Review

Advance in the Stripping Voltammetry Using Alloy Electrodes for the Determination of Heavy Metal Ions

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Excessive (or even trace of very toxic species) heavy metal ions can cause serious problems on the environment and human health. Therefore, sensitive and practical methods for the determination of them are of great significance. Stripping voltammetry is leading in the development of capable heavy metal ions detection tools by employing environmental-friendly alloy electrodes, including Bi, Sb and Sn. Herein the mainstream advance in recent half-dozen years is reviewed briefly. In particular, attention is paid to the integration of alloy electrodes and nanomaterials, which enhances significantly the selectivity, sensitivity, and reproducibility of detection.

1. INTRODUCTION

Concerns about the effects of heavy metal ions on human health and the environment [1,2] trigger the necessity and urgency for developing practical methods of determination. Compared to atomic absorption spectroscopy (AAS), mass spectroscopy (MS), inductively coupled plasma-mass spectrometry (ICP-MS) and X-ray fluorescence spectroscopy (R-FS), electrochemical methods, especially stripping voltammetry, show some essential advantages in the determination of trace heavy metal ions, such as the inherent miniaturization and portability of instrumentations, the low cost of operation, fast response and high sensitivity [3,4]. On occasions, greater sensitivity is required than can be achieved on bare solid working electrodes, even when the electrodes are made very high surface area such as columnar glassy carbon electrode [5]. Therefore, to improve sensitivity to meet some

important scale, for example, the limit concentrations of heavy metal ions in drink water recommended by the World Health Organization (WHO) [4], alloy electrodes and amalgam electrodes are often employed. Since the middle of the 20th century, Hg-based electrodes coupled with stripping techniques have been the most frequently used methods for the determination of heavy metal ions because of the amalgam-forming ability [6]. However, there is a tendency to avoid the use of Hg because of its toxicity. Furthermore, its low mechanical stability complicates the use in flowing systems and in portable devices [4,6-9]. Fortunately, a few metals, which show the potential to replace Hg, have been realized at the right time for the development of "green chemistry". Bismuth (Bi), antimony (Sb) and tin (Sn) based electrodes also show attractive stripping behaviour resulting from the ability to form 'fused' multicomponent alloys with heavy metals, and are more environmental-friendly since the toxicity of them and their salts is negligible compared to Hg compounds.

The research and application of these new alloy electrodes for the determination of heavy metal ions have been blossoming since the beginning of this century. In particular, the use of Bi-based electrodes has attracted interest all over the world. Landmark reviews on Bi-based electrodes have been published in 2005 [10,11] and 2010 [12]. Over the last few years research interest in this field has accelerated with many more achievements having been reported on the determination of heavy metal ions by employing alloy electrodes, including not only Bi but Sb and Sn in this time. In particular, considerable evidence shows that the integration of alloy metals and nanomaterials can improve the sensitivity significantly. Herein, the main advance of the application of Bi-, Sb- and Sn-based alloy electrodes, as well as the integration of nanomaterials, in the determination of heavy metal ions, is reviewed, covering the period of 2008-early 2015.

2. ALLOY ELECTRODES IN THE DETERMINATION OF HEAVY METAL IONS

2.1. Bi

Compared to Hg, Bi not only is more environmental-friendly, but also has some other attractive properties for voltammetric electroanalysis [12-14], such as the insensitivity to the presence of oxygen, the wide potential window, the versatility of coupling with an inert electrode substrate and the excellent mechanical stability. As emphasized by Wang *et al* in 2010 [12], the attractive and unique behaviour of Bi-based electrodes was attributed to the formation of multi-components alloys, as well as the enhanced sensitivity derived from the combination of the great properties of the nanostructure materials. The recent use of Bi materials as the working electrode material for stripping voltammetry can be subdivided into four categories which are bulk Bi, Bi nanoparticles, Bi film and Bi precursor modified electrode. Significant factors, including the substrate upon which the Bi is attached, the method of coupling the Bi and the employments of nanostructure materials, affect the electrochemical properties of the final working electrodes [15]. Therefore, these factors, as well as the electrochemical parameters and the apparent ability displayed in the applications, are all considered in this review.

2.1.1. Bulk Bi

Armstrong *et al* [16] fabricated a bulk Bi disk electrode in 1.5 mm diameters, and evaluated its ability for determining Pb(II), Cd(II), and Zn(II) by square wave voltammetric stripping (SWASV). The results showed that the limits of detection of 93, 54, and 396 ng/L for Pb(II), Cd(II) and Zn(II) were obtained, respectively, with an accumulation time of 180 s. After extensive use of the electrode for multiple runs (without polishing), misshapen and broad peaks were observed due to the formation of a Bi oxide.

In 2012, Morales *et al* [17] reported the employment of a rotating bulk Bi disk electrode for the determination of Pb(II), Cd(II) and Zn(II) by SWASV. With an accumulation time of 120 s, limits of detection for Cd(II) and Pb(II) were 5.64 and 5.85 μg/L, respectively. Using a shorter accumulation time of 60 s, a limit of detection for Zn(II) was 59.1 μg/L. Successful application to the determination of Pb(II) in samples of fortified rainwater and sewage sludge from a steel industry was achieved.

2.1.2. Nano Bi

Bi nanoparticles have been proven to be highly sensitive and reliable for trace analysis of heavy metal ions in conjunction with stripping voltammetry [4]. Table 1 summarizes the significant employments of Bi nanoparticles to the determination of heavy metals reported over the year of 2008-2014.

Table 1. Employments of Bi nanoparticles to the determination of heavy metal ions and the applications.

Basal electrode	Modification	Analyte	Technique	Accumulation time (s)	Detection limit (μg/L)	Linear range (μg/L)	Real sample	Ref.
GCE	Coating	Pb Cd	SWASV	30	Pb: 0.21 Cd: 0.56	Pb: 83-1243 Cd: 45-674	Leached from Toy leachate	[18]
SPE	Adsorption	Pb Cd Zn	SWASV	120	Pb: 1.3 Cd: 1.7 Zn: 4.9	- - -	Tap water	[19]
Al/Au	Self-assemble	Pb	SWASV	60	-	Pb: 2.5-50	-	[20]
GCE	Coating	Pb Cd	SWASV	120	Pb: 0.8 Cd: 0.4	Pb: 5-60 Cd: 5-60	Natural water	[21]

The data were obtained in acetate buffer of pH 4.0 [18], 4.5 [19,21] and 4.4 [20], respectively.
GCE –Glassy carbon electrode; SPE -Screen-printed electrode.

In 2009, a new mode of employing Bi nanoparticles was reported [22]. In this report, Bi powder and glassy carbon powder were mixed to fabricate a composite electrode. During electrode operation, dissolution of Bi was performed at 0.3 V. Then the dissolved Bi(III) reduced onto the surface of electrode to form nanoparticles, accompanying the deposition of Pb(II) and Cd(II) in 0.1 M

acetate buffer solution of pH 4.5. With an accumulation time of 300 s, limits of detection for Cd(II) and Pb(II) were 0.49 and 0.41 μg/L, respectively.

2.1.3. Bi film

As an alternative to Hg-based electrode, Bi films are the most frequent employed material for the determination of heavy metal ions [12,15], in particular, *in situ* or *ex situ* deposition on a commercially GCE. Moreover, it has been demonstrated that Bi films can easily be formed on many kinds of substrates, either conductive or nonconductive ones. This section will discuss some typical cases only where Bi films are formed onto the substrates directly, without the combination with other materials.

1) *Ex situ* modifying mode. Serrano *et al* [23, 24] electrodeposited a Bi film onto the surface of a commercial SPE with *ex situ* modifying mode, and evaluated its properties for the determination of heavy metal ions by differential pulse anodic stripping voltammetry (DPASV). At the Bi-based electrode, limits of detection for Pb(II), Cd(II) and Zn(II) were 0.5, 3.9 and 3.5 μg/L, respectively, with an accumulation time of 120 s.

2) *In situ* modifying mode. Zong *et al* [25] described a method for the determination of Sb(III) and Sb(V) by Osteryoung square wave cathodic stripping voltammetry, employing an *in situ* plated Bi film on an edge-plane graphite substrate as working electrode. The limit of detection was as low as 2 ng/L for Sb(III) with an accumulation time of 30 s. Khairy *et al* [26] demonstrated that *in situ* Bi film modified SPE might be used for the bio-monitoring of Cd(II) in artificial and diluted human oral (saliva) fluid by SWASV. With an accumulation time of 200 s, a limit of detection of 2.3 μg/L was obtained in buffer solution of pH 1.0. Santos *et al* [27] fabricated a Bi film modified SPE by *in situ* electrodeposition mode. Using it as working electrode, limits of detection of 0.60 and 0.10 μg/L for Cd(II) and Pb(II) could be obtained by SWASV with an accumulation time of 180 s. Based on the *In situ* modifying mode, Intarakamhang *et al* [28] also developed an automatic device for determining Cd(II) and Pb(II). Outstandingly, a method based on double deposition and stripping steps was proposed to increase the detecting sensitivity of Pb(II) and Cd(II) by employing *in situ* plated Bi film electrode [29]. Calibration was performed following deposition times of 300 and 120 s at the first and the second electrode, respectively. Under such conditions the detection limits of 0.037 μg/L for Pb(II) and 0.005 μg/L for Cd(II) were obtained, indicating that this method was excellent for accomplishing the routine analysis of these metals according to standards and guidelines for heavy metals in drinking water recommended by the WHO and EPA [4].

3) Comparison between *ex situ* and *in situ* modifying mode. Commonly, Bi film generated by *ex situ* electroplating metallic Bi on a conductive substrate requires a separate step, which complicates the experimental procedure and extends the analysis time. However, in one reaction cell many basal electrodes can be modified using the same Bi(III) solution. Therefore less usage is needed than that by *in situ* modifying mode. Quintana *et al* [30] carried out an analytical comparative study of SPEs modified by Bi using "*in situ*" and "*ex situ*" mode, respectively. For Pb(II) detection, they confirmed that the "*in situ*" procedure resulted in better analytical performances. This result may be the

explanation for the less employment of "*ex situ*" mode. However, in certain cases the application of the *in situ* mode is not convenient, undesired or even impossible, e.g., when performing measurements in environments where Bi(III) cannot be added to the medium.

4) Sputtering Bi film electrode. Apart from the "*in situ*" and "*ex situ*" electroplating Bi film in chemical reaction cell, another important microfabrication method has been developed rapidly, basing on a sputtering technique.

Table 2. Sputtering Bi film electrodes and their applications in the determination of heavy metal ions.

Basal electrode	Analyte	Technique	Solution pH	Accumulation time (s)	Detection limit (µg/L)	Linear range (µg/L)	Real sample	Ref.
Silicon	Ni	SWASV	9.2	90	Ni: 0.1	-	River water	[31]
SPE	Pb	DPASV	6.0	300	Pb: 0.16	0.53-19.8	Groundwater	[32]
	Cd				Cd: 0.10	0.33-12.3		
SiO$_2$	Tl	SWASV	4.5	240	-	10-80	Lake water	[33]
Silicon	Pb	SWASV	4.5	120	Pb: 0.7	Pb: 2.5-15	Lake water	[34]
	Cd		4.5	120	Cd: 0.6	Cd: 2.5-15		
	Ni		9.2	60	Ni: 0.7			

It has been shown that the application of such a thin-film approach for the fabrication of Bi film electrode offers several advantages over the traditional electroplating: i) a Bi(III) plating solution is not required so that the experimental procedure can be simplified, the analysis time can be shortened while waste products are minimised; ii) a conductive substrate is not necessary, because the sputtered Bi coating serves as both the sensing element and the transducer of the current to the measuring instrument; iii) the electrode geometry and the thickness of the Bi film can be easily controlled with the view to manufacture sensors of different configurations; iv) the use of standard thin film technology offers increased scope for mass-production of inexpensive and disposable devices in a reproducible fashion [15,31]. Table 2 summarizes the typical fabrication and application of this technique. Moreover, from Table 1 and Table 2 it can be found that the sputtering Bi film electrodes, as well as bulk Bi electrodes, are applicable to media covering a relative wider pH range.

2.1.4. Bi precursor

Sopha *et al* [35] developed a carbon paste electrode (CPE) bulk-modified with ammonium tetrafluorobismuthate (BiF4). It revealed a favourable performance in acidic solutions (pH 0.5-2.5) in the presence of dissolved oxygen for the determination of Cd(II) and Pb(II) by ASV. Limits of detection of 1.2 µg/L for Pb(II) and 9.8 µg/L for Cd(II) were obtained with an accumulation time of 240 s. Bi$_2$O$_3$ was also employed to modified electrode [36] to conducting a simultaneous multi-elemental stripping voltammetry. Limits of detection of 5, 10 and 30 µg/L for Cd, Pb and Zn were obtained, respectively.

2.1.5. Integration of Bi with nanostructure materials

Carbon nanotubes (CNTs) and graphene have been shown to be ideal for sensor applications since they possess unique physical and chemical properties including high surface area, strong mechanical strength, excellent thermal conductivity and electric conductivity. CNTs exhibit excellent properties because of the presence of edge-plane-like sites and reactive groups on the surface. It was recently discovered that they can transport charge ballistically over relatively large distances at room temperature [37]. Similarly, graphene exhibits a lower charge-transfer resistance than graphite and glassy carbon electrode (GCE) and a comparable wide electrochemical potential window due to in which sp^2 bonded carbon atoms are arranged into honeycomb structure [38]. While, gold nanoparticle (Au NP) has received increasing attention in electrochemical detection since they enhance the electrode conductivity and facilitate the electron transfer due to quantum size effects [39]. In addition, some other carbon-based nano-composites containing metal receptors, such as cysteine, can react with metal ions and produce stable complexes [40]. Moreover, some other materials have also been proved to be useful for improving the properties of the stripping voltammetry. Therefore, many functional materials, in particular, nano-scale materials, are known to play important role in the improvement of electrochemical capacity for stripping analysis of heavy metal ions. In the closely recent years, the integration of organic ligand [41], ionic liquid [3], polymer [42], carbon-based nanoparticles [14] and even their combination [40], etc. with Bi modified electrode has been reported frequently [43].

1) Binary combination.

In some cases, Bi was modified onto the surface of electrode substrate by combining with another kind of functional material to form a binary combination. Due to their unique characteristic and strong adsorption ability, carbon-based nanomaterials have been the most frequently used ones. [1,6,37]. More than two dozen papers on it have been published in recent six years according to Google Scholar Research. The SWASV grams of Cd(II) and Pb(II) at Bi film modified SPE, electrochemically reduced graphene oxide modified SPE, Bi film combining electrochemically reduced graphene oxide modified SPE, and Bi film combining chemically reduced graphene oxide modified SPE were studied, respectively. Highest peaks for target metal ions were obtained at the Bi film combining electrochemically reduced graphene oxide modified SPE due to the presence of nanosheets provided more effective active area for the nucleation of target metal ions with Bi in short time during the electrodeposition procedure [44]. The SWASV grams of 50 μg/L Cd(II) and Pb(II) at the CPE, multi-walled carbon nanotubes (MWCNT) modified CPE, and Bi film combining MWCNT modified CPE were studied, respectively. Similar to the above report, the best response was obtained at the Bi film combining MWCNT modified CPE, indicating the ability of electrochemical analysis for these heavy metal ions was improved significantly by employing the combination of Bi and CNT [45]. Moreover, there are a few other binary combination reports by employing carbon-based nanomaterials and Bi. The maim contents, including their applications, are listed in Table 3 in comparison.

Some other kinds of nano- or micro-scale particles have also been employed by combining to Bi to improve the performance of stripping voltammetry for the determination of heavy metal ions. For example, zeolite, polyaniline, montmorillonite, etc, all can help, mainly because they can provide large area platforms. The typical examples, including their applications, are also listed in Table 3. Notably,

Saturno *et al* [46] designed a distinctive protocol. They electroplated Bi onto a hydrated aluminum oxide template, which was previously coated on a GCE. Then, the template was selectively removed by soaking the electrode in a 0.1 M NaOH solution, leaving a dispersed Bi film covering the electrode surface.

Table 3. Representative examples of binary combination for the determination of heavy metal ions.

Basal electrode	Functional Species	Plating mode of Bi	Analyte	Technique	Supporting solution	pH	Accumulation time (s)	Detection limit (µg/L)	Linear range (µg/L)	Real sample	Verification technique	Ref.
SPE	MWCNT	*In situ*	Pb Cd Zn	SWASV	0.1 M acetate buffer	4.5	300	Pb: 1.3 Cd: 0.7 Zn: 12	2-100 2-100 2-100	River water	ICP-MS	[47]
SPE	MWCNT	*In situ*	Pb Cd	SWASV	acetate buffer	4.0	180	Pb: 0.2 Cd: 0.8 Zn: 11	2-100 2-100 12-100	Herb medicine	ICP-AES	[8]
Graphite	MWCNT	*In situ*	Pb	CPSA	0.1 M acetate buffer	4.6	120	Pb: 1.0	10-100	Soil	ICP-AES	[48]
CPE	MWCNT	*In situ*	Cd	SWASV	0.1 M acetate buffer	5.0	120	Cd: 0.3	1.0-60.0 -	Tap water	-	[49]
CPE	MWCNT	*Ex situ*	Pb Cd	SWASV	0.1 M acetate buffer	4.5	300	- -	- -	-	-	[45]
SPE	MWCNT	*Ex situ*	Pb Cd	SWASV	0.1 M acetate buffer	4.5	240	Pb: 0.1 Cd: 0.1	5-150 5-150	Air	-	[50]
SPE	Electrochemically reduced graphene	*In situ*	Pb Cd	SWASV	0.1 M acetate buffer	4.5	150	Pb: 0.8 Cd: 0.5	1-60 1-60	Milk	ICP-MS	[44]
CPE	Graphene	*In situ*	Pb Cd	SWASV	0.05 M HCl	-	-	Pb: 0.04 Cd: 0.07	0.1-50 0.1-50	Tap water Surf clam tissue	ICP-OES	[51]
CPE	Reduced graphene	*Ex situ*	Pb Cd Zn Cu	DPASV	0.1 M acetate buffer	5.5 5.5 6.5 5.5	400	Pb: 0.55 Cd: 2.8 Zn: 17 Cu: 26	20-120 20-120 - -	Ground water Lake water	-	[52]
CPE	Zeolite	*In situ*	Pb Cd	DPASV	0.1 M acetate buffer	4.5	120	Pb: 0.1 Cd: 0.08	1-20 1-20	Tap water Sewage water	AAS	[53]
GCE	Polyaniline	*In situ*	Pb Cd	SWASV	20 mM H_2SO_4 + 30 mM KCl	-	160	Pb: 3.42 Cd: 0.12	5.2-31.1 2.8-16.9	- -	- -	[42]
GCE	Silica nanoparticle	*In situ*	Pb Cd	SWASV	0.1 M acetate buffer	4.5	120	Pb: 0.2 Cd: 0.6	2-150 2-150	Lake water	ICP-MS	[42]
CPE	Montmorillonite	*In situ*	Zn	SWASV	0.1 M acetate buffer	5.0	240	Zn: 0.18	1-64	Honey	ICP-AES	[54]

| SPE | Porous CaCO$_3$ | *In situ* | Pb Cd | SWASV | 0.1 M acetate buffer | 4.5 | 300 | Pb: 0.03 Cd: 0.34 | 0.05-30 1-30 | River water | ICP-MS | [55] |

2) Ternary combination.

Ternary composite films have also been employed to facilitate the determination of heavy metal ions. The peak current of 0.19 mM Pb(II) was 2 times greater at the MWCNT/Nafion/SPE modified with a Bi film than without a Bi film. These results can be explained by the fact that: 1) Bi can form an alloy with Pb and cause Pb(II) to be reduced more easily; 2) the strong adsorptive ability and large electroactive area of MWCNT attracts Pb(II) and Bi(III) from bulk solution to the electrode surface [14]. Similarly, the highest stripping peak currents for Pb(II) and Cd(II) were obtained on the graphene/poly(sodium 4-styrenesulfonate)/Bi/SPE [56]. It demonstrated that the ternary composite film possesses very attractive electrochemical characteristics with high sensitivity, compared with other three film electrodes. The phenomenon of high sensitivity could be attributed to the small size with larger surface, high adsorptive ability and outstanding electrochemical properties of graphene. In addition, the defective structure and the existence of some functional groups, such as carboxylic and hydroxyl groups are beneficial for the adsorption of metal ions. Furthermore, the improvement may be related to the morphology features of the poly(sodium 4-styrenesulfonate) (PSS), which could wrap around graphene, providing more absorbing sites for metal binding without affecting the electronic property of the graphene. The typical examples of ternary combination, including their applications, are listed in Table 4.

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3) Quadruple combination.

It has been evidenced that some combinations containing quadruple ingredients could also be capable for the determination of trace heavy metal ions. Using a Bi/GCE modified with Nafion, poly (2,5-dimercapto-1,3,4-thiadiazole) and MWCNTs as working electrode, He *et al* [67] obtained limits of detection of 0.03 and 0.05 μg/L for Cd(II) and Pb(II), respectively, by DPASV. Zhu *et al* [40] modified gold nanoparticle/graphene/cysteine composite onto the surface of GCE, following by an *in situ* electrodeposition of Bi. The currents and the concentrations of Cd(II) and Pb(II) in the both range between 0.50-40 μg/L with the limits of detection of 0.10 μg/L for Cd(II) and 0.05 μg/L for Pb(II), respectively, were obtained with an accumulation time of 800 s. Recently, the same research group also reported the employment of graphene oxide/thionine/Nafion, instead of gold nanoparticle/graphene/cysteine composite. Linear calibration curves for both Cd(II) and Pb(II) were 1-40 μg/L with limits of detection of 0.1 μg/L for Cd(II) and 0.05 μg/L for Pb(II) [68] . Besides, it has been evidenced that the sensitivity of a 3-D Bi/graphene/CNT composite coated SPE is over 50 times of that coated only with Bi for determining Pb(II) [69].

Table 4. Representative examples of ternary combination for the determination of heavy metal ions.

Basal electrode	Functional Species	Plating modei	Analyte	Technique	Supporting solution	pH	Accumulation time (s)	Detection limit (μg/L)	Linear range (μg/L)	Real sample	Verification technique	Ref.
GCE	MWCNT Nafion	*In situ*	Pb Cd	SWASV	0.1 M acetate buffer	4.5	600	Pb: 0.05 Cd: 0.08	- -	Tap water	ICP-MS	[57]
SPE	MWCNT Nafion	*Ex situ*	Pb Cd Zn	SWASV	0.1 M acetate buffer	4.6	120	Pb: 0.15 Cd: 0.17 Zn: 0.72	0.5-4.0 1.0-7.9 5.9-49.7	-	-	[14]
GCE	MWCNT Nafion	*In situ*	Pb Cd	DPASV	M acetate buffer	4.5	600	Pb: 0.025 Cd: 0.040	0.05-100 0.05-100	Tap water	AAS	[58]
SPE	MWCNT Nafion	*In situ*	Pb Cd Zn	DPASV	0.1 M acetate buffer	4.0	120	Pb: 0.01 Cd: 0.01 Zn: 0.01	0.05-100 0.5-80 0.5-100	Lake water	AAS	[59]
GCE	Graphene Nafion	*In situ*	Pb Cd	DPASV	0.1 M acetate buffer	4.5	120	Pb: 0.02 Cd: 0.02	0.5-50 1.5-30	Lake water	-	[60]
PGE	Graphene Nafion	*In situ*	Pb Cd Zn	SWASV	0.1 M acetate buffer	4.6	120	Pb: 0.13 Cd: 0.09 Zn: 0.17	- - -	Tap water	-	[61]
SPE	Graphene PSS	*In situ*	Pb Cd	DPASV	acetate buffer	4.5	120	Pb: 0.089 Cd: 0.042	0.5-120 0.5-120	Tap water Lake water	AAS	[56]
SPE	Graphene Ionic liquid	*In situ*	Pb Cd	SWASV	0.1 M acetate buffer	4.5	120	Pb: 0.1 Cd: 0.08	1.0-80 1.0-80	Rice	AAS	[3]
Silicon	Graphene Polyaniline	*In situ*	Pb Cd	SWASV	0.1 M acetate buffer	5.3	180	Pb: 0.07 Cd: 0.04	- -	-	-	[62]
GCE	Nafion 2,2-bipyridyl	*In situ*	Pb Cd Zn	SWASV	acetate buffer	4.5	120	Pb: 0.077 Cd: 0.12 Zn: 0.56	0.21-414 0.11-224 0.07-131	Wine Tap water Natural Water	ICP-AES	[41]
SPE	Nafion Crown ether	*In situ*	Pb Cd	SWASV	hydrochloric acid	-	180	Pb: 0.11 Cd: 0.27	0.5-60 0.5-60	Rice	ICP-OES	[63]
GCE	Nafion Ionic liquid	*In situ*	Pb Cd	SWASV	acetate buffer	4.5	120	Pb: 0.2 Cd: 0.5	10-120 10-120	Lake water	-	[64]
GCE	Nafion Nitrogen doped microporous carbon	*In situ*	Pb Cd	DPASV	acetate buffer	4.5	150	Pb: 0.05 Cd: 1.5	0.5-100 2-100	Tap water	-	[65]
Graphite	Nafion Nanomedical stone	*In situ*	Pb Cd	SWASV	acetate buffer	4.5	300	Pb: 0.07 Cd: 0.47	2-12 2-12	Wastewater	AAS	[66]

2.2. Sb

Sb-based electrodes could be as a probable alternative for electrochemical stripping analysis of trace heavy metal ions, attributing to the ability to form multi-components alloys [4]. It compared favourably to Bi film electrodes in better performance in acidic conditions [70], narrower stripping signals for Cd(II) and Pb(II), and improved overall response to Cd(II) [13]. Similar to the Bi-based electrodes, commonly there are four models to use Sb as working material for stripping voltammetry, including bulk electrode, Sb nanoparticle modified electrode, Sb film and Sb precursor modified electrode. In this section all the typical modes, as well as the electrochemical parameters and the apparent ability displayed in the applications, were reviewed.

2.2.1. Bulk Sb

Carbon paste bulk-modified with Sb powder has been presented for the determination of Cd(II) and Pb(II) by SWASV in non-deaerated solution of 0.01 M hydrochloric acid (pH 2) [71]. With an accumulation time of 120 s, the limits of detection for the two kinds of ions were 1.4 and 0.9 μg/L, respectively. This mode is environment-friendly because of the elimination of toxic Sb (III) compounds, which is being criticized as the major disadvantage.

2.2.2. Sb film

Sb film is also a popular employment as Hg-free electrodes. The study on the fundamental mechanism and applications are proceeding. *In situ* deposition, *ex situ* deposition and sputtering fabrication are the common modes to prepare Sb film.

1) *Ex situ* modifying mode. Bassie *et al* [72] developed a film modified GCE by *ex situ* electrodepositing Sb. It was found that −500 mV depositions potential and 45 s deposition time are the optimized conditions for sensitive film fabrication in supporting solution of pH 1. At the modified working electrode, the striping response of Pb(II) and Cd(II) was sensitive in 0.1 M acetate buffer supporting electrolyte at pH 2.5 and 5.5, respectively. Besides, the Sb film can also be formed by *ex situ* on CPE [73] using 0.02 M HCl as supporting solution. In 2010, a strategy to create macroporous Sb modified Au electrode is developed by Urbanová *et al* [74] based on the replication of colloidal crystal templates. The electrode of controlled porosity showed an increased internal electroactive area and a significantly improved electrochemical performance. The typical applications of Sb film electrodes are summarized in Table 5.

2) *In situ* modifying mode. Similar to the Bi-based electrodes, *in situ* mode is the mainstream modification due to the same advantages. In 0.1 M HCl solution (pH 1) Sb nanoparticles could be formed on the surface of boron doped diamond (BDD) electrode to produce a good platform for the simultaneous electroanalytical determination of Pb(II) and Cd(II) [75]. An *in situ* Sb film modified SPE was successfully used for the determination of Cu(II) simultaneously with Cd(II) and Pb(II) ions, by mean of DPASV with a very high reproducibility and good trueness [76]. The electrode was proposed as a valuable alternative to *in situ* Bi film electrodes, since no competition between the

electrodeposited Cu and Sb for surface sites was noticed. Compared to the *in situ* mode for forming Bi film, the formation of Sb film can be carried out in a wider pH range. For example, 1.0 M solution of hydrochloric acid [77], 0.01 M acetate buffer of pH 4.5 [76] and 0.1 M ammonium buffer of pH 9.0 [78] all can work well as supporting electrolyte. Tesarova *et al* [79] found that the Sb film modified CPE exhibited superior electroanalytical performance in more acidic medium (pH 2) associated with favourably low hydrogen evolution, improved stripping response for Cd(II), and moreover, stripping signals corresponding to Cd(II) and Pb(II) at Sb film were slightly narrower than those observed at Bi and Hg counterparts. Consequently, more varietal heavy metal ions can be determined by employing *in situ* modifying Sb. The typical applications are also summarized in Table 5.

Table 5. Representative examples of the employments of Sb film modified electrodes by *ex situ* and *in situ* modes for the determination of heavy metal ions.

Basal electrode	Plating mode of Bi	Analyte	Technique	Supporting solution	pH	Accumulation time (s)	Detection limit (µg/L)	Linear range (µg/L)	Real sample	Verification technique	Ref.
GCE	*Ex situ*	Pb	DPASV	0.1 M acetate buffer	2.5	140	Pb: 0.61	-	Tap water	-	[72]
		Cd			5.5	130	Cd: 0.17	-			
CPE	*Ex situ*	Pb	DPASV	0.1 M acetate buffer	6.0	300	Pb: 2.65	-	Tap water	-	[73]
		Cd					Cd: 2.32	-			
		Cu					Cu: 9.73	-			
Au	*Ex situ*	Pb	DPASV	0.01 M hydrochloric acid	2.0	100	Pb: 0.5	20-120	-	-	[74]
		Cd					Cd: 0.7	20-120			
BDD	*In situ*	Pb	LSASV	0.1 M hydrochloric acid	1.0	120	Pb: -	50-500	-	-	[75]
		Cd					Cd: -	50-500			
SPE	*In situ*	Pb	DPASV	0.01 M acetate buffer	4.5	120	Pb: 4.8	16.1-55.5	groundwater	-	[76]
		Cd					Cd: 3.4	11.5-72.4			
		Cu					Cu: 0.28	0.95-54.8			
GCE	*In situ*	Hg	ASV	1 M hydrochloric acid	1.0	120	Hg: 0.39	2.5-80	Real water	ICP-MS	[77]
GCE	*In situ*	Ni	AdSV	0.1 M ammonium buffer	9.0	60	Ni: 0.11	2-20	-	-	[78]
CPE	*In situ*	Pb	SWASV	0.01 M hydrochloric acid	2.0	120	Pb: 0.2	5-50	Lake water	-	[79]
		Cd					Cd: 0.8	5-50			
GCE	*In situ*	Pb	ASV	0.5 M hydrochloric acid	1.0	-	Pb: 1.2	-	-	-	[80]
		Cd					Cd: 1.4	-			
GCE	*In situ*	Pb	SWASV	hydrogen potassium tartrate	3.6	120	Pb: 1.5	-	Rain water	-	[81]
		Cd					Cd: 0.7	-			
		Zn					Zn: 3.8	-			
		Tl					Tl: 1.0	-			
		Cu					Cu: 0.5	-			
		In					In: 1.4	-			
GCE	*In situ*	Tl	SWASV	0.1 M acetate buffer	3.5	120	Tl: 2	20-100	River water	-	[82]
		In					In: 8	20-100	Tap water		

3) Comparison between *ex situ* and *in situ* modifying mode. Similar to the employment of Bi, the *ex situ* and *in situ* modifying modes for forming Sb film have respective advantages. Sopha *et al* [78] reported that the electrodes modified by *in situ* revealed superior performance over its *ex situ* prepared analogue. However, in the performance of *ex situ* electrodeposition less Sb (III) was needed, causing less risk of environmental pollution.

4) Sputtering Sb film electrode. Sputtering technique was also used to form Sb film modified electrodes for the determination of heavy metal ions. And the method has the similar features as by employing Bi. In 2009, Kokkinos *et al* [83] reported a method for fabricating working electrode by sputtering Sb onto the surface of silicon substrate. In 1 M ammonia buffer of pH 9.2, the limit of detection for Ni(II) was 0.2 μg/L by SWASV with an accumulation time of 60 s. Latterly, they reported that the modified electrode could also be used to determine Pb(II) and Tl(I) using 0.05 M phosphoric acid as supporting electrolyte [84].

2.2.3. Sb precursor

Svobodová *et al* [85] fabricated a working electrode by modifying CPE with Sb_2O_3 powder. It could work in both mild and more acidic supporting media. In both acetate buffer of pH 4.4 and 0.01 M hydrochloric acid of pH 2, Cd(II) and Pb(II) exhibited well-defined anodic stripping signals. The limits of detection were 1.0 and 0.7 μg/L respectively, with an accumulation time of 90 s.

2.2.4. Integration of Sb with other materials

The integration of Sb with nanostructure materials has been investigated for the determination of heavy metal ions. Dey *et al* [73] co-deposited Sb and Au onto the surface of a CPE to fabricate a Sb–Au nano-composite electrode. On the electrode, Hg(II) could be determined as low as 0.052 μg/L in acetate buffer supporting electrolyte of pH 6 with an accumulation time of 300 s. Ashrafi *et al* [86] modified a CPE with nano-Sb coated MWCNT by *ex situ* mode. In 0.01 M hydrochloric acid, the limits of detection of 0.65 μg/L for Pb(II) and 0.77 μg/L for Cd(II) were obtained by SWASV with an accumulation time of 120 s. Niu *et al* [87] fabricated a disposable Sb film modified MWCNT/SPE by *in situ* mode. Using it as working electrode, Pb(II) in hydrochloric acid of pH 1.51 was measured sensitively. They also found that the integration of Sb and ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate could improve the ability of the CPE for determining Hg(II) . Yi *et al* [88] used a GCE modified with Sb and poly (p-aminobenzene sulfonic acid) to determine Pb (II) by SWASV. In hydrochloric acid solution of pH 2, the limit of detection was 0.1 μg/L with an accumulation time of 240 s.

2.3. Sn

Compared with Bi and Sb, Sn is a more 'environmentally friendly' material. It has also been employed as alloy electrode for the determination of heavy metal ions, through it was a niche method.

In 2013, Wang *et al* [89] electrodeposited a Sn film onto a CPE modified with Nafion by *in situ* mode. The formed electrode displayed highly sensitive response to the stripping analysis of Cd(II). With an accumulation time of 120 s, a limit of detection of 0.13 µg/L could be obtained in 0.11 M acetate buffer solution of pH 4.0. In the next year, they reported the other strategy by electrodepositing Sn film onto a GCE modified with poly(p-aminobenzene sulfonic acid)/graphene composite [90]. The formed electrode displayed higher sensitivity- a limit of detection of 0.05 µg/L could be obtained. And it was used to determine trace Cd(II) in wastewater and lake water samples with a satisfactory results.

2.4. Synergy of alloy metals

Chen *et al* [91] reported a Bi-Sb film coated SPE by *in situ* co-electrodepositing Bi(III) and Sb(III). They found that The Bi-Sb film modified SPE provided an enhanced electrochemical stripping signal for Pb(II) compared to solo Bi or Sb film modified SPE. Under optimized conditions, the limit of detection was 0.07 µg/L. Ashrafi *et al* [92] also found at the co-deposited film modified CPE the current responses of Pb(II) and Cd(II) were favourably higher than those obtained at solo Bi or Sb film modified electrode.

Xiong *et al* [93] fabricated a Bi-Sn film modified electrode by *in situ* co-electrodepositing Bi(III), Sn(II) and target metal ions onto the poly(p-aminobenzene sulfonic acid) coated GCE. Compared with the solo Bi film modification, as-prepared electrode displayed higher stripping current response. In addition, it had the advantages of better stability and less toxicity. Under the optimum conditions, the linear calibration graph for Cd(II) in the concentration range of 0.5-55 µg/L was obtained and the detection limit was 0.32 µg/L. The method was applied to the analysis of Cd(II) in tap water sample with satisfactory results. Latterly, the same research group confirmed again that the Bi-Sn film modified electrode revealed better electroanalytical performance for electrochemical stripping analysis of trace heavy metals [94].

3. CONCLUSIONS AND OUTLOOK

As discussed in the above sections, there have been many exciting developments in the employment of environmental-friendly alloy electrodes, i.e. Bi, Sb and Sn, for the determination of heavy metal ions by stripping methods. In particular, the combination of alloy metals and other nanostructure materials paves a promising way for developing ultrasensitive electrochemical sensor [7]. Moreover, the synergy of two kinds of alloy metals allows more enhanced electrochemical stripping signal for some heavy metal ions. It is reasonable to believe that the screen printed methodologies, which offer the advantage of production of simple, economical, disposable, portable and mass produced devices suitable for on-site analysis [15,95], are bound to grow continuously and find new application domains by coupling the alloy electrodes.

Low-cost devices and methods that offer portability, simplicity in operation and the ability for high-throughput and quantitative analysis are needed for the point of care detection, as well as the

measurement in lab. To meet the goal it is expected that future work shall focus on the integration of micro-devices and more stable alloy electrodes. There are challenges and opportunities include but not limited to the followings. 1) The electrode based on Bi has a relatively narrow cathodic potential range and suffers from the instability in air due to its natural oxidation [96,97]. And there is the same problem when Sb and Sn are employed. The solution of this obstacle will benefit the *ex situ* mode greatly. 2) The toxic feature of these alloy metal ions, Sb (III) in particular [71], cannot be ignored completely. Thus it is clear that the less usage of them the better. 3) More efforts are worthy of making on the integration of alloy metals and nanostructure materials. 4) As pointed by Li *et al* [6], many heavy metals in the real samples are present in the form of metal-organic complexes instead of free ions. Therefore the methods of pretreatment must be coupled to the employment of suitable alloy electrode for practical applications. 5) Are there some more kinds of heavy metal ions can be determined by employing these alloy electrodes? And how to carry out? 6) Moreover, there is another interesting question: are there any other metals, which are more environmental-friendly than these have been revealed, can be employed as alloy electrode, too?

Reference

1. J. Chang, G. Zhou, E. R. Christensen and R. Heideman, J. Chen, *Anal. Bioanal. Chem*. 406 (2014) 3957.
2. D. Sud, G. Mahajan and M. P. Kaur, *Bioresource Technol*. 99 (2008) 6017.
3. Z. Wang, H. Wang, Z. Zhang and G. Liu, *Sensor. Actuat. B-chem*. 199 (2014) 7.
4. G. Aragay, J. Pons and A. Merkoci, *Chem. Rev*. 111 (2011) 3433.
5. X. Zhang, S. Ma, Z. Cui, J. Chen, Y. Cui, J. Zhao and X. Feng, *J. Chin. Chem. Soc*. 58 (2011) 681.
6. M. Li, H. Gou, I. Al-Ogaidi and N. Wu, *ACS Sustainable Chem. Eng*. 1 (2013) 713.
7. G. Aragay and A. Merkoci, *Electrochim. Acta* 84 (2012) 49.
8. U. Injang, P. Noyrod, W. Siangproh, W. Dungchai, S. Motomizu and O. Chailapakul, *Anal. Chim. Acta* 668 (2010) 54.
9. B. Yosypchuk and J. Barek, *Crit. Rev. Anal. Chem*. 39 (2009) 189.
10. A. Economou, *TrAC-Trends Anal. Chem*. 24 (2005) 334.
11. J. Wang, *Electroanalysis* 17 (2005) 1341.
12. I. Švancara, C. Prior, S. B. Hočevar and J. Wang, *Electroanalysis* 22 (2010) 1405.
13. B. J. Privett, J. H. Shin and M. H. Schoenfisch, *Anal. Chem*. 82 (2010) 4723.
14. A. Mandil, R. Pauliukaite, A. Amine and C. M. A. Brett, *Anal. Lett*. 45 (2012) 395.
15. N. Serrano, A. Alberich, J. M. Díaz-Cruz, C. Ariño and M. Esteban, *TrAC- Trends Anal. Chem*. 46 (2013) 15.
16. K. C. Armstrong, C. E. Tatum, R. N. Dansby-Sparks, J. Q. Chambers and Z. Xue, *Talanta* 82 (2010) 675.
17. M. G. Morales, M. R. P. Marín, L. C. Blázquez and E. P. Gil, *Electroanalysis* 24 (2012) 1170.
18. Y. Li, G. Sun, Y. Zhang, C. Ge, N. Bao and Y. Wan, *Microchim Acta* 181 (2014) 751.

19. M. Á. G. Rico, M. Olivares-Marín and E. P. Gil, *Talanta* 80 (2009) 631.
20. Z. Zhang, K. Yu, D. Bai and Z. Zhu, *Nanoscale Res. Lett.* 5 (2010) 398.
21. D. Yang, L. Wang, Z. Chen, M.u Megharaj and R. Naidu, *Microchim Acta* 181 (2014) 1199.
22. G.-H. Hwang, W.-K. Han, S.-J. Hong, J.-S. Park and S.-G. Kang, *Talanta* 77 (2009) 1432.
23. N. Serrano, J. M. Díaz-Cruz , C. Ariño and M. Esteban, *Anal. Bioanal. Chem.* 396 (2010) 1365.
24. N. Serrano, J. M. Díaz-Cruz, C. Ariño and M. Esteban, *Electroanalysis* 22 (2010) 1460.
25. P. Zong and Y. Nagaosa, *Microchim. Acta* 166 (2009) 139.
26. M. Khairy, R. O. Kadara, D. K. Kampouris and C. E. Banks, *Anal. Methods* 2 (2010) 645.
27. V. B. dos Santos, E. L. Fava, N. S. de Miranda Curi, R. C. Faria and O. Fatibello-Filho, *Talanta* 126 (2014) 82.
28. S. Intarakamhang, W. Schuhmann and A. Schulte, *J. Solid State Electrochem.* 17 (2013) 1535.
29. I. Rutyna and M. Korolczuk, *Sensor. Actuat. B-chem.* 204 (2014) 136.
30. J. C. Quintana, F. Arduini, A. Amine, F. Punzo, G. L. Destrid, C. Bianchini, D. Zane, A. Curulli, G. Palleschi and D. Moscone, *Anal. Chim. Acta* 707 (2011) 171.
31. C. Kokkinos, A. Economou, I. Raptis and T. Speliotis, *Anal. Chim. Acta* 622 (2008) 111.
32. V. Sosa, N. Serrano, C. Ariño, J. M. Díaz-Cruz and M. Esteban, *Talanta* 119 (2014) 348.
33. C. Kokkinos, I. Raptis, A. Economou and T. Speliotis, *Procedia Chem.* 1 (2009) 1039.
34. C. Kokkinos, A. Economou and I. Raptis, *Anal. Chim. Acta* 710 (2012) 1.
35. H. Sopha, L. Baldrianová, E. Tesařová, G. Grincienė, T. Weidlich, I. Švancara and S. B. Hočevar, *Electroanalysis* 22 (2010) 1489.
36. R. O. Kadara, N. Jenkinson and C. E. Banks, *Electroanalysis* 21 (2009) 2410.
37. A. K. Wanekaya, *Analyst* 136 (2011) 4383.
38. M. Zhou, Y. Zhai and S. Dong, *Anal. Chem.* 81 (2009) 5603.
39. L. Zhu, L. Xu, L. Tan, H. Tan, S. Yang and S. Yao, *Talanta* 106 (2013) 192.
40. L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan and S. Yao, *Electrochim. Acta* 115 (2014) 471.
41. F. T. M. Kádár, K. Tóth and E. Tatár, *Anal. Chim. Acta* 619 (2008) 173.
42. Z. M. Wang, H. W. Guo, E. Liu, G. C. Yang and N. W. Khun, *Electroanalysis* 22 (2010) 209.
43. D. Yang, L. Wang, Z. Chen, M. Megharaja and R. Naidu, *Electrochim. Acta* 132 (2014) 223.
44. J. Ping, Y. Wang, J. Wu and Y. Ying, *Food Chem.* 151 (2014) 65.
45. N. Pikroh and P. Vanalabhpatana, *ECS Transactions* 45 (2013) 39.
46. J. Saturno, D. Valera, H. Carrero and L. Fernández, *Sensor. Actuat. B-chem.* 159 (2011) 92.
47. G. H. Hwang, W. K. Han, J. S. Park and S. G. Kang, *Talanta* 76 (2008) 301.
48. H. Xiong, X. Li, G. Li, Z. Yang, Y. Gao and M. Chen, *Int. J. Electrochem. Sci.* 9 (2014) 4974.
49. J. Luo, X. Jiao, N. Li and H. Luo, *J. Electroanal. Chem.* 689 (2013) 130.
50. P. Rattanarat, W. Dungchai, D. Cate, J. Volckens, O. Chailapakul and C. S. Henry, *Anal. Chem.* 86 (2014) 3555.
51. W. Wonsawat, S. Chuanuwatanakul, W. Dungchai, E. Punrat, S. Motomizu and O. Chailapakul, *Talanta* 100 (2012) 282.
52. P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. Li and D. Bahadur, *Biosen. Bioelectron.* 43 (2013) 293.
53. L. Cao, J. Jia and Z. Wang, *Electrochim. Acta* 53 (2008) 2177.
54. J. Meng, F. Li, L. Luo, X. Wang and M. Xiao, *Monatsh Chem* 145 (2014) 161.
55. C. Chen, X. Niu, Y. Chai, H. Zhao and M. Lan, *Sensor. Actuat. B-chem.* 178 (2013) 339.
56. C. Huangfu, L. Fu, Y. Li, X. Li, H. Du, J. Ye, *Electroanalysis* 25 (2013) 2238.
57. N. Wang and X. Dong, *Anal. Lett.* 41 (2008) 1267.
58. H. Xu, L. Zeng, S. Xing, Y. Xian and G. Shi, *Electroanalysis* 20 (2008) 2655.
59. L. Fu, X. Li, J. Yu and J. Ye, *Electroanalysis* 25 (2013) 567.
60. J. Li, S. Guo, Y. Zhai and E. Wang, *Anal. Chim. Acta* 649 (2009) 196.
61. K. Pokpas, N. Jahed, O. Tovide, P. G. Baker and E. I. Iwuoha, *Int. J. Electrochem. Sci.* 9 (2014) 5092.

62. Z. Wang, L. Li and E. Liu, *Thin Solid Films* 544 (2013) 362.
63. K. Keawkim, S. Chuanuwatanakul, O. Chailapakul and S. Motomizu, *Food Control* 31 (2013) 14.
64. D. Yang, L. Wang, Z. Chen, M. Megharaj and R. Naidu, *Electroanalysis* 26 (2014) 639.
65. L. Xiao, H. Xu, S. Zhou, T. Song, H. Wang, S. Li, W. Gan and Q. Yuan, *Electrochim. Acta* 143 (2014) 143.
66. H. Lia, J. Li, Z. Yang, Q. Xu, C. Hou, J. Peng and X. Hu, *J. Hazard. Mater.* 191 (2011) 26.
67. X. He, Z. Su, Q. Xie, C. Chen, Y. Fu, L. Chen, Y. Liu, M. Ma, L. Deng, D. Qin, Y. Luo and S. Yao, *Microchim Acta* 173 (2011) 95.
68. Z. Li, L. Chen, F. He, L. Bu, X. Qin, Q. Xie, S. Yao, X. Tu, X. Luo and S. Luo, *Talanta* 122 (2014) 285.
69. C.-H. Lien, K.-H. Chang, C.-C. Hu and D. S.-H. Wang, *J. Electrochem. Soc*. 160 (2013) B107.
70. B. Sebez, B. Ogorevc, S. B. Hocevar and M. Veber, *Anal. Chim. Acta* 785 (2013) 43.
71. E. Svobodova-Tesarova, L. Baldrianova, M. Stoces, I. Svancara, K. Vytras, S. B. Hocevarb and B. Ogorevc, *Electrochim. Acta* 56 (2011) 6673.
72. T. Bassie, K. Siraj and T. E. Tesema, *Adv. Sci. Eng. Med*. 5 (2013) 275.
73. M. K. Dey, A. K. Satpati and A. V. R. Reddy, *Anal. Methods* 6 (2014) 5207.
74. V. Urbanová, K. Vytřas and A. Kuhn, *Electrochem. Commun.* 12 (2010) 114.
75. K. E. Toghill, L. Xiao, G. G. Wildgoose and R. G. Compton, *Electroanalysis* 21 (2009) 1113.
76. V. Sosa, C. Barceló, N. Serrano, C. Ariño, J. M. Díaz-Cruz and M. Esteban, *Anal. Chim. Acta* 855 (2015) 34.
77. S. D. Borgo, V. Jovanovski and S. B. Hocevar, *Electrochim. Acta* 88 (2013) 713.
78. H. Sopha, V. Jovanovski, S. B. Hocevar and B. Ogorevc, *Electrochem. Commun*. 20 (2012) 23.
79. E. Tesarova, L. Baldrianova, S. B. Hocevar, I. Svancara, K. Vytras and B. Ogorevc, *Electrochim. Acta* 54 (2009) 1506.
80. V. Guzsvány, H. Nakajima, N. Soh, K. Nakano and T. Imato, *Anal. Chim. Acta* 658 (2010) 12.
81. A. Bobrowski, M. Putek and J. Zarębski, *Electroanalysis* 24 (2012) 1071.
82. J. Zhang, Y. Shan, J. Ma, L. Xie and X. Du, *Sensor Lett.* 7 (2009) 605.
83. C. Kokkinos, A. Economou, I. Raptis and T. Speliotis, *Electrochem. Commun*. 11 (2009) 250.
84. C. Kokkinos and A. Economou, *Sensor. Actuat. B-chem*. 192 (2014) 572.
85. E. Svobodová, L. Baldrianová, S. B. Hocevar and I. Švancara, *Int. J. Electrochem. Sci*. 7 (2012) 197.
86. A. M. Ashrafi, S. Cerovac, S. Mudri, V. Guzsvány, L. Husáková, I. Urbanováand K. Vytras, *Sensor. Actuat. B-chem.* 191 (2014) 320.
87. X. Niu, H. Zhao and M. Lan, *Electrochim. Acta* 56 (2011) 9921.
88. W. Yi, Y. Li, G. Ran, H. Luo and N. Li, *Microchim. Acta* 179 (2012) 171.
89. Z. Wang, G. Liu, L. Zhang and H. Wang, *Ionics* 19 (2013) 1687.
90. Z. Wang, H. Wang, Z. Zhang, X. Yang and G. Liu, *Electrochim. Acta* 120 (2014) 140.
91. C. Chen, X. Niu, Y. Chai, H. Zhao, M. Lan, Y. Zhu and G. Wei, *Electroanalysis* 25 (2013) 1446.
92. A. M. Ashrafi and K. Vytřas, *Int. J. Electrochem. Sci* 8 (2013) 2095.
93. 93 C. Xiong, H. Luo and N. Li, *J. Electroanal. Chem.* 651 (2011) 19.
94. N. Li, W. Zhu, J. Luo and H. Luo, *Analyst* 137 (2012) 614.
95. A. Hayat and J. L. Marty, *Sensors* 14 (2014) 10432.
96. D. Pan, Y. Wang, Z. Chen, T. Lou and W. Qin, *Anal. Chem*. 81 (2009) 5088.
97. M. Korolczuk, A. Moroziewicz and M. Grabarczyk, *Anal. Bioanal. Chem*. 382 (2005) 1678.