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Review Paper

Screen-printed Electrochemical Sensors and Biosensors for Monitoring Metal Pollutants

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Abstract: The present review (with 231 references) focuses on developments made in the area of screen-printed biosensors and sensors for the determination of metal ions in industrial, environmental and biomedical applications. The year 2012 represents the twentieth anniversary of the first reported application of screen-printed electrodes for the determination of metal ions. Focus is placed on fabrication techniques, operating details and performance characteristics for the selected applications. The greater proportion of articles have utilised the technique of stripping voltammetry, gaining detection limits in the low ng/mL (ppb) region. An increasing percentage of these have explored bismuth as an alternative to mercury for the modification of the carbon electrode surface. However, a steady number of applications have shown the possibility of utilising the unmodified screen-printed carbon, gold or silver electrode surface. More recently the alternative approach of electrochemical biosensors has become a growing area. The majority of these have exploited the inhabitation metal ions exhibit on the enzyme activity of urease, acetylcholinesterase and glucose oxidase gaining detection limits in the sub µg/mL region, however recent applications utilising thiol-functionalised oligonucleotides have been shown the possibility of gaining detection limits as low as 120 ng/L for Hg^{2+}.

Keywords: screen-printed carbon electrode; stripping voltammetry; biosensors; nano; metal; sensors; bismuth; review.

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1. Introduction

Metals have long been industrially processed and used in numerous applications since antiquity. Ice core and peat bog samples have shown the planetary wide metal contamination that has existed as far back as the early Mediterranean societies [1-3]. Their utilisation has soared since the industrial revolution [4], with the natural fluxes of these elements greatly affected resulting in a marked increase in their potential as pollutants and spreading their impact across a wide number of ecosystems [5-7]. They are inherently non-biodegradable which distinguishes them from other pollutants [8] making them ubiquitous and long lived pollutants. As toxicology studies have advanced, knowledge on levels that no adverse effects occur has become progressively lower. However, many are also known to be essential for life such as Cu, Mg and Zn, but also can exert toxic effects at elevated levels, with some exhibiting narrow windows of acceptability; speciation is also very important and none act solely in isolation. Awareness of such problems has generated a demand for sensitive methods that are rapid, inexpensive, reproducible, and accurate in fields such as, environmental monitoring, occupational hygiene, biomedicine and food quality. One growing area which has been shown capable of meeting these demands is that of electrochemical measurements with screen-printed sensors.

The present review focuses on developments made in this area since our last review given in 2003 [9] with reports made prior to this are given in a series of tables; pre-2003 reports have been summarised in appendix 1. The field is now a mature area with the year 2012 representing the twentieth anniversary of the first reported application of screen-printed electrodes for the determination of metal ions [10]. Particular focus is given for fabrication techniques, operating details and performance characteristics for the selected applications. The review is divided into two main sections detailing with the development of screen-printed biosensors and the application of stripping voltammetry. A number of reviews and monographs describing the theory underlying electrochemistry have already been given [11-21] and the history of the development of electroanalytical chemistry has recently been reviewed [21-23].

2. Applications of Screen-printed Electrodes for Metal Ion Analysis

2.1 Mercury Modified Screen-printed carbon Electrodes for the Stripping Voltammetric Determination of Metal Ions

Mercury offers a number of advantages as an electrode material [24,25]; it can be obtained as a very pure liquid at ambient temperatures, and allows for the sensitive analysis as a fresh surface can be easily formed. Coupled to this is a wide usable potential range is obtainable, from +0.1 V (vs. SCE) to reportedly potentials as low as -2.6 V (vs. SCE) in aqueous solutions, and in non-aqueous solutions at potentials as low -3.0 V (vs. SCE) [25]; however the range is curtailed in the anodic range due to the oxidation of Hg itself. In 1957 Demars and Shain [26] first showed the sensitivity that could be obtained at a hanging Hg drop electrode (HMDE), determining Cd levels in the sub ppb region by stripping voltammetry, proving the technique at the time to be the most sensitive instrument based technique available to the analytical chemist. However, long platting times were required, due mainly to the low surface to volume ratios at the HMDE reduces plating efficiency and the relative large drop volume results in a low concentration of metal in the Hg, resulting in a broadening of the resulting stripping peak. Such problems lead to development of alternative approaches such as Hg thin film electrodes (MTEs). Investigations at metal electrodes proved problematic as the metal substrate to some extent dissolves into the Hg altering its chemistry [25]. In this respect carbon has been found to be superior, allowing stable Hg films formation. Originally first described by Matson and Roe in 1965 [27] and Florence [28] in 1970, utilising *in situ* film formation. These are characterised by a Hg layer in the order of 10 to 1000 nm in thickness [28,29], covering an inert support, giving a very large surface area to volume ratio, and hence high amalgam concentration in stripping step. Due to the close contact of the Hg to the underlying electrode high stirring rates can be employed without risk of dislodging the Hg film all of which greatly improves sensitivity compared to the HMDE. Selectivity can also be much greater than the HMDE due to the much higher diffusion rates of metals from the bulk to the surface resulting in improved peak shapes. Pre-plated films were first employed but best results are generally found by the forming of *in situ* plated Hg films. For this mercury nitrate was added directly into the sample solution at concentrations of *ca.* 1 – 5 x 10^{-5} M and simultaneously deposited with the target analytes obtaining films thickness of the order of >100 nm [15].

A number of authors explored the use of Hg in conjunction with screen-printed carbon electrodes (SPCEs) for thin film formation [9]. In these investigations, Hg was utilised as either *ex situ* deposited thin film plated this on before in a separate solution, or co-deposited, *in situ* with the target analyte by addition of a soluble Hg salt to the sample solution. The thin Hg film can also be formed by incorporation as a suitable Hg salt as part of the working electrode ink which can be electrochemically reduced to give the Hg film on the electrode surface [30].

Determination of metal ions at these electrodes involves two separate stages; initially a pre-concentration step to accumulate the analyte as an amalgam at the working electrode, (eq.1), which is then electrochemically stripped back into the solution in the current measurement step (eq.2).

$$M^{n+} + ne^- + Hg \rightarrow MHg \qquad \text{(eq.1)}$$

$$MHg \rightarrow M^{n+} + Hg + ne^- \qquad \text{(eq.2)}$$

As mentioned in section 1, the first reported example of the utilisation of screen-printed electrodes for the determination of metal ions was made by Wang and Tian [10] in 1992 using such an approach. Here, commercially available ExacTech screen-printed glucose biosensors were investigated for the determination of Pb^{2+} and Cd^{2+} ions by both potentiometric stripping analysis (PSA) and differential pulse anodic stripping voltammetry (DPASV). These biosensors consisted of planar working and Ag/AgCl reference electrodes printed on a PVC substrate. As the original working electrode had been modified with enzyme and mediator layers, the unadulterated carbon contacts pads (2 mm x 8 mm) were employed as the working electrodes instead. At the beginning of each day a Hg film was plated on the working electrode surface from an 80 mg/L Hg 0.02 M HCl solution to form the thin Hg film SPCE (TF-SPCE). Using DPASV detection limits of 30 ng/L and 50 ng/L for Pb^{2+} and Cd^{2+} were reported respectively, utilising an accumulation time of 10 minutes. PSA was shown to give detection limits of 300 ng/L and 500 ng/L for Pb^{2+} and Cd^{2+} respectively. Both human urine and drinking water were investigated, and results were shown to be comparable with both Hg thin film glassy carbon and hanging Hg drop electrodes.

Subsequently, a large number of reports have been made, utilising dedicated screen-printed electrodes modified by *in situ* or *ex situ* electrochemically plated Hg films. Up until the early part of the last decade this was the generally prevailing approach [9]. Table 1 summaries a number of these applications, demonstrating the low limits of detection and versatility that these devices offer.

One advantage of electrochemical techniques such as stripping voltammetry offers is the possibility to determine the relative concentrations of free and complexed metal fractions [8]. This is an important parameter as the relative toxicities of different metal species and complexes can be quite notable. Recently TF-SPCEs have been utilised with a technique referred to as absence of gradients and Nernstian equilibrium stripping (ANGES) [31,32]. This is a relatively new technique which has been developed to measure the free ion concentration alone. In this approach, in the deposition stage a potential a few mV more negative than the standard potential of the couple is applied. This concentrates the metal inside the amalgam until the redox couple reaches Nernstian equilibrium and there is no concentration gradient in the amalgam or in the solution. This results in a gain or pre-concentration factor in the amalgam with respect to the solution, which is controlled via the applied deposition potential according to Nernst’s law. The subsequent measurement stripping step is achieved by applying a potential sufficient to produce an oxidation stripping current.

However, even with the relative smaller concentrations of Hg used in these approaches they still suffered from the perceived problems of toxicity and disposal, especially with on-site applications. In light of this alternative approaches have been sort. Two differing strategies have been followed to overcome these issues and are discussed in the next sections.

Analyte	**Modifier**	**Accumulation media**	**Measurement technique**	**Linear range**	**Detection limit (time)**	**Sample(s)**	**Ref.**
Pb^{2+}, Cd^{2+}, Cu^{2+}	Hg thin film	Sample acidified with HCl pH 2	SWASV, -1.1 V (120 s)	0 ng/mL – 500 ng/mL in acidified seawater	Cd^{2+} 7.0 ng/mL, Pb^{2+} 0.31 ng/mL, Cu^{2+} 0.53ng/mL	seawater	[33]
Sb^{3+}	Hg thin film	HCl 3M	DPASV, -0.9 V (600 s)	0.99×10^{-8} – 8.26×10^{-8} M	1.27×10^{-8} M.	Glucantime and seawater	[34]
Cd^{2+}	Hg modified microelectrode array formed by and femtosecond laser ablation	acetate buffer 0.2 M, pH 4.5	SWASV	1 ng/mL – 10 ng/mL	1.3 ng/mL, 300 s	River water	[35]
Cd^{2+}	Ex situ Hg plated thin film	acetate buffer 0.2 M pH 4.5	SWASV, -1.0 V	0.2 ng/mL – 40 ng/mL	0.2 ng/mL, (60 s)	River water	[36]
Pb^{2+}, Cd^{2+}	Thin-film Hg	0.6 M NaCl solution at pH 8	SWASV, -1.1 V	10 ng/mL – 2000 ng/mL	Pb^{2+} 1.8 ng/mL, Cd^{2+} 2.9 ng/mL (120 s)	seawater	[37]
Cd^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}	Cd^{2+}, Cu^{2+}, Pb^{2+} by thin Hg film, Hg^{2+} Au screen-printed electrode	0.1 M HCl	SWASV, Hg^{2+} +0.2 V, Cd^{2+}, Cu^{2+}, Pb^{2+}, -1.1 V	1 ng/mL – 1 µg/mL for all	Hg^{2+} 0.9 ng/mL, (120 s), Cd^{2+}, 1.0 ng/mL Cu^{2+} 0.5 ng/mL, Pb^{2+} 0.3 ng/mL (300 s)	Dogfish muscle, mussel tissue, Atlantic hake fillets	[38, 39]
Pb^{2+}	Pre-anodized Hg plated	0.1 M H_2SO_4	SWASV, Tl^{3+} used as internal standard	1-300 ng/mL	0.23 ng/mL	Blood from battery factory workers	[40]
Pb^{2+}, Cd^{2+}	Hg thin film	0.1 M HCl	SWASV, -1.1 V	Pb^{2+}, Cd^{2+} both 5-100 ng/mL	-	Herbal drugs (St. John's Wort)	[41]
Cd^{2+}, Pb^{2+}, Zn^{2+}	Carbon based mercury thin film electrode	0.10 M KNO_3 with 50 mM HCl	CV and Differential pulse anodic stripping voltammetry (DPASV)	8.0-220 ng/mL Zn^{2+}, 0.3-50.0 ng mL^{-1} $Cd^{2+,}$ 0.15-60.0 ng/mL Pb^{2+}	0.25, 0.08 and 5.5 ng/mL for Cd^{2+}, Pb^{2+}, Zn^{2+} (60 s deposition step at –1.10 V)	Water, wastewater, lake water, certified reference material samples	[42]

Table 1. Mercury modified screen-printed electrodes for Metal Ion Determination.

2.2 Trace Metal Determination at Unmodified Screen-printed Carbon Electrodes

An alternative approach has been to utilise unmodified screen-printed carbon electrodes, with the deposition and measurement of the target metal ion at the carbon surface [9]. This has been shown successful for the trace determination of a number of elements and has been previously reviewed [9] and a number of previous reported examples of this approach are given in table 2. These studies have shown that identification and optimisation of the supporting electrolyte is important, governing the character and number of stripping peaks developed. Recently, using such an approach, Crew *et al* [43] have determined Zn^{2+} concentrations in human sweat, an important indicator of stress and fatigue utilising anodic stripping voltammetry at an unmodified Hg-free SPCE. Cyclic voltammetric studies identified the optimum electrolyte as pH 6.0 0.1 M acetate buffer containing 0.1 M NaCl. Further studies showed that by using a deposition potential of -1.6 V a well-defined stripping peak at -1.2 V could be obtained which was found to exhibit a linear response with concentration from 1×10^{-8} to 5×10^{-6} M Zn^{2+} for a deposition time of 60 s. A coefficient of variation of 5.6 % was obtained for six replicate measurements of a $2x10^{-6}$ M Zn^{2+}. The method was applied to the determination of Zn^{2+} in sweat from ten human volunteers. The concentrations were found to between 0.39 and 1.56 µg/mL, in agreement with that reported in previous studies.

Investigations have shown the possibility of directly screen-printing microarrays of electrodes [44,45]. The use of microelectrodes offers a number of advantages, including high mass transport, low ohmic drop and enhanced signal to noise ratios [46]. One important factor related to stripping analysis is the increased mass transport which occurs as a result of this type of diffusion. Further increases in sensitivity can be made if a number of these microelectrodes are wired together in parallel, with each electrode diffusionally independent an amplified signal output can be gained, allowing improved sensitivity and a lower detection limit. This possibility has been explored by Kadara *et al* [44] by screen-printing shallow recessed microarrays directly with a reportedly reproducible disc radius of 116 (±6) µm. Using a screen printed 16 microelectrode shallow recessed array, with discs in a hexagonal pattern separated by 1.250 mm, the electroanalytical determination of Mn^{2+} via cathodic stripping voltammetry was shown to be possible achieving a limit of detection of 81 (±1.2) nM. Changing the arrangement of the array by reducing the number of discs to six and increasing the separation to 2.500 mm, a detection limit of 64 (±1.5) nM was reported.

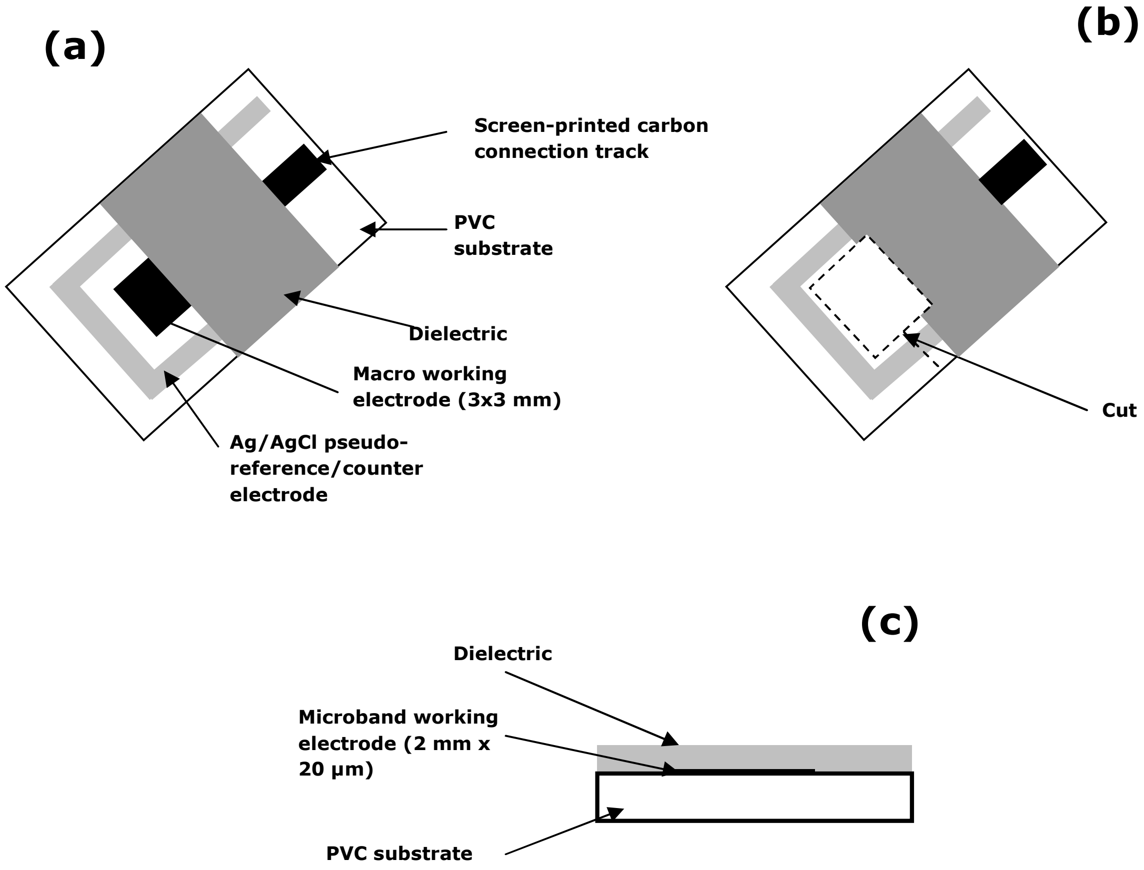
In further studies the possibility of determining traces Pb concentrations in river water utilising the six disc array in this case by cathodic stripping voltammetry as described by equations 3 and 4. This approach utilises the oxidation of the Pb^{2+}cation in the presence of water to accumulate the metal as a thin-film of insoluble PbO_2 at the electrode surface (eq. 3). By the application of a negative going voltage scan the accumulated PbO_2 undergoes a two electron reduction back to Pb^{2+} giving the analytical signal (eq. 4) [47].

$$Pb^{2+}_{(aq)} \quad + \quad 2H_2O \quad \rightarrow \quad PbO_{2(s)} \quad + \quad 4H^+ \quad + \quad 2e^- \qquad \text{(eq.3)}$$

$$PbO_{2(s)} + 4H^{+} + 2e^{-} \rightarrow Pb^{2+}_{(aq)} + 2H_2O \quad \text{(eq.4)}$$

A detection limit of 3 µM, with a linear response to 50 µM was reported using a conditioning potential of +0.5 V and a deposition potential of +1.65 V (vs. SCE) applied for 120 s. By increasing the deposition time to 320 s two linear ranges were reported, from 0.4 µM to 1 µM, and second from 1.5 µM to 10 µM. Based on the first linear range a detection limit of 39 nM was reported. Ten replicate measurements of river water fortified with 0.4 µM were found to give a coefficient of variation of 8 %.

Figure 1. Diagrammatic representation of method for the manufacture of microband SPCEs. (a) Plain view of 3×3mm SPCE, (b) and µBSPCE (c) end on view of µBSPCE. Reprinted from Talanta, 84, Honeychurch K.C., Al-Berezanchi S., Hart J.P., The voltammetric behaviour of lead at a microband screen-printed carbon electrode and its determination in acetate leachates from glazed ceramic plates. 717–723, Copyright 2011, with permission from Elsevier.



The determination of Pb^{2+} has recently been reported at a microband screen-printed carbon electrode (µBSPCE) [48]. These µBSPCE can be manufactured by exposing a cross section of the 2 mm x 20 µm printed layer of the ink working electrode, sandwiched between the dielectric and the PVC substrate, as depicted in figure 1. This was shown to be relative simple and cost effective manner of manufacture, with the possibility to form several µBSPCEs from a single screen-printed sensor by simple further cutting to reveal a fresh carbon surface. Cyclic voltammetric investigations undertaken on a 0.1 M KCl 5 mM ferrocyanide solution demonstrated microelectrode type behaviour with sigmoidal shaped voltammograms being reported. Utilising linear sweep anodic stripping voltammetry with an accumulation time of 1500 s in a quiescent 0.1 M pH 4.1 acetate 13 mM NaCl solution, a linear relationship with Pb^{2+} concentration was obtained from 50 µg/L to 1.7 mg/L with an associated detection limit of 2.3 ng/mL was obtained. The developed sensor was shown to be able to successfully determine the concentration of Pb leached from ceramic plates and tableware.

Sue *et al* [49] have utilised a flow injection device system shown in figure 2 for the determination of As^{3+} at a screen-printed ring disc electrode, via its interaction with electrochemically produced I_2 formed at the inner disk electrode (eq.5). In the presence of As^{3+}, the electrochemically generated I_2 is rapidly reduced to I^-, in the "gap" between the disk and ring electrodes (eq.6). This results in a subsequent depletion in the concentration of I_2 arriving at the ring electrode [50]. Hence this reduction in the current collected at the ring electrode allows for the determination of the concentration of As^{3+} introduced into the cell (eq.7). The developed method was utilized for As^{3+} measurements in groundwater of 'Blackfoot' endemic disease affected areas of south-western coast of Taiwan.

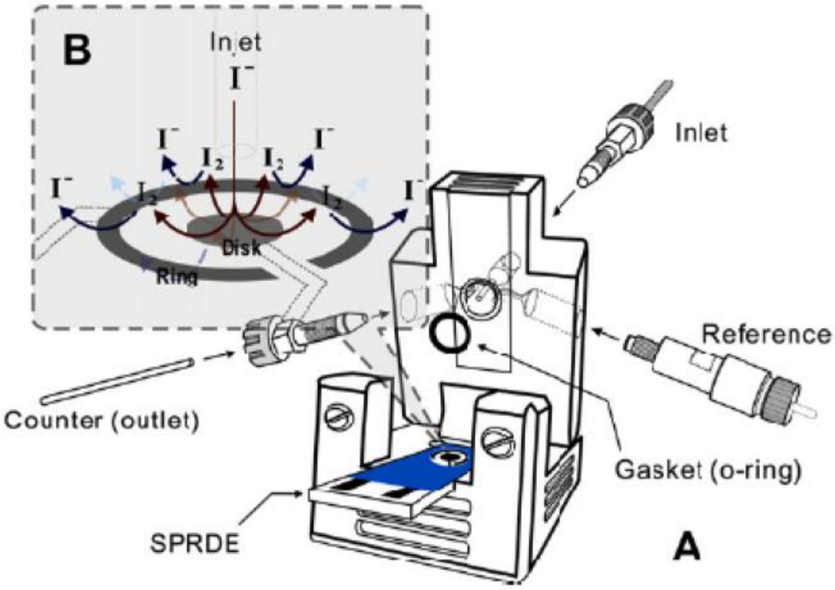
Inner disk electrode reaction $$2I^-_{(aq)} \rightarrow I_{2\,(aq)} + 2e^- \qquad \text{(eq.5)}$$

"Gap" reaction $$I_{2\,(aq)} + As^{3+}_{(aq)} \rightarrow 2I^-_{(aq)} + As^{5+}_{(aq)} \qquad \text{(eq.6)}$$

Outer ring electrode reaction $$I_{2\,(aq)} + 2e^- \rightarrow 2I^-_{(aq)} \qquad \text{(eq.7)}$$

A screen-printed lab-on-paper device has been recently reported for the stripping voltammetric determination of Au with the simultaneous colorimetric determination of Fe [51]. The use of paper as a substrate has a number of reported advantages including being inexpensive and readily available. In this study, the authors showed the possibility of utilising a Whatman No. 1 filter paper as the substrate to screen-print a three electrode system. The filter paper was pre-treated in a similar manner as described by Martinez *et al* [52] by spin coating with SU-8 negative photoresist. The three electrodes design was then screen-printed on to this modified filter paper, using a carbon ink for the working and counters electrodes and Ag/AgCl ink for the reference electrode and conductive pads.

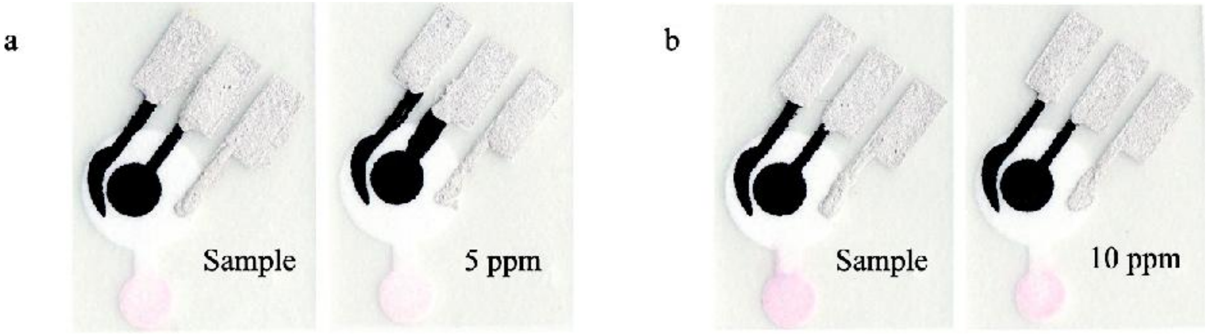
Figure 2. Schematic representation (A) and reaction mechanism (B) of the flow injection electrochemical detector setup. Reprinted from Electrochem. Commun. 10, Sue J.-W., Ku H.-H., Chung H.-H., Zen J.-M., Disposable screen-printed ring disk carbon electrode coupled with wall-jet electrogenerated iodine for flow injection analysis of arsenic(III), 987–990, Copyright 2008, with permission from Elsevier.



Cyclic voltammetric investigations of 50 µg/mL Au^{3+} in dilute *aqua regia* electrolyte showed a well-defined reduction peak of Au^{3+} at +260 mV vs. Ag/AgCl corresponding to the 2 e^- reduction of $AuCl_4^-$ to $AuCl_2^-$. To determine the low concentrations of Au present in waste and environmental water samples further investigation were made with square wave cathodic stripping voltammetry; the optimized system (pulse amplitude = 50 mV, square wave frequency of 15 Hz, and step height pulse height of 5 mV) was capable of achieving a linear range between 1 and 200 µg/mL with a detection limit of 1 µg/mL for Au^{3+} requiring an one minute assay time.

The analytical performance of the sensor was investigated on gold-refining waste solutions, obtained from the precious metals assay laboratory of the Gem and Jewellery Institute of Thailand. Results for two different samples showed levels of 17.5 ± 0.5 and 46.0 ± 1 µg/mL, Au^{3+} and exhibited good agreement with that gained by ICP-AES. The average percentage recovery values obtained for a gold waste sample fortified with Au^{3+} were found to be in the range 91 %–93 % with a coefficient of variation of between 2.7%–4.4 %. It was found that a 50-fold excess of Cu^{2+}, Ni^{2+}, Zn^{2+}, Pt^{2+}, Rh^{2+}, and Ag^+ did not interfere with the determination of Au^{3+}. However, the peak current for Au^{3+} decreased in the presence of a 2.5-fold excess concentration of Fe^{3+} with no response seen Au^{3+} in the presence of a 25-fold excess of Fe^{3+}. This was concluded to result from the reduction current response of Fe^{3+} overlapping with that of Au^{3+}, and the possible formation of intermetallic compounds. Due to the interferences resulting from the present of Fe, the authors included a colorimetric test, incorporated into the same paper device, based on the reaction of Fe^{2+} with 1,10-phenanthroline (figure 3). As the Fe ion is in acidic solution it will be predominantly present as Fe^{3+}. Consequently, ascorbic acid was added to reduce this Fe^{3+} to the Fe^{2+}. The resulting colour intensity being proportional to the concentration of the Fe^{2+} complex with 1,10-phenanthroline, and was able to be assessed visually. The colour developed was compared to the calibration chart by the naked eye, hence allowing for samples containing high Fe concentrations to be identified.

Figure 3. Intensity of the observed colour is proportional to the complex concentration of (a) sample 1 and (b) sample 2, compared to the Fe^{3+}. Reprinted with permission from Apilux A., Dungchai W., Siangproh W., Praphairaksit N., Henry C.S., Chailapakul O., Lab-on-Paper with Dual Electrochemical/Colorimetric Detection for Simultaneous Determination of Gold and Iron. Anal. Chem. 2010, 82, 1727-1732. Copyright 2010 American Chemical Society.



Aurothiomalate (gold(I)thiomalate) is widely used in the treatment of rheumatoid arthritis. Recently, Bergamini and Zanoni [53] have determined this by an indirect anodic stripping voltammetric stripping at a SPCE. This was achieved by reducing the Au^+ to Au^0 metal on the surface of the SPCE by applying a potential of -1.5 V (*vs.* printed carbon) and then stripping the accumulated Au from the SPCE surface. This was found to give to oxidation peaks corresponding to the oxidation of Au^0 to Au^+ and then Au^+ to Au^{3+}. Interestingly in this approach a screen-printed carbon reference electrode was utilised rather than the standard Ag/AgCl. A negative shift of *ca.* 400 mV in Ep was recorded, compared to potential measured against the Ag/AgCl, but no other differences were found. Utilising an accumulation potential of -1.5 V (vs. printed carbon) and accumulation time of 60 s a detection limit of $6.5x10^{-7}$ M, with a linear range from $1.43x10^{-6}$ M to $1.55x10^{-4}$M was obtained.

Analyte	**Modifier**	**Accumulation media**	**Measurement technique**	**Linear range**	**Detection limit (time)**	**Sample(s)**	**Ref.**
Cr^{6+}	Unmodified carbon	0.1 M H_2SO_4	LSCSV	100 ng/mL – 1000 ng/mL	19 ng/mL	Canal water	[54]
Pb^{2+}		0.1 M KCl	DPASV, -1.1 V (400 s)	10 - 60 µg/dL	2 µg/dL	-	[55]
Hg^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}	Unmodified carbon	0.1 M NaCl, adjusted to pH 1.35	DPASV, -1.4 V	Hg^{2+} 5 µg/mL – 100 µg/mL, Pb^{2+}2 µg/mL – 50 µg/mL , Ni^{2+} 5 µg/mL – 50 µg/mL, Cd^{2+} 2 µg/mL – 30 µg/mL, Cu^{2+} 2 µg/mL – 50 µg/mL	500 ng/mL Pb^{2+}, 750 ng/mL Cd^{2+}, 2 µg/mL Zn^{2+}, 1 µg/mL Ni^{2+}, 2 µg/mL Hg^{2+}, 2 µg/mL Cu^{2+} (60 s)	Pollution monitoring and mapping	[56]
Hg^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}	Unmodified carbon	0.1 M NaCl, adjusted to pH 1.35	DPASV, -1.4 V	-	-	Soil	[57]
Pb^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}	Unmodified carbon	0.1 M NaCl, adjusted to pH 1.35	DPASV, -1.4 V	-	-	Forensic soil analysis	[58]
Cd^{2+}, Pb^{2+}	Unmodified carbon	0.2 M CH_3COOH + 0.2 M CH_3COONa	DPASV, -1.0 V	Cd^{2+} 2 µM–100 µM, Pb^{2+} 5 µM–100 µM	Cd^{2+} 500 nM, Pb^{2+} 800 nM (120 s)	Rainwater, flour, maize and sunflower seedlings	[59]
Cd^{2+}, Cu^{2+}, Pb^{2+}	Injection modelled flow cell containing screen-printed sensor	Cu^{2+} 0.1 M HNO_3, Cd^{2+} 0.1 M pH 9 ammonium citrate buffer, Pb^{2+} 0.1 M pH 9 glycine buffer	Cu^{2+}, Cd^{2+} DPASV and Pb^{2+} SWASV	Pb^{2+} 30 ng/mL – 70 ng/mL (300 s), Cu^{2+} 9 ng/mL – 26 ng/mL (500 s)	Cu^{2+} 4.4 ng/mL (300 s) Pb^{2+} 5.9 ng/mL (500 s), Cd^{2+}	Lake water, industrial waste water	[60]
Cd^{2+}, Cu^{2+}, Pb^{2+},	microchip capillary electrophoresis	MES buffer (pH 7.0, 25 mM)	-0.8 V	100 – 1000 µM	Pb^{2+} 1.74 µM, Cd^{2+} 0.73 µM, 0.13 µM	Green vegetable, Tomato and pine apple juices	[61]
K^+, Na^+, Li^+, Mg^+, Cl^-, NO_3^-, SO_4^{2-}	Microchip capillary electrophoresis	50mM Acetic acid and 10 mM His at pH 3.6 for inorganic cations and anions	LTCC, Contactless conductivity	100µM to 5mM for K^+	8, 13, 6 and 6 µM for K^+, Na^+, Ca^+ and Mg^{2+}; 39, 44 and 22 µM for Cl^-, NO_3^-, SO_4^{2-}	Standard solution and water samples: Wöslauer and Urquelle mineral water, tap water	[62]

Table 2. Unmodified Screen-printed Electrodes for Determination of Metal Ions.

2.3 Chemical Modified Screen-printed Carbon Electrodes for Metal Ion Determination

The expression ‘chemically modified electrodes’ (CMEs) was first used by Murray and co-workers [63] to designate an electrode with a chemically active species deliberately immobilised onto the surface of the electrode. It is now generally used to denote the modification of the electrode with a ligand or similar compound. CMEs have been used for the determination of a large number of both organic and inorganic analytes and a number of reviews have been produced on its scope and application [64-68].

Early applications of “non-electrolytic” pre-concentrations have been described by Brainina [69], Kalvoda and Kopanica [70] Cheek and Nelson [71] and Wang [72], with developments on the chemical modification of electrode surfaces beginning about 1975 [73,74]. Direct mixing of the modifying agent into the carbon paste was suggested by Ravichandran and Baldwin [75], which led to the application of modified carbon paste electrodes. Wang and co-workers developed chemically modified SPCEs have utilising a similar approach of mixing ion exchange [76] and chelating agents [77] with the screen-printing ink prior to printing for the determination of Cu and Ni respectively. Simple drop coating of the SPCEs has been developed by Honeychurch *et al* [78-80] for Cd and Pb.

In this approach, metal ions (M^{n+}) are chemically accumulated at the ligand modified electrode surface ($L_{surface}$), in the absence of an applied potential eq. 8.

$$M^{n+} + L_{surface} \rightarrow M^{n+}L_{surface} \qquad \text{(eq. 8)}$$

Once accumulated at the electrode, the metal ion can be measured by either a negative going potential ramp, (cathodic stripping) or a positive going one (anodic stripping). For cathodic stripping voltammetry the electrode potential is swept in a negative direction, to a potential low enough to cause the reduction of the surface accumulated metal ions to their native metal, ($M_{surface}$) as in equation (eq. 9).

$$M^{n+}L_{surface} + ne^{-} \rightarrow M_{surface} + L_{surface} \qquad \text{(eq. 9)}$$

Where ne^{-} is the number of electrons transferred, and other terms have the same meanings as equation 8. Measurement is based upon the electrons consumed in the reduction of the metal ion to form the lower oxidation state metal. The case of anodic measurement is however more complicated as the metal ions need to be first converted to a metal layer on the electrode. This can be achieved by the application of sufficiently negative voltage, before the measurement step. The application of this potential, needs to be as short as possible to ensure that any metal ions present in the stripping solution are not accumulated, hence leading to erroneous results. Once reduced, the resulting thin metal layer adsorbed upon the electrode surface can then be stripped from the electrode by the application of a positive going linear voltage ramp, as for ASV, in equation (eq. 10).

$$M_{surface} + L_{surface} \rightarrow M^{n+}_{aq} + ne^{-} + L_{surface} \qquad \text{(eq. 10)}$$

Where terms used have the same meanings as equation 8.

2.3.1 Medium Exchange

Optimum conditions necessary for the chemical accumulation of metal ions from the sample solution are generally very much different from that of those needed by the electrochemical-stripping measurement step. The relatively low ionic strength and alkaline to neutral pH values employed in most complexing reactions makes them unattractive as stripping media which are generally acidic and of higher ionic strength. This problem can be easily overcome by the use of the well-established technique of medium exchange [81,82] employed recently with chemically modified SPCEs by Honeychurch *et al* [78-80]. The basis of which involves the deposition of the target analyte from the sample solution followed by stripping of the accumulated analyte into a separate more suitable electrolyte. The use of the two separate media for the accumulation and stripping step means that both can be optimised independent of each other, allowing for a number of other advantages. Interferences resulting from the presence of other electroactive species in the sample can often cause problems, due to their associated background current swamping out the target analyte signal, or their voltammetric peaks being unresolved from the target species. The exchange to a clean optimised stripping electrolyte has been shown to be able to eliminate these problems. Similarly, Interferences from co-accumulated metals have been minimised by the addition of a suitable complexing agent to the stripping media [83-85].

2.3.2 Application of Modified Screen-printed Carbon Electrodes for Metal Ion Analysis

Honeychurch and Hart [9] reviewed the reported applications of chemically modified screen-printed electrodes and a number of these earlier reported applications of chemically modified screen-printed electrodes are given in table 3.

Concentrations of Au in human urine have been quantified at a poly-L-histidine modified SPCE [86]. It was found possible to complex Au, present as tetrachloroaurates, at the modified electrode surface under open circuit conditions. This was then quantified by a cathodic stripping voltammetry in 0.1 M KCl (pH 1.0). Linear sweep (LSV), differential pulse (DPV), and square wave voltammetry (SWV) were investigated and detection limits of 6.0 μM, 1.7 μM and 4.0 μM were obtained respectively. SWV was found to be the most sensitive waveform, however, DPV was shown to obtain the lowest detection limit, and consequently was utilised in further studies.

Shi *et al* [87] have synthesized an 8-hydroxyquinoline ferrocenoate (Fc-Q) ligand and applied this as the recognition element in the development of a multi-channel sensor for the detection of Hg^{2+}. In the presence of Hg^{2+} ions Fc-Q was shown to give colorimetric, fluorescent and electrochemical responses. With increasing complexation with Hg^{2+} ion, the absorption peak was reported to be red-shifted ($\Delta\lambda$= 45 nm), with the fluorescent intensity being quenched at 303 nm. Electrochemical investigations at a screen-printed electrode showed that in the presence of Hg^{2+} the FcQ oxidation peak to shift catholically by −149 mV. This behaviour was reported to result from the presence of the positively charged Hg^{2+} ion increasing the electron density at the ferrocenyl redox centre of the Fc-Q molecule. DPV investigations showed that with increasing Hg^{2+} concentration the Fc-Q oxidation peak current magnitude was found to decrease linearly. Utilising this behaviour it was found possible to determine Hg^{2+} concentration in the ng/mL region, with Investigations by DPV exhibiting a linear response over the range 0–300 ng/mL Hg^{2+}. Possible interferences from other metal cations (Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}) and anions (Cl^{-}, acetate and ClO_4^{-}) were investigated with no notable interferences reported. The possibility of determining Hg^{2+} in both river and tap water sample were investigated by immobilising the Fc-Q on the SPCE surface. The average recovery is >94% (%CV <3.4) for water samples fortified at 40, 50 and 60 ng/mL.

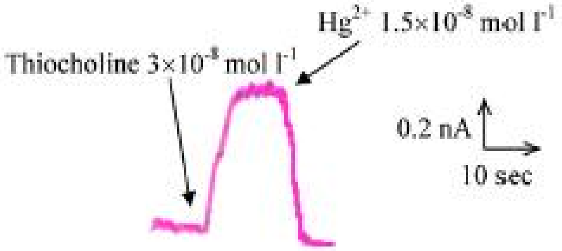
Stozhko *et al* [88] have investigated seven different hetarylated formazans as modifiers for the determination of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. Higher analytical signals of metals were detected at 1-(o-chlorophenyl)-3-phenyl-5-(6-methyl-4-oxo-pyrimidinyl-2)formazan modified electrodes. The modified electrodes were obtained by mixing a 0.02 g portion of carbon ink with 0.02 mL of a 10 % formazan solution in chloroform. A thin layer (*ca.* 100 μm) of the resulting mixture was applied onto a polymeric substrate and then dried at 50 ˚C for 2 h. The simultaneous electrochemical pre-concentration of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} was carried out at using an accumulation potential of -1.4 V. The anodic differential voltammogram measurement step was recorded from –1.0 to -0.05 V. The response was reported to be linear over the concentration range from 2 to 50 mg/L for Cu^{2+}, Pb^{2+}, Cd^{2+} and from 10 to 50mg/L for Zn^{2+}. The detection limits for Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} were reported to be 1.0 μg/L, 0.8 μg/L, 0.9 μg/L and 1.8 μg/L respectively.

Prasek *et al* [89-92] have presented a number of reports focused on both the development of SPCE and their modification with nanoparticles. Recently, utilising SPCEs modified with carbon nanoparticles, Arduini *et al* [93] have reported an amperometric based sensor capable of determining Hg^{2+} levels as low as 1 ng/mL with a response time of less than three minutes. Their sensor was based on a screen-printed electrode modified with an acetonitrile dispersion of commercially available carbon black N220. This was shown to give significantly enhanced electrochemical activity compared to an unmodified screen-printed electrode when tested with thiocholine, cysteine, glutathione and cysteamine. Amperometric investigations were undertaken in a stirred 0.05 M pH 7.4 phosphate buffer solution containing 0.1 M KCl, at an applied potential of +0.3 V vs. Ag/AgCl. Responses for thiocholine and cysteine were found to be highly sensitive and linear up to 1×10^{-5} M. The reported enhancement seen at the carbon black modified electrodes was concluded to result from the electrocatalytic properties gained from the carbon nanoparticles, resulting from the high number of defect sites present in their nanostructure; similar to that reported for carbon nanotubes. The electrochemical oxidation of thiols such as thiocholine and cysteine resulted in the formation of the corresponding disulphide (eq. 11).

$$2RSH \rightarrow RSSR + 2e^- + 2H^+ \qquad \text{(eq. 11)}$$

However, the addition of Hg^{2+} ions to this system resulted in formation of a non-electroactive thiol complex with a subsequent depletion in the amperometric response proportional to the concentration of Hg^{2+} ions present. Figure 4 shows the amperometric response for the sensor, when challenged with 1.5×10^{-8} M Hg^{2+} (3.0 ng/mL). The analytical application of the developed sensor was investigated by determining Hg^{2+} levels in fortified drinking water samples. Samples were analysed without any pre-treatment with the effect on the thiocholine signal being recorded. Using a thiocholine concentration of 1×10^{-7} M was no signal decrease was reported for the control drinking water samples. However, for drinking water samples fortified with 5×10^{-8} M and 5×10^{-9} M of Hg^{2+}, signal decreases of 98±2% and 14±3% respectively were observed. The effects for various other metal ions, such as, Cu^{2+}, Ag^+, Pb^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Mn^{2+} and As^{3+} were investigated at a concentration of 5×10^{-6} M with a thiocholine concentration of 1×10^{-5} M only the addition of Ag^+ ions was reported to give any notable decrease in the amperometric response.

Figure 4. Typical current–time curve obtained before and after adding mercury ions: applied potential +0.3 V vs. Ag/AgCl, phosphate buffer 0.05 M + KCl 0.1 M, pH 7.4, thiocholine 3×10^{-8} M. Reprinted from Electrochim. Acta, 56, Arduini F., Majorani C., Amine A., Moscone D., Palleschi G., Hg^{2+} detection by measuring thiol groups with a highly sensitive screen-printed electrode modified with a nanostructured carbon black film, 4209–4215, Copyright 2011, with permission from Elsevier.



Analyte	Modifier	Accumulation media	Measurement technique	Linear range	Detection limit (time)	Sample(s)	Ref.
Hg^{2+}	polyanilinemethylene blue coated	0.5 M HCl	DPASV,-0.3 V	$1x10^{-8}$ M - $1x10^{-5}$ M	54.27 ng/mL (120 s)	Ultra-pure water	[94]
UO_2^{2+}	4-carboxyphenyl	Ammonium acetate	15 minutes	$8.5×10^{-10}$ to 10^{-7}M	$2×10^{-9}$ M	Estuarine water	[95]
Hg^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}	polyaniline, or polyaniline-poly(2,2'–dithiodianiline)	0.1 M H_2SO_4; 0.5M HCl	DPASV, -0.4 V (120 s)	1 x 10^{-9} M and 1 x 10^{-6} M	-	-	[96]
Hg^{2+}	Electrochemically coated polyaniline-poly(2,2'-dithiodianiline)	0.5 M HCl	DPASV, -0.3 V	$1x10^{-8}$ M - $1x10^{-5}$ M	56 ng/mL (120 s)	-	[97]
Hg^{2+}	poly(4-vinlylpyridine)	pH 4 acetate buffer solution with 2 M KCl	SWASV	100 – 1000 ppb	69.5 ppb	Skin-lightening cosmetics	[98]
Cd^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}	Chitosan	0.1 M HCl/KCl	DPASV, -1.0 V	10 – 200 ng/mL	Pb^{2+} 3.4 ng/mL, Cu^{2+} 5 ng/ml, Cd^{2+} 5 ng/mL Hg^{2+} 2 ng/mL (30 s)	Tap water	[99]
Eu^{3+}	self-assembled salicylamide on mesoporous silica	open circuit, 50 mM acetate buffer pH 4.6 – 6.5	electrolysis at -0.9 V for 60 s in a new medium (0.1–0.2 M NH_4Cl, pH 3.5), by square-wave voltammetric	75 to at least 500 ppb	10 ppb (10 min)	-	[100]
Pb^{2+}	functionalized mesoporous silica	0.2 M HCl	SWASV, -1.2 V	1 ng/mL – 30 ng/ml	0.1 ng/mL, 5 min accumulation , 120 s electrolysis	Drinking water, river water, groundwater	[101]
Pb^{2+} and Cd^{2+}	Crown-ethers (dibenzo-24-crown-8 and tetrathiacyclododecane 12-crown-4 membranes investigated)	0.1 M KNO_3 – 0.2 M HNO_3	LSAV, -1.0 V	Up to $7.5x10^{-7}$ M for both Pb^{2+} and Cd^{2+}, using tetrathiacyclododecane 12-crown-4 membranes	Pb^{2+} $0.8x10^{-8}$ M, Cd^{2+} $0.6x10^{-8}$ M, using tetrathiacyclododecane 12-crown-4 membranes	Soil and river water	[102]
Cd^{2+}	ETH 1062 across water|PVC-NPOE gel microinterface, PVC-NPOE Gel (PVC 2.8% m/m in a solution of 10 mM BTPPATPBCL or TBATPBCL and 10 mM ETH 1062 in NPOE			Up to 391 nM, 30 s.	20 ppb for Cd^{2+} ions (20 s without pre-concentration step)	Aqueous solution	[103]

Table 3. Chemical modified screen-printed Electrodes for the Determination of Metal Ions.

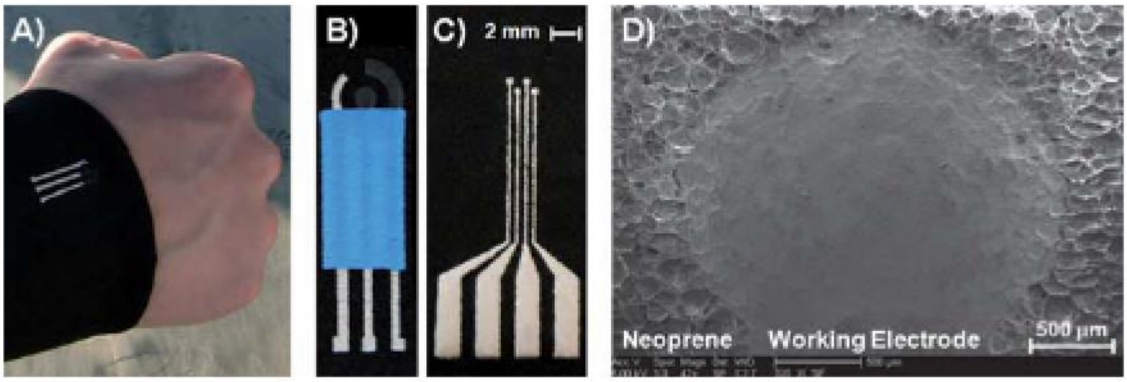
2.4 Platinum, Gold and Silver Screen-printed Carbon Electrodes

Electrode materials other than carbon such have been successfully utilised for the manufacture of screen-printed metals sensors. Principally, these have focused on the application of Au, Ag and Pt (table 4). Aluminium chlorohydrate is important compound in antiperspirant deodorants, known to reduce sweat production. However, recently concern has focused on Al relationship with the development of Alzheimer's disease. Consequently, there is need for its determination of Al in such formulations. Chiu *et al* [104] have utilised a screen-printed silver sensor system as part of a flow injection system for its determination. The sensor consisted of Ag working and counter electrodes and a Ag/AgO reference electrode. In the presence of water chloride is liberated from aluminium chlorohydrate which reacts with the Ag working electrode to form free Cl^-. Conditions were optimised for this reaction and it was found that a 0.1 M pH 6 phosphate buffer with a flow rate of 0.5 mL/min using an applied potential of -25 mV obtained a linear range of 1 to 200 mg/L with a corresponding detection limit calculated for a signal to noise ratio of 3 of 0.295 mg/L was obtained. Four different antiperspirants deodorant samples were investigated and the values obtained were found to be in good agreement with the product labels. Samples were fortified with 20, 40 and 60 mg/L aluminium chlorohydrate and good recoveries were obtained for all samples investigated (95.65–106.36 %).

Recently, Malzahn *et al* [105] have shown the possibility of screen-printing electrochemical sensors onto neoprene diving wet and dry suits. As is illustrated in figure 5 the neoprene material was found to be a suitable substrate to print the working, counter and reference electrodes and could be utilised for the anodic stripping voltammetric determination of Cu^{2+}, together with sensors for the voltammetric determination of 2,4,6-trinitrotoluene and a tyrosinase based biosensor for the determination of phenolic compounds. Each printed three-electrode assembly consisted of a circular carbon working electrode (geometrical area: 3 mm^2) inscribed inside of a hemispherical carbon counter electrode (area: 10 mm^2) and a Ag/AgCl reference electrode (area: 2 mm^2). The carbon working electrodes were modified with a thin Au film by electroplating at 0.0 V in a pH 7 phosphate buffer containing 50 mg/L Au. Copper determination was shown to be possible in quiescent unmodified seawater, using square-wave stripping voltammetry (frequency = 10 Hz, 25 mV step amplitude, 4 mV step potential). Using a two minute accumulation time at -1.00 V (vs. Ag/AgCl) a detection limit of 13 ng/mL and a linear range from 10 to 90 ng/mL was reported. The authors also described a miniaturized 19 mm x 19 mm PCB-mounted CMOS potentiostat encapsulated into a watertight compartment integrated into the wetsuit. However, this was not utilised for the determination Cu, but was operated in free-running chronoamperometric mode only.

Noh and Tothill [106] have described a three-electrode configuration screen-printed gold sensor developed for the determination of Pb^{2+} by square-wave stripping voltammetry using an applied potential of -0.7 V (vs. screen-printed Ag/AgCl). The gold working electrode was fabricated as part of a three electrode sensor by printing a gold layer on the working electrode track (planar area 1.3 mm^2) using Au ink. A linear concentration range of 10–50 µg/L and 25–300 µg/L with detection limits of 2 µg/L and 5.8 µg/L were obtained for Pb^{2+} for measurement times of four and two minutes, respectively. It was shown possible to determine Pb^{2+} in wastewater samples and in acetic acid and *aqua regia* extracts of soil samples. To perform this analysis each sample was diluted 10 to 62.5-fold, depending on the original concentration of Pb^{2+} in the samples. Before analysis every new electrode was cleaned by cyclic voltammetry from 0 to 1.5 V, 10 times, at 100 mV/s, in 0.5 M H_2SO_4–0.01 M KCl. The electrodes could be reused up to 20 times after cleaning with 0.5 M H_2SO_4. The pre-treatment method was postulated to increase surface functionality and/or remove surface contaminants, resulting in enhanced electrochemical activity. The peak area of the Pb stripping peak was reported to be significantly enhanced in the presence of Cd, making their simultaneous determination impossible. However, the determination of Pb was still possible, as the method of multiple standard additions was shown to overcome these problems. Interferences from other ions including, Cr, Hg, As, Fe, Zn, Cu and Ca were also investigated, with an enhancement in the Pb stripping current reported in the presence of Cu and a decrease in the presence of As^{3+}. Comparisons were made with Hg-film electrodes and ICP–MS, and some disagreement with the concentrations determined. It was concluded that the formation of intermetallic species may explain the differences between the results obtained.

Figure 5. (A) Screen printed electrode (SPE) on an underwater garment. The three-electrode configuration comprises an Ag/AgCl reference electrode as well as carbon working and counter electrodes printed directly onto neoprene. Centre: Two different SPE designs on neoprene—(B) three-electrode configuration equivalent to (A) comprising an additional insulator layer (blue); (C) an array of four silver electrodes (the feature width of each contact line is ~195 µm, the pitch between adjacent electrodes is ~280 µm, and the diameter of the active area of each electrode is ~440 µm). (D) Scanning electrode micrograph illustrating the working electrode area on the neoprene substrate (42x, 5 kV). Malzahn K., Windmiller J.R., Valdés-Ramírez G., Schöning M.J., Wang J., Wearable electrochemical sensors for in situ analysis in marine environments. Analyst, 2011, 136, 2912-2917. – Reproduced by permission of The Royal Society of Chemistry, http://dx.doi.org/10.1039/C1AN15193B.



Analyte	**Modifier**	**Accumulation media**	**Measurement technique**	**Linear range**	**Detection limit**	**Sample(s)**	**Ref.**
Hg^{2+}, Pb^{2+}	Au film, with accumulation with thiol-modified magnetic particles	0.05 M HCl	SWASV, -1.0 V	Hg^{2+} 2 – 16 ng/mL, Pb^{2+} 4 – 16 ng/mL	Hg^{2+} 1.5 ng/mL, Pb^{2+} 0.5 ng/mL, (120 s)	Drinking water	[107]
Cd^{2+}	Screen-printed carbon and screen-printed Au	0.1 M KCl	DPASV	0 – 150 µM	500 nM	-	[108]
Sb^{3+}	Electrochemical generated silver nanoparticles	pH 2 Britton–Robinson buffer	DPASV, -0.6 V, (200 s)	9.90×10^{-8} - 9.09×10^{-7} M	6.79×10^{-10} M	Seawater, pharmaceutical preparations	[109]
Sb^{3+}	Electrochemical generated gold nanoparticles	pH 2 Britton–Robinson buffer	DPASV, -0.55 V (200 s)	9.90×10^{-8} - 9.09×10^{-7} M	9.44×10^{-10} M	Seawater, pharmaceutical preparations	[110]
Pb^{2+}	Random micro-array formed by spraying screen-printed working with a commercial deodorant (200 mm for 12 s).	0.1 M HNO_3	SWASV, -0.5 V	20 µM to 50 µM and 75 µM to 200 µM	9.5 µM	-	[111]
As^{3+}	Au array for ASV, Pt array for direct oxidation, formed by spraying screen-printed working with a commercial deodorant (200 mm for 6 s).	1 M H_2SO_4	LSASV, -1.2 V	1 µM to 5 µM by LSASV	4.8×10^{-7} M	-	[112]
As^{3+}	platinum nanoparticle	1 M H_2SO_4	Cyclic voltammetry, -0.2 V to +1.3 V, 100 mV/s	1.6×10^{-7} - 1.3×10^{-6} M	5.68 ±1.18 mg/L	Certificated water sample	[113]
Pb^{2+}	Au nanostructured	0.1 M HCl	SWASV, -0.5 V (under potential deposition)	2.5 – 250 mg/mL, Fe^{3+} as internal standard	0.09 ng/mL	Capillary and venous blood	[114]
Hg^{2+}	Gold surface conditioned by applying five cycles of CV potential range 0 to +0.7V; scan rate 50 mV/s,	Sample acidified with HCl pH 2, +0.3V for 60 s.	SWASV	5 to 30 ng/mL	1.1 ng/mL (deposition time 60 s)	Industrial waste, fortified rain water, ambient water	[115]

Table 4. Screen-printed carbon Au, Ag and Pt electrodes.

2.5 Bismuth Modified Screen-printed Electrodes for Metal Ion Determination

Bismuth has been successfully shown by a number of authors [116-119] to be an effective alternative to the more toxic Hg (Bi rat oral LD_{50} = 5 g/kg, Hg LD_{50} = 1 mg/kg). The use and history relating to Bi modified electrodes has recently been reviewed [116-119] and a number of elements including chromium [120], zinc [121] and lead [122] have been determined, utilising a similar approach to that used for Hg thin-film electrodes (eq. 12-14). A number of examples of these are summarised in table 5.

$$Bi^{3+} + 3e^{-} \rightarrow Bi^{0} \qquad \text{(eq. 12)}$$

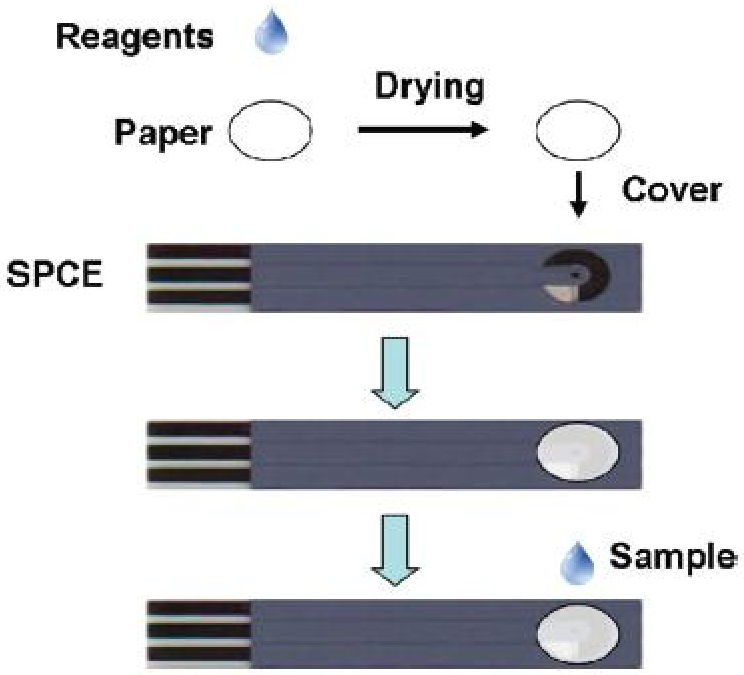
$$M^{n+} + ne^{-} + Bi^{0} \rightarrow MBi \qquad \text{(eq. 13)}$$

$$MBi \rightarrow M^{n+} + ne^{-} + Bi^{0} \qquad \text{(eq. 14)}$$

The formation of a suitable Bi film can be subject to a number of factors, which need to be optimised. Khairy *et al* [123] have utilised an *in situ* Bi film formation approach for the determination of Cd^{2+} in artificial and diluted oral fluid at a SPCE using square wave stripping voltammetry. In this approach, a soluble Bi^{3+} salt is added to sample solution and co-deposited with target analyte. The effect of solution pH upon the *in situ* formed Bi film was explored using a 30 µg/L Cd. At pH values above three the magnitude of the stripping peak decreased reportedly due to hydrolysis. Unstable film formation was also reported if the Bi concentration were too great and a 0.4 mg/L Bi concentration was found optimum for a 30 µg/L Cd solution. Investigations into the effect of deposition potential were then made, and the magnitude of the Cd stripping peak increased with increasing negative potential up to -1.2 V, beyond which it was found to plateau for a 200 s deposition time. Using these conditions investigations into the determination of trace Cd concentrations in oral fluid were however problematic as the adsorption of samples proteins and other components interfered with the *in situ* deposition of Bi. However, by adjusting the pH of the oral fluid samples to pH 1 with HCl this problem was greatly elevated. Additions of Cd were found to be linear over the range 10 to 80 µg/L. Concentrations above this resulted in decreased voltammetric responses, due to the saturation of the Bi nucleation sites. A detection limit of 2.9 µg/L was calculated based on three times the standard deviation of the blank. Real oral fluid samples needed to be diluted 100 times and as above the pH adjusted to pH 1. A linear range of 10 to 50 µg/L and a detection limit of 2.3 µg/L were found.

The alternative approach is to incorporate some insoluble form Bi, such as Bi_2O_3 [121,124] or $BiPO_4$ [125] into the ink and hence the body of the screen-printed electrode during the manufacturing step. This can then be reduced to Bi during the electrochemical deposition step forming a metal film on the electrode surface. The method avoids the need to add Bi to sample or the *ex situ* plating of Bi. Wang and co-workers have demonstrated the possibility modifying the SPCE with all the reagents required for the ASV determination of Pb^{2+} in surface waters [126,127]. This was simply achieved by drying the buffer salts, $Bi(NO_3)_3$ and the internal standard, zinc nitrate on to a 7 mm diameter Whatman No. 1 filter paper placed over the screen-printed working electrode (figure 6). Upon addition of a ten µL aliquot of the water sample these components are reconstituted allowing for the SWASV determination. A detection limit of 2.0 ng/mL Pb^{2+} was reported with a linear range 0 to 100 ng/mL for a 120 s deposition time at -1.4 V.

Figure 6. *Preparation and application of the paper disk integrated SPCE. Typically 10 µL of buffer with an internal standard were dropped on the filter surface and dried in the air; the paper with pre-storage of reagents was left on the electrode surface; then a fixed volume of sample (10 µL) was dropped on the paper for electrochemical detection. Reprinted with permission from Tan S.N., Ge L., Wang W., Paper Disk on Screen Printed Electrode for One-Step Sensing with an Internal Standard. Anal. Chem. 2010, 82, 8844-8847. Copyright 2010 American Chemical Society.*



The technique of cathodic adsorptive stripping voltammetry (CAdSV) with Bi modified SPCEs for the determination of metal ions such as Co [128] has also been studied. Here an *ex situ* Bi coated SPCE was used in CAdSV of Co with dimethylglyoxime (DMG) as complexing agent. A series of soil extracts with varying Co concentrations were analysed, and the results obtained compared to those determined using ICP–MS. The results revealed the suitability of stripping analysis for the determination of 0.1 µg/L levels of heavy metals in soil extracts.

An interesting hybrid stripping voltammetric-colorimetric method has recently been reported by [129] for the determination of Pb^{2+}, Cu^{2+} and Cd^{2+}. Screen-printed carbon electrodes were modified *in situ* with Bi during the accumulation step for the co-deposition the target metal ions, by the application of an applied potential of -1.2 V for Cd^{2+} and Pb^{2+} and -0.6 V for Cu^{2+}. The modified electrode was then transferred from the sample solution to a second separate solution for the subsequent stripping measurement step to be performed, in a similar manner to that undertaken in previously reported medium exchange assays. However, in this approach, this second stripping solution contained the metal indicator dye, xylenol orange. Consequently, the metal ions generated in the electrochemical stripping step, react in solution with this dye, producing a coloured complex, the concentration of which can then be determined via UV spectroscopy. The relatively high levels of Bi^{3+} ions generated were reported not to interfere with the spectroscopic analysis. Linear relationships with metal ion concentrations and UV absorbances obtained at 575 nm for Pb^{2+} (acetate buffer) and Cu^{2+} (acetate buffer), 580 nm for Cd^{2+} (hexamethylenetetramine buffer), respectively. Limits of detection were reported as 10, 10 and 100 nM for Cd^{2+}, Pb^{2+} and Cu^{2+} respectively. Analysis of waste water samples were successfully undertaken and good agreement was reported with that gained by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Some drawbacks with the use of Bi modified SPCEs have been highlighted by Serrano *et al* [130]. The stripping of the Bi film itself can result in narrowing of the potential range that can be successfully utilised, an affect that can be exacerbated by extremes of pH. However, such issues can also be said for Hg. These effects can interfere with the determination of elements such as Cu and Hg. The presence of relatively large concentrations of Bi^{3+} in solution required for the *in situ* plating of the Bi film can also result in disruptions in speciation of the target analytes. As with most thin-film techniques peak splitting can be observed, but by correct optimisation the assay can be generally avoided. However, in their recent comparison of *ex situ* plated Bi electrodes, Serrano *et al* [130] have shown Bi SPCEs to be superior to Bi thin film glassy carbon electrodes, which exhibited splitting of the Cd stripping peak.

Analyte	**Modifier**	**Accumulation media**	**Measurement technique**	**Linear range**	**Detection limit**	**Sample(s)**	**Ref.**
Pb^{2+}	Bi thin film	Acetate buffer pH 4.5	SWASV, -1.0 V, 2 minutes	10-100 ng/mL	0.3 ng/mL, 3 minutes	Drinking water	[131]
Zn^{2+}, Cd^{2+} Pb^{2+}	Chemically synthesized Bi nanoparticles	pH 4.5 0.1M acetate buffer	SWASV, -1.4 V, flow cell and convective cell		0.52 ng/mL Zn^{2+}, 0.45 ng/mL Cd^{2+}, 0.41 ng/mL Pb^{2+}, (120 s)	Waste water certified reference material, drinking water	[132]
Zn^{2+}, Cd^{2+} Pb^{2+}	bismuth oxide modified ink	0.1 M sodium acetate solution containing 0.05 M HCl or 0.1 M HCl	SWASV, -1.2 V	Cd^{2+} 10 – 150 ng/mL, Pb^{2+} 10 – 150 ng/mL, Zn^{2+} 40 to 150 ng/mL	5, 10 and 30 ng/mL	River water	[133]
Cd^{2+}	Microband *ex situ* Bi plated	acetate buffer 0.2 M, pH 4.5	SWASV, -1.0 V	5.6 ng/mL – 45 ng/mL	1.3 ng/mL	River water sample from a mine area	[134]
Cd^{2+}, Pb^{2+}	bismuth oxide modified ink	0.5M ammonium acetate containing 0.1M HCl (pH 4.6)	Chronopotentiometric	20–300 ng/mL	Pb^{2+} 8.0 ng/mL, Cd^{2+} 16 ng/mL	soil and water samples	[135]
Zn^{2+}, Pb^{2+}	*Ex situ* deposited bismuth	0.01 M KNO_3 and maleic/maleate buffer at pH 6.	DPASV, -1.5 V, 60 s. stripping chronopotentiometry	Up to: Zn^{2+} 250 ng/mL, Pb^{2+} 50 ng/mL, Cd^{2+} 600 ng/mL.	Zn^{2+} 3.5 ng/mL Pb^{2+} 0.5 ng/mL, Cd^{2+} 3.9 ng/mL	Barcelona tap water	[136]
Pb^{2+}	Bi, 0.5% nafion	100 mM acetate 50 mM KCl buffer containing 500 mg/L Bi	SWASV, -1.0 V, 120 s	5 ng/mL - 80 ng/mL	4 ng/mL	Leachates from Moroccan ceramic tajines (cooking vessels)	[137]
Zn^{2+}, Cd^{2+} Pb^{2+}	Dip coated hydrogel modified Bi doped ink	Volatile metal species generated at room temperature by the addition of sodium tetrahydroborate (III) to an acidified solution.	SWASV, -1.2 V	10–80 ng	1 ng (120 s)	Metal vapours	[138]

Zn^{2+}, Cd^{2+} Pb^{2+}	*In situ* plated Bi	1 M HCl	SIA-ASV, -1.4 V	2–100 ng/mL Pb^{2+} and Cd^{2+}, 12–100 ng/mL Zn^{2+}.	0.2 ng/mL Pb^{2+}, 0.8 ng/mL, Cd^{2+} and 11 ng/mL Zn^{2+}	Herbs	[139]
Zn^{2+}, Cd^{2+} Pb^{2+}	*In situ* plated Bi	1 M HCl	SIA-ASV, -1.4 V	0 – 70 ng/mL $Pb^{2+}$and Cd^{2+}, 75 – 200 ng/mL Zn^{2+}.	0.89 ng/mL Pb^{2+} 0.69 ng/mL Cd^{2+}	Drinking water	[140]
Cd^{2+} Pb^{2+}	*In situ* plated Bi	0.2 M, pH 4.6 acetate buffer	SI-MSFA, -1.1 V	10 ng/mL – 100 ng/mL	Cd^{2+} 1.4 ng/mL Pb^{2+} 6.9 ng/mL	Water from a zinc mining draining pond	[141]
Zn^{2+}, Cd^{2+} Pb^{2+}	*In situ* plated Bi	0.1 M pH 4.5 acetate buffer, 10^{-2} M KCl	SWASV	10 ng/mL – 100 ng/mL	Zn^{2+}8.2 ng/mL, Cd^{2+} 3.6 ng/mL, Pb^{2+} 2.5 ng/mL	tap water and waste water	[142]
Cd^{2+}, Pb^{2+}	bismuth oxide modified ink	0.1M, pH 4.5 acetate buffer	SWASV, -1.2 V	20 ng/mL – 100 ng/mL	2.3 ng/mL Pb^{2+}, 1.5 ng/mL Cd^{2+}	River water	[143]
Pb^{2+}	*In situ* plated Bi Lab on a chip	0.1 M acetate buffer pH 4.5	SWASV, -1.2 V	2.5 ng/mL – 100 ng/mL	1.0 ng/mL (120 s)	-	[144]
Pb^{2+}	SPCE modified with Whatman No. 1 filter paper containing electrolyte, Bi and internal standard (Zn) salts.	0.1 M pH 4.5 acetate buffer, containing Zn (60 ng/mL) as internal standard	SWASV, -1.4 V	10 ng/mL - 100 ng/mL	2.0 ng/mL (120 s)	-	[127]
Zn^{2+}, Cd^{2+} Pb^{2+}	Sequential flow injection *in situ* plated Bi	1 M HCl	SWASV, -1.2 V, following pre-concentration at ME-1 chelating resin column	20–50 µg/L Zn^{2+}, 0–14 µg/L Cd^{2+}, 0–14 µg/L Pb^{2+}	17 µg/L Zn^{2+}, 0.3 µg/L Cd^{2+} 0.05 µg/L Pb^{2+}	Drinking water	[145]

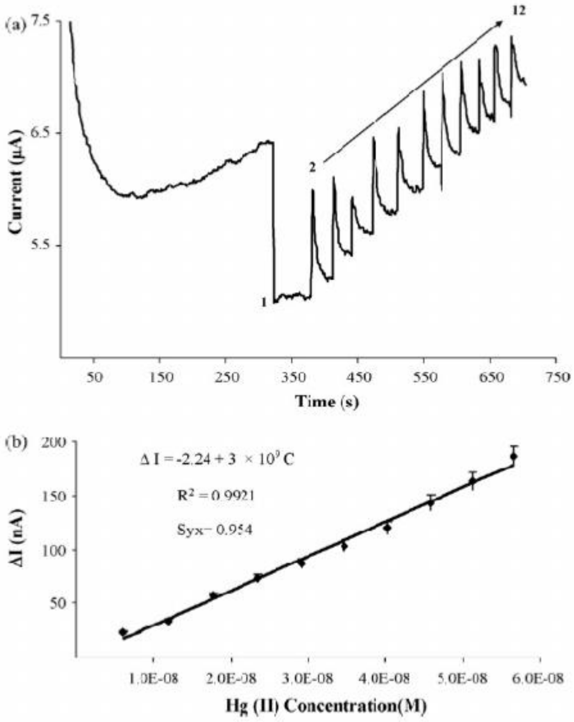
SIA-ASV, sequential injection analysis-anodic stripping voltammetry, SI-MSFA, Sequential injection monosegmented flow voltammetry

Table 5. Bismuth modified screen-printed carbon electrodes for trace metal determination.

3. Screen-printed Biosensors for Metal Ion Detection

Several very good reviews regarding the history and development of biosensor technology have already been given [21,146-151]. For the purposes of this review, biosensors have been defined using a version of the definition given by Théavenot *et al.* [152] as analytical devices incorporating some kind of biological material, such as tissue, microorganisms, organelles, cell receptors, enzymes, antibodies, nucleic acids, *etc.* These biological components are intimately associated with or integrated within a physicochemical transducer or transducing microsystem such as a SPCE. Such devices usually produce a digital electronic signal proportional to the concentration of a specific analyte. The more recent applications of screen-printed based biosensors have recently been reviewed [153]. The following section details with their recent applications to metal ion analysis in more detail.

Figure 7. Amperometric recording obtained at a: (a) urease/SPCE: (1) Addition of urea ((urea) = 0.33M), (2–12) additions of 100 μL of a 10^{-4} M mercury (II) solution. (b) urease/AuNPs/SPCE: Relation between ΔI vs. [Hg (II)]. Eap = -1.5V vs. Ag/AgCl, pH= 7. Reprinted from Talanta, 79, Domínguez-Renedo O., Alonso-Lomillo M.A., Ferreira-Goncalves L., Arcos-Martínez M.J., Development of urease based amperometric biosensors for the inhibitive determination of Hg (II), 1306–1310, Copyright 2009, with permission from Elsevier.



3.1 Enzyme and Amino Acid Modified Metal Ion Biosensors

The application of biosensor technology for metal ion determination is a more recent development; a number of examples are given in table 6. Recently, such an approach has been employed for the determination of Hg^{2+} based on the inhibition of urease activity at a gold nano-particle modified SPCE [154]. Urease was immobilized to the SPCE surface by cross-linking with bovine serum albumin and glutaraldehyde. Metallic gold nano-particles were found to enhance the sensitivity of the sensor and were electrochemically deposited on the working electrode surface, from a 0.1 mM solution of $HAuCl_4$ in 0.5 M H_2SO_4. Figure 7a shows the resulting amperometric response of the sensor. A steady-state current was obtainable in the presence of urea and additions of Hg^{2+} resulted in a current decrease which was shown to be proportional concentration (figure 7b). Using this approach a detection limit of 5.6 x 10^{-8} M was obtainable and the biosensor was shown to be able to determine Hg^{2+} levels of 1.0 µM in fortified human plasma samples.

Sanllorente-Méndez *et al* [155] have recently determined As^{3+} at an acetylcholinesterase modified SPCE. Arsenic inhibits acetylcholinesterase conversion of acetylthiocholine iodide to thiocholine iodide and acetic acid (eq.15).

$$\text{Acetylthiocholine iodide} + H_2O \rightarrow \text{thiocholine iodide} + \text{acetic acid} \qquad \text{(eq. 15)}$$

The former is electrochemically active and can, as in this case, be monitored amperometically at an applied potential of +0.6 V. A corresponding drop in the amperometric signal is gained with increasing As^{3+} concentration. A detection limit of 1.1×10^{-8} M with a corresponding linear range up to 1×10^{-7} M As^{3+} was obtained. The developed biosensor was capable of determining 1.0 µM As^{3+} concentrations in tap water. Further investigation on a certified As^{5+} water sample were possible following the addition of sodium thiosulphate to reduce the acetylcholinesterase inert As^{5+} to As^{3+}.

The interaction of arsenate with L-cysteine has been successfully utilised as the basis of a biosensor for the determination of As [156]. L-cysteine reduces arsenate to arsenite and is itself in process oxidized to L-cystine. The reaction involves electron transfer at the working electrode and can be monitored amperometically. By immobilising L-cysteine to the surface of the screen-printed carbon electrode, it was found possible to gain a limit of detection of between 1.2 and 4.6 ng/mL. Interferences from other oxidising agents such as nitrate were investigated, and no effects were reported for concentrations commonly present in drinking water.

The widely used glucose oxidase enzyme system has also been described for the determination of a number of metal ions including; Hg^{2+}, Ag^{+}, Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} [157]. As part of a flow injection system the sensor was able to obtain detection limits in the low µg/mL with Ag^{+} detection limits in the µg/L region.

3.2 Bacteria Modified Screen-printed Metal Ion Biosensors

Shewanella sp. is known as a metal-reducing bacterium, involved in the cycling of iron, manganese, trace elements as well as phosphates. Prasad *et al* [158] have demonstrated the use of this bacterium as the electron transfer material for electrochemical sensors for the determination of arsenite, hydrogen peroxide, and nitrite. A *Shewanella sp.* CC-GIMA-1 bacterial suspension (prepared in 0.1 M, pH 7.4 phosphate buffered saline) was drop-coated on the electrode surface and allowed to settle under room temperature for 1 h. This approach was found to superior to growing bacterial biofilms on the electrode, reported to be laborious and time consuming. Oxygen functional groups, known to be present on the electrode surface, offer similar properties to humates which are a favourable environment for bacterial growth. The bacteria films were found to be able to utilise these functional groups as electron acceptors for respiration. The effects of arsenite (50-500 µM), hydrogen peroxide (50 µM-2.5 mM) and nitrite (100-500 µM) were studied by cyclic voltammetry and the reduction peak current of the *Shewanella sp.* modified electrode was found to increase in the case of As from *ca.* 6 µA to 10 µA for an addition of 500 µM arsenite. Additions of Fe^{3+} were also found to exhibit similar voltammetric behaviour.

3.3 Peptide Modified Screen-printed Electrode for Metal Ion Determination

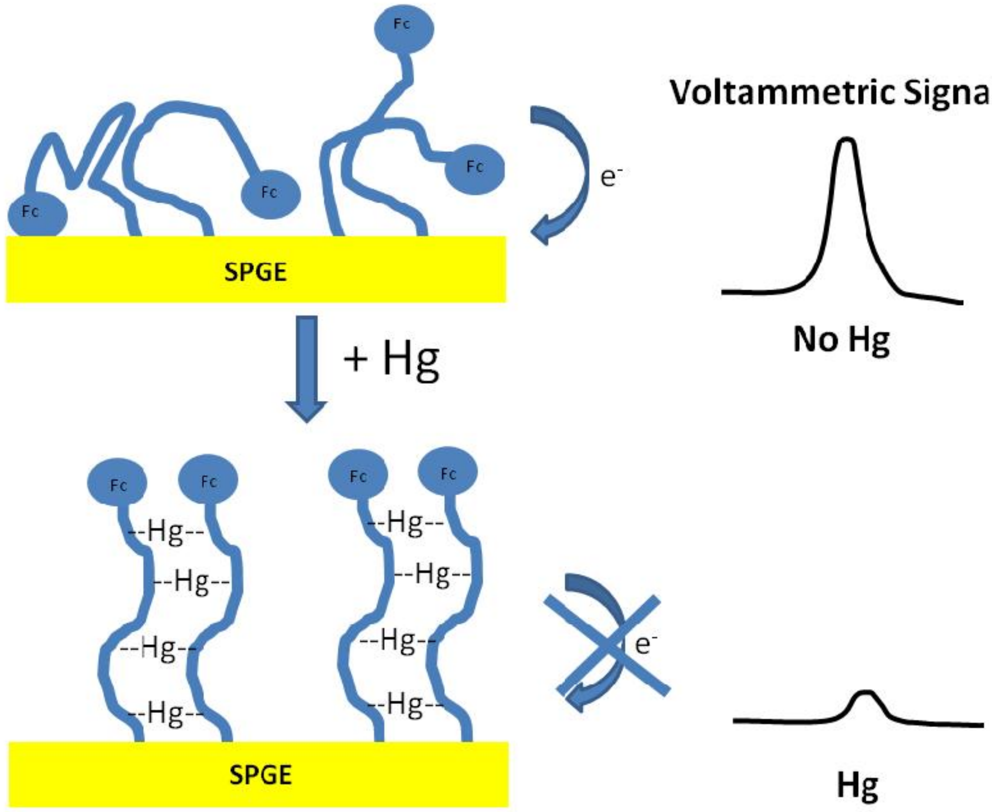
Self-assembled peptide nanofibrils formed at screen-printed Au electrodes have been investigated as a possible biosensor for the determination of Cu^{2+} ions [159]. Four different cysteine containing variants of the octapeptide were investigated as nanofibrils; N-S-G-A-I-T-I-G (NS), N-C-G-A-I-T-I-G (NC), C-N-G-A-I-T-I-G (CN) and C-S-G-A-I-T-I-G (CS). The peptide nanofibrils were prepared from lyophilized peptide powders dissolved in double-distilled water and incubated for six days to allow the fibrils to form. The Au screen-printed electrodes were modified by the addition of a 5 µL drop of a solution containing self-assembled nanofibrils was deposited on top of the metal working electrode, incubated overnight at 4 ˚C. The electrodes were washed with double-distilled water prior to the electrochemical measurements to remove any unbound nanofibrils. The functionalized gold electrode was evaluated by cyclic voltammetry, impedance spectroscopy, energy dispersive X-ray and atomic force microscopy. Copper ions were accumulated on the NC-modified gold electrodes at open circuit potential by immersing the electrode into 5 mL of an aqueous solution of Cu^{2+} in 50 mM ammonium acetate (pH 6.8) and 50 mM NaCl for electrochemical measurements by SWV. The pulse amplitude was 25 mV with a step of 4 mV and a frequency of 25 Hz. The SW voltammograms were recorded between -250 and 500 mV. After the measurement step, bound copper was eliminated from the NC-modified electrode at by applying a potential of +500 mV during 20 s in a 0.1 M $HClO_4$. The biosensor was shown to give a linear response with Cu^{2+} concentration from 15 µM to 50 µM for a 2 minute open circuit accumulation time. The possible interferences resulting from Ca^{2+} and Mg^{2+} were commented upon but were not investigated in this report.

3.4 DNA Modified Screen-printed Metal Ion Biosensors

Niu *et al.* [160] have utilised a DNA modified Au screen-printed electrode (SPGE) biosensor for the trace determination of Hg^{2+}, gaining a detection limit of 0.6 nM (120 ng/L). The working electrode was modified with a self-assembled mono layer of the thiol-functionalized oligonucleotide, 5'-SH-$(CH_2)_6$-TTGCTCTCTCGTT-3' (P1) and a second ferrocene (Fc) substituted oligonucleotide, 5'-TTCGTGTGTGCTT-ferrocene-3' (P2). As shown in figure 8a, in the absence of Hg, hybridisation does not occur between the two oligonucleotides due to the T–T mismatched bases. The flexibility of the single oligonucleotide, P2 allows close enough contact with to the SPGE and hence a voltammetric peak is recorded from interaction with the Fc. However, in the presence of Hg, (figure 8b) hybridisation via the thymine–Hg^{2+}–thymine (T–Hg^{2+}–T) complex can occur and the ferrocene molecule is no longer able to interact with the SPGE and the voltammetric peak decreases in proportion to the Hg concentration.

The developed biosensor showed a linear response for Hg^{2+} over the concentration range 0.001-10 µM, and no interferences were reported for several metal ions including, Mg^{2+}, Ba^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Na^{+} and K^{+} at 1 mM concentrations for the response gained for a 1 nM Hg^{2+} solution.

Figure 8. Schematic of the electrochemical Hg^{2+} biosensor based on T-Hg^{2+}-T induced DNA hybridization.



Analyte	**Enzyme**	**Immobilisation technique**	**Electrolyte**	**Measurement technique**	**Linear range, mM**	**Detection limit, mM**	**Sample(s)**	**Ref.**
Cu^{2+}, Cd^{2+} and Pb^{2+}	Urease	Sol-Gel	pH 7.0 0.02 mM phosphate buffer	conductometric	0.1- 10	-	-	[161]
Hg^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}	Urease	Sol-Gel	pH 7.5 5.0 mM imidazole-HCl buffer at room temperature	conductometric	Hg^{2+} 0.005-0.5, Cu^{2+} 0.02-1.0, Cd^{2+} 0.1-10, Pb^{2+} 0.9-10	Hg^{2+} 0.005, Cu^{2+} 0.02, Cd^{2+} 0.1, Pb^{2+} 0.9	-	[162]
Ag^{+} and Cu^{2+}. Ag^{+}, Pb^{2+}, Sb^{3+}, Cd^{2+}, Co^{2+} and Ni^{2+} also investigated	Urease	Bio-compatible ink	5.0 mM phosphate buffer composed of equal amounts of KH_2PO_4 and K_2HPO_4 in 0.1 M KCl, containing 10 mM urea.	potentiometric	Cu^{2+} 0.001-0.1	Sub ppm	-	[163]
Hg^{2+}, Cu^{2+} and Cd^{2+}	urease and the NADH–glutamic dehydrogenase system	alginate gel and nafion	pH 8.0 Tris/HCl–KCl buffer	amperometric	Hg^{2+} 0.075–1 mg/L, Cu^{2+} 0.05–1 mg/L, Cd^{2+} 1–50 mg/L	Hg^{2+} 63.6 µg/L, Cu^{2+} 55.3 µg/L, Cd^{2+} 4.3 mg/L	Water, sediments and soils	[164]
Hg^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}	urease and the NADH–glutamic dehydrogenase system	Reaction undertaken in solution and 100 µL added to SPCE surface	pH 8 Tris/HCl buffer (50 mM, 0.1M KCl)	amperometric, rhodinised screen-printed carbon electrode for NADH measurement	$Hg^{2+}$and Cu^{2+} 10-100 µg/L, Cd^{2+}, Zn^{2+} 1-30 mg/L. No inhibition seen for Pb^{2+}	Hg^{2+} 7.2 µg/L, Cu^{2+} 8.5 µg/L, Cd^{2+} 0.3 mg/L, Zn^{2+} 0.2 mg/L	As mine leachate	[165]
Ni^{2+}, Cu^{2+} and Cd^{2+}	Acetylcholinesterase			amperometric, TCNQ as mediator	Cu^{2+} 0.001–0.1	-	-	[166]

Table 6. Screen-printed Metal Ion Biosensors.

5. Conclusions

The predominant analytical technique would still seem to be stripping voltammetry. However, notably since our last review, there has been marked increase in the volume of work reported on Bi modified SPCEs with a similar reduction the utilisation of Hg based assays. We believe that this reduction in the utilisation of Hg will continue as legislation becomes more stringent on its application. The number of reports focused on screen-printed ion-selective metal sensors has stayed relative constant, presumably due to competing technologies, such as PVC membrane based electrodes [167-190].

The majority of reported work has focused on the heavy metal ions, Pb, Cd and Cu, but there are increasing numbers of reports on the determination of other elements. A number of biosensors based approaches have been reported predominated by urease based systems and are generally less sensitive than approaches based on stripping voltammetry. However, recent studies with oligonucleotide based biosensors have shown comparable sensitivities [160]. The application of new technology such as nanoparticles, plastic electronics [191] and synthetic biology [192] will become increasingly more important. Although outside the scope of this review, the utilisation of screen-printed electrodes in the stripping voltammetric determination of metal nanoparticle labels in immunoassays is an area we believe will continue to increase importance [193-196].

Appendix

Analyte	**Modifier**	**Medium exchange**	**Accumulation media**	**Measurement technique**	**Linear range**	**Detection limit (time)**	**Sample(s)**	**Ref.**
Cu^{2+}	Cation exchanger, Dowex 50W-X8 (H^+ form, 20 - 50 mesh)	Yes	Phosphate buffer, 5 mM pH 5.7, open circuit (10 min)	DPASV -0.4 V (15 s)	0 - 110 ng/mL (2 min)	0.5 ng/mL (10 min)	Drinking water, groundwater	[76]
Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}	Hg thin film	No	20 mM KH phthalate, 0.1 M $MgCl_2$	DPASV -1.4 (300 s)	10 -500 ng/mL			[197]
Pb^{2+}	0-cresolphthlexon (OCP), Hg thin film	No	OCP 1 µM, in 1 mM acetate buffer pH 4.0, 0.0 V.	PSA constant current -10 µA stop at -0.9 V	1 – 15 ng/mL (2 min)	40 pg/mL (2 min)	Drinking water, human albumin	[198]
Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}	Hg coated micro array	No	-1.2 V, 0.1 M pH 4.0 acetate buffer	PSA, SWASV	PSA = 2 – 25 ng/mL SWASV = 10 – 80 ng/mL	0.1 ng/mL Pb^{2+} (4 min) PSA	Drinking water, wine	[199]
Pb^{2+}	micro array	No	No supporting electrolyte	LSASV	10 – 50 ng/mL	0.8 ng/mL	blood	[200]
Pb^{2+}	Au coated	No	-0.7 V, 0.05 M acetate buffer pH 4.5.	PSA	0 -25 ng/mL (4 min), 50 – 250 ng/mL (30 s).	0.1 ng/mL (20 min), 0.6 ng/mL (4 min).	Drinking water, urine	[201]
U	Hg thin film	No	5 mM pH 4.5 acetate buffer, 5 mM cupferron. Adsorption of uranium-cupferron complex at -0.05 V	PSA	0 – 35 ng/mL	0.2 ng/mL (5 min)	Groundwater	[202]
Cu^{2+}	Cu-bis-cyclohexanone oxaldihydrazone	No	Tris-HCl, pH 8.0, 50 mM	Amperometric	1.91-19.1 µg/mL	1.91 µg/mL	-	[203]
Pb^{2+}	Palintest, Hg thin film	No	2.5 % v/v	DPASV		2.5 µg per sample	Paint, soil, particulate and dust matrices	[204]
Pb^{2+}	Palintest, Hg thin film	No		DPASV		1-2 ppb	Filtered particulates in workplace air	[205-207]
Pb^{2+}	Palintest, Hg thin film	No		DPASV			Drinking water	[208]
Zn^{2+},Cd^{2+},	Hg thin film	No	120 mg/mL Hg_2Cl_2	DPASV	0 - 1000 ppb	Zn^{2+} (55.71	water	[209]

Pb^{2+}, Cu^{2+}			20 mM potassium hydrogen phthalate, 0.1 $MgCl_2$			ng/mL),Cd^{2+} (71.64 ng/mL), Pb^{2+} (64 ng/mL), Cu^{2+} (123 ng/mL)		
Cd^{2+}, Pb^{2+}, Cu^{2+}	Hg thin film generated from HgO incorporate in ink	No	0.1 M KNO_3, 0.024 M HCl, -1.2 V, 2 minutes	LSASV	Cd^{2+}, Pb^{2+}, 0-30 ng/mL, Cu effected by carry over		Lake water	[30]
Cd^{2+}, Pb^{2+}, Cu^{2+}	Pre-plated Hg thin film	No	SWASV 30 mM acetate buffer pH4.7. PSA 10 mM KCl and 30 mM acetate buffer pH4.7.	SWASV, -1.0 V and PSA		SWASV Cd^{2+} (1.0 ng/mL), Pb^{2+} (0.4 ng/mL), Cu^{2+} (8.0 ng/mL) 3 minutes. PSA Cd^{2+} (0.4 ng/mL), Pb^{2+} (0.6 ng/mL), Cu^{2+} (0.8 ng/mL) 75 s.	Tap water	[210]
Pb^{2+}	Thin-film [Hg/Cu] ratio of 2	No	0.02 M acetate buffer pH 2	SWASV, -0.8 V	0-100 ng/mL	0.81 ng/mL (60 s)	Ground, tap and seawater	[211]
Pb^{2+}	Thin film Hg coated array. Cd internal standard.	No	hydrochloric acid solution, containing 3 mg/L and 50–100 µg/L mercury and cadmium ions, respectively	PSA	20 -300 µg/L (50 s)	5 ng/mL (2.5 minutes)	Blood	[212, 213]
Cd^{2+}, Pb^{2+}	Hg thin film	No	0.01M HCl.	SWASV	50 - 200 µg/L	-	-	[214]
Pb^{2+}	Ag SPE	No	0.1 M pH 3 KNO_3/HNO_3	SWASV, -0.5 V	5-80 ng/mL (60 s)	46 pg/mL	Pond water, ground water	[215]
Ag^{+}	Unmodified SPCE, thin layer cell	No	photographic fixer solution	SWASV -0.9 V and chronamperometry	SWASV 0.6-13 mg/L, chronamperometry 0.25 g/L – 5.0 g/L	-	Photographic waste solution	[216]
Pb^{2+}	Unmodified SPCE	No	0.1 M HCl	DPASV, -1.4 V	6.3 ng/mL– 24	2.5 ng/mL (180 s)	Pond water	[217]

					ng/mL and 24 ng/mL – 50 ng/mL			
Cu^{2+}	Unmodified SPCE	No	0.1 M malonic acid	DPASV	8.0 ng/mL - 450 ng /mL	8.2 ng/mL	Bovine serum, tap water, river water	[218]
Pb^{2+}, Cd^{2+}, Cu^{2+}	Unmodified SPCE and Hg thin film	No	0.1 M KNO$_3$	LSASV	10^{-6} M – 10^{-9} M Pb^{2+}	-	-	[219]
Pb^{2+}	SPCE microarray	No	No supporting electrolyte	LSASV (-1.2 V)	10 – 50 ng/mL	0.8 ng/mL (300 s)	Water	[220]
Pb^{2+}	Hg thin film screen-printed microarray	No	HCl	SWASV	Up to 100 ng/mL	5 ng/mL (60 s)	Blood	[221]
Pb^{2+}	Drop coated PAN	Yes	Accumulation media pH 10 ammonia buffer, open circuit, measurement 0.1 HCl	DPASV (-1.4 V)	0-700 ng/mL and 700-5000 ng/mL	15 ng/mL	Water	[78]
Pb^{2+}	Drop coated calix[4]arene	Yes	Accumulation media pH 10, ammonia buffer, open circuit, measurement 0.1 HCl	DPASV (-1.4 V)	5 ng/mL – 100 ng/mL	5 ng/mL	River water	[79]
Cd^{2+}	Drop coated calix[4]arene	Yes	Accumulation media pH 10, measurement	DPASV	2.8 ng/mL – 350 ng/mL	2.8 ng/mL	River water	[80]
Ni^{2+}	Screen-printing ink doped 5-20 % w/w dimethylglyoxime	No	0.1 M ammonia buffer pH 9.2	DPASV	40 ng/mL – 200 ng/mL	5 ng/mL	River water	[77]
Hg^{2+}	Screen-printing ink doped with Sumichelate Q10R	No	0.5M NaCl, 0.1M acetate buffer, pH 4.5	DPASV	2.4 pg/mL – 2.0 ng/mL and 2.0 ng/mL – 8.0 ng/mL	2.4 pg/mL (30 minutes open circuit)	Channel water	[222]
Al^{3+}	Screen-printing ink doped with 5 % Alizarin	No	pH 9	DPASV	18 ng/mL – 486 ng/mL	5.4 ng/mL	Soil, water	[223]
Cr^{6+}	Self-assembled monolayer 4-(-2-mercaptoethyl)pyridinium	Yes	Accumulation 0.15 M NaF, buffered at pH 4.5, measurement 0.15 M NaF buffered pH 7.8	SWCSV, 5 minutes open circuit	4.2x10^{-11}M – 5.4x10^{-10}M	2.3x10^{-11}M	-	[224]
Cr^{6+}	12.5% diphenylcarbohydrazide	No	0.1M NaNO$_3$ solution at pH 3	Potentiometric batch and flow	static mode 3.16×10^{-7} M -	static mode 2.1×10^{-7}M and	Leachates from municipal solid	[225]

				analysis	1.00×10^{-4} M, flow injection analysis 1.00×10^{-6} M – 1.00×10^{-4} M	flow injection analysis 9.4×10^{-7} M	waste landfills	
Pb^{2+}	Dithizone, nafion membrane, nafion membrane modified with S,S'-methylenebis(N,N'-diisobutyldithiocarbmate	Yes	Accumulation, open circuit pH 11, 10 minutes. Measurement 0.1 M HCl	SWASV (-1.0 V, 15 s) or PSA	25-250 ng/mL (dithizone)	12 ng/mL (dithizone)	-	[226]
Cu^{2+}	Ion-selective	No	0.1 M KNO_3	Potentiometric		<318 ng/mL	-	[227-230]
Hg^{2+}, Se^{4+} and dimethylmercury also investigated	Au thin film	No	0.05 M HCl	Potentiometric stripping analysis	0-30 ng/mL	Hg^{2+} 0.5 ng/mL	-	[231]

Appendix 1. pre 2003 applications of screen-printed electrodes for metal ion analysis.

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