells have been reported for SA of metals.¹⁰³ A relatively recent development is the lab-on-a-valve (LOV) arrangement which allows integration of on-line miniaturized sample manipulation and detection modules within a specially-designed multi-port selection valve.^{104–106} Flow systems also allow easy hyphenation of SA with spectroscopic techniques (mass spectroscopy (MS) inductively coupled plasma-MS (ICP-MS) and atomic emission spectrometry (ICP-AES)) for metal analysis.^{107–111}

Different flow probes for monitoring of trace metals by SA in the environment have been reported.^{5,112–116} On the other hand, portable on-line systems can be used as personal exposure monitors to trace metals.¹¹⁷

1.3.8 Biosensing Based on SA of Metals

SA of metals can be exploited for the indirect detection of different biomolecules (oligonucleotides, proteins) or whole cells.^{118–122} The principle of these assays is to label the target biomolecules with a reported biomolecular probe (*via* hybridization or bioaffinity interactions) tagged with metal (silver, gold) nanoparticles or quantum dots (nanocrystals composed of metal sulfides or selenides). After labelling, the metal nanoparticles and quantum dots are oxidized or dissolved, respectively, to release the respective metal cations, which are then detected and quantified by SA. Specific strategies to implement detection of several biomolecules and cells through SA of metal-containing labels are reported in recent reviews.^{118–122} An example is illustrated in Figure 1.4 that demonstrates a method for the

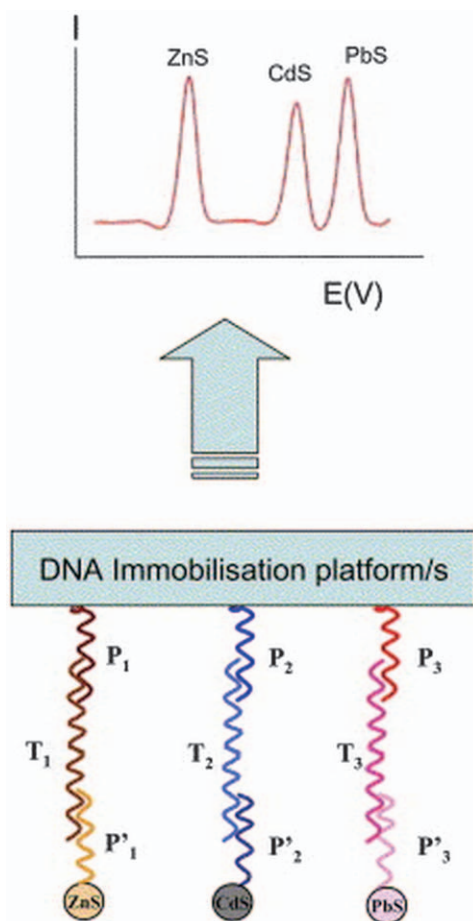


Figure 1.4 Schematic of multiple detection of DNA. DNA probes P'_1 , P'_2 and P'_3 bearing different DNA sequences with different nanoparticles (ZnS, CdS and PbS, respectively) that enable the simultaneous detection of three DNA targets T_1 , T_2 and T_3 hybridized with corresponding DNA-capturing probes P_1 , P_2 and P_3 immobilized onto a direct or an indirect (magnetic particles) transducing platform(s). (Reproduced with permission from ref. 123.)

simultaneous assay of three oligonucleotide targets after labelling DNA probes with different nanoparticles (ZnS, CdS and PbS quantum dots); the quantum dots produce well-defined and resolved stripping peaks for Zn, Cd and Pb at a mercury-coated glassy carbon electrode.¹²³

1.4 Conclusions

SA, more than 80 years after its first application, is still an active field of research. While the basic principles and instrumentation remain

unchanged, the recent research trends revolve around new materials, microfabrication technologies and biosensing. Undoubtedly, the introduction of bismuth electrodes (as well as antimony and tin electrodes) as substitutes of mercury electrodes has brought about a revival of SA as a viable and environment-friendly trace metal analysis technique. Screen-printing electrodes and microelectrodes continue to receive attention as sensors in SA using both electrolytic and non-electrolytic accumulation. Microfabricated lab-on-a-chip and microfluidic devices as well as paper-based and wearable sensors constitute emerging fields in which SA plays a predominant role as detection technique. Finally, the applicability of SA is further extended by its ability to detect metallic labels in order to indirectly monitor biomacromolecules in clinical samples.

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