

Electrodes Modified with Bismuth, Antimony and Tin Precursor Compounds for Electrochemical Stripping Analysis of Trace Metals. A Short Review

Nikolitsa Lezi¹, Anastasios Economou^{1*}, and Jiří Barek²

¹ *Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, 157 71 Athens, Greece.*

² *Charles University in Prague, Faculty of Science, University Research Centre UNCE “Supramolecular Chemistry”, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Chemistry, Hlavova 2030/8, 128 43 Prague 2, Czech Republic.*

Abstract: Over the last decade, intensive research is being carried out towards the development of “green” electrochemical sensors. Bismuth, antimony and tin electrodes have been proposed as potential substitutes of mercury electrodes in electrochemical stripping analysis of trace metals. The main advantage of these metals as electrode materials is their lower toxicity compared to mercury. Among the different configuration of bismuth, antimony and tin electrodes, one of the most attractive involves the modification of a support material with a bismuth, antimony or tin precursor compound (oxide, hydroxide or sparingly soluble salt). When the electrode is polarized to a sufficiently cathodic potential, the metal precursor is reduced to the respective metal which forms a thin “film” on the surface of the support material. The present article is an overview of the existing state-of-the-art in the field of bismuth, antimony and tin precursor-modified sensors. This review covers and critically discusses the various fabrication approaches (support materials, types of precursor compounds, modification approaches, precursor reduction methods) and also lists typical applications of these precursor-modified sensors to electrochemical stripping analysis of metals.

Keywords: Bismuth, tin, antimony electrodes; Screen-printed electrodes; Carbon paste electrodes; Precursor compounds; Trace metals.

*) Author to whom correspondence should be addressed. E-mail: aeconom@chem.uoa.gr

Introduction

Mercury, in the form of the hanging mercury drop electrode (HMDE) or the mercury film electrode (MFE), is, without doubt, the ideal electrode material for cathodic electroanalysis. MFEs [1] are particularly suited as electrodes in electrochemical stripping analysis which is currently the most sensitive electroanalytical technique and a viable alternative to optical atomic absorption and emission techniques for the determination of trace metals [2]. Although the alleged toxicity of mercury is challenged by many electrochemists [3], it remains a fact that there is strong political pressure worldwide to minimize the use of mercury [4]. In order to address the impact of this environmental move to electroanalysis, new “green” electrode materials have been developed over the last decade.

The invention of the bismuth film electrode (BiFE) in 2000 has been both a landmark and a starting point for further research in this direction [5]. Nowadays, bismuth electrodes of different configurations have been established as viable alternatives to mercury electrodes exhibiting performance that approaches that of mercury in electrochemical stripping analysis [6–9]. Bismuth was later followed by the introduction of antimony (in the form of the antimony film electrode, SbFE) as another potential electrode material exhibiting enhanced performance in acidic media as well as a weaker antimony stripping peak [10,11]. More recently, the tin film electrode (SnFE) has also been proposed for stripping analysis [12,13]. The attraction of the trio of “green” metals (bismuth, antimony and tin) as electrode materials is that their toxicity is considerably lower than that of mercury [14].

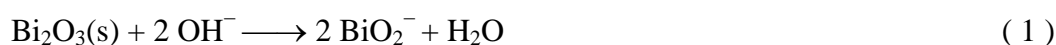
There are several approaches to fabricate bismuth, antimony, and tin electrodes. By far the most common methodology involves *in situ* or *ex situ* electroplating of a thin metal “film” on a conductive substrate [6,7]. Metal–film sensors can also be fabricated by microelectronic approaches [15–17]. In addition, different types of metal–modified electrodes have been developed by incorporating metal powder in highly conductive matrices (such as carbon paste) [18,19].

Another alternative fabrication methodology (which is the subject of the present review) is the incorporation of “green” metal precursor compounds within the bulk, or sometimes on the surface, of a conductive substrate. So far, three types materials have been reported as supports for metal precursors: carbon paste, screen–printed ink and graphite–epoxy composites. Insoluble oxides, hydroxides or salts of bismuth, antimony or tin are normally used as a precursor. After fabrication of the sensor, the metal precursor is electrochemically reduced to the respective metal forming a thin deposit on the electrode surface.

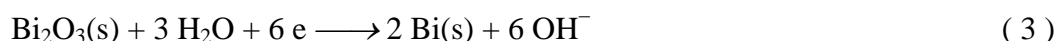
There are two modes of reduction: (i) in the *ex situ* mode, the precursor is reduced to the respective metal in a separate solution and then the electrode is transferred to the sample solution for analysis; (ii) in the *in situ* mode, the electrode is placed in the sample solution and the precursor is reduced to the respective metal during the potentiostatic accumulation step. The attractions of metal precursor–modified sensors are the experimental simplicity (since they do not require a separate metal plating step), the flexibility in the selection of the support material and the modifier compound, the low cost as well as the ease and speed of fabrication. The existing applications of “green” metal precursor–modified sensors are summarized in Table 1 with data on type of modifier, type of substrate, method of film formation, type of sample, stripping technique and limits of detection.

Carbon Paste Precursor–Modified Electrodes

Carbon pastes are very convenient materials for electroanalysis due to their low cost, easy and fast preparation, flexibility in varying the electrode composition and good conductivity [20]. In the context of metal precursor–modified electrodes, carbon pastes are particularly attractive since the respective electrodes can be easily and rapidly bulk–modified by simple mixing of the modifier with the paste. The reduction mechanism of Bi₂O₃ mixed with carbon paste in strongly alkaline media was reported in 1991 [21]. According to the authors, a chemical reaction occurs between bismuth oxide and OH[−] ions while the proper electrochemical reduction of the resulting BiO₂[−] occurs at −0.8 V:



Another reduction can be observed at −1.0 V (vs. SCE), corresponding to:



Based on these results, the first proof–of–concept report of the metal precursor–modified electrode utilized a carbon paste electrode prepared by mixing graphite, silicone oil and Bi₂O₃ powder for the determination of Zn(II) by ASV [22]. Although no analytical figures of merit were established, this work paved the way for the first analytical applications of bismuth precursor–modified carbon paste electrodes [23,24].

In the first one, a carbon paste electrodes containing Bi_2O_3 powder was used for the assay of Pb(II) in mineral water, drinking water and urine but the linearity for Cd(II) was not satisfactory [23]. In a second report by the same group in the same year, Cd(II) , Pb(II) and Zn(II) were determined by DPASV in water using a carbon paste electrode modified with bismuth trioxide, Bi_2O_3 [24].

Carbon paste electrodes modified with ammonium tetrafluorobismuthate (NH_4BiF_4 , an ionic liquid) exhibited satisfactory performance for the detection of Pb(II) and even Cd(II) in strongly acidic media [25]. BiF_3 (another highly insoluble bismuth salt) was used to modify a carbon paste electrode which was used for the SWASV measurements of Cd(II) and Pb(II) [26]; the analytical features of this sensor compared favorably with those of the classical Bi_2O_3 -modified carbon paste electrodes.

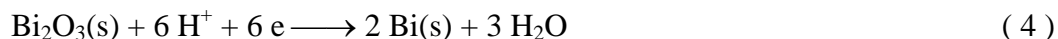
A novel type of antimony sensor was fabricated by mixing carbon paste with a reaction product of the hydrolysis of SbCl_3 [27]. The modifier compound was prepared by reacting acidic SbCl_3 with NaOH and subsequent drying of the precipitate; the final product was speculated to be composed of a mixture of SbOCl , SbO(OH) and Sb_2O_3 . The electrode was tested for the detection of Cd(II) , Pb(II) , Tl(I) , Zn(II) and Sn(II) in highly acidic solutions. Finally, a carbon paste electrode modified with SbF_3 was used in SWASV detection of Cd(II) and Pb(II) [28]. Although SbF_3 is highly soluble in water (and therefore, unlike its bismuth counterpart BiF_3 , is not an obvious choice as a precursor), it reacts with water forming a polymer-like, water-resistant structure. An important feature of this electrode displays improved performance in strongly acidic media (0.1 M and 1 M HCl).

So far, carbon paste-based electrodes modified with tin precursor compounds have not been yet reported.

Screen-Printed Precursor-Modified Electrodes

Screen-printing is an attractive technology for the fabrication of electrochemical sensors since it enables large-scale rapid fabrication of low cost, reproducible and disposable electrodes with extended scope for modification [29,30]. Screen-printed electrodes bulk-modified with metal precursors are commonly fabricated by mixing the precursor compound with graphite ink and printing. The first proof-of-principle analytical application of a screen-printed electrode modified with Bi_2O_3 appeared in 2004 [31]. It was recommended that a weakly acidic solution was used as a supporting electrolyte because in alkaline solutions the precursor reacts with OH^- .

The modifier was reduced *in situ* to metallic bismuth at -0.68 V:



This sensor was compared to a Sb_2O_3 -modified screen-printed electrode fabricated in an identical way. The authors found that the Bi_2O_3 -loaded electrode provided more satisfactory results for both Cd(II) and Pb(II) analysis by DPASV.

This concept was not revisited until 2008 when another type of screen-printed electrode bulk modified with Bi_2O_3 was described utilizing a multi-layer screen-printing fabrication approach [32]: a layer of Bi_2O_3 in terpineol and ethyl cellulose was screen-printed on a base layer of screen-printed glassy carbon paste. In this report, a comparative study of the reduction of the Bi_2O_3 precursor was conducted in acetate buffer and 0.1 M KOH media and the results indicated that reduction in 0.1 M KOH provided better reduction efficiency of the precursor.

Later screen-printing approaches reverted again to the more conventional fabrication method by direct screen-printing a mixture of conductive ink and Bi_2O_3 powder. A series of publications were devoted to this subject. In the first report, the formation of the bismuth film was performed *in situ* in 0.1 M HCl or acetate buffer; both being also used as the supporting electrolytes [33]. In this case, the stripping step was carried out by chronopotentiometry but the simultaneous detection of Cd(II) and Pb(II) was not possible. The previous sensor was improved by using square-wave voltammetry which enabled the simultaneous determination of Cd(II), Pb(II) and Zn(II) [34] or Zn(II) alone [35].

A study comparing *ex situ* reduction in 0.1 mol Γ^{-1} KOH and *in situ* reduction in 0.1 mol Γ^{-1} acetate buffer (pH 4.5) for the determination of Pb(II) and Cd(II) by SWASV using screen-printed electrodes modified with Bi_2O_3 , revealed that the *ex situ* mode in 0.1 M KOH improved the sensitivity for Cd(II) but did not significantly effect the Pb peak height [36].

In another report, some new bismuth precursor compounds (bismuth titanate, $\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2$, and bismuth aluminate, $(\text{Bi}_2(\text{Al}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O})$) were assessed to modify screen-printed electrodes for the determination of Pb(II) by ASV and these were compared to Bi_2O_3 [37]. It was found that bismuth aluminate yielded the highest sensitivity for the detection of Pb(II) with a LOD of $0.6 \mu\text{g L}^{-1}$. An extension of this study introduced additionally bismuth zirconate ($2\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_2$) and bismuth citrate ($([\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2)\text{CH}_2\text{CO}_2]\text{Bi})$) as modifiers of screen-printed electrodes, this time for the simultaneous determination of Pb(II)

and Cd(II) [38]; among all the precursors, bismuth citrate provided the lowest limits of detection and the best sensitivities for both metals. The same bismuth precursors were used in screen-printed electrodes for the determination of trace Tl(I) [39]; interestingly, it was found that bismuth citrate produced a double stripping peak for Tl while bismuth zirconate, bismuth aluminate and Bi₂O₃ yielded comparable sensitivities.

A rather unusual application of a screen-printed electrode surface-modified with BiPO₄ has been reported for the determination of Cd(II), Zn(II) and Pb(II) [40]. The sensor was prepared by chemical synthesis of the precursor directly at the electrode surface: a solution containing Na₂HPO₄, Bi(NO₃)₃ and Nafion were applied on the electrode surface. Nafion was added to improve the mechanical adherence of the resulting Bi nanoparticles and to prevent fouling by surfactants.

As far as tin precursor-modified electrodes are concerned, there is a single application which compares the performance of Sb₂O₃-, Bi₂O₃-, antimony oxalate hydroxide (Sb(C₂O₄)OH)- and antimony tin oxide (SnO₂/Sb₂O₅) - modified screen-printed electrodes [41]. It is interesting that the antimony tin oxide-modified sensor responds like an electroplated SnFE, presumably because the reduction of Sb(V) was not possible under the specific experimental conditions.

A comparison of the stripping responses for the determination of Cd(II) and Pb(II) at Sb₂O₃-, Bi₂O₃-, Sb(C₂O₄)OH- and SnO₂/Sb₂O₅- modified screen-printed electrodes is illustrated in Fig. 1; the drawback of the SnO₂/Sb₂O₅- modified electrode is the vicinity of the Pb- and Sn oxidation potentials, which has resulted in partially overlapping the Pb- and Sn stripping signals.

Composite Precursor-Modified Electrodes

Apart from the carbon paste and screen-printed electrodes described in the previous sections, two types of composite bismuth precursor - modified sensors have been developed. The first such application made use of an electrode fabricated by mixing Bi(NO₃)₃, graphite powder and epoxy resin, which was used for the determination of Cd(II) and Pb(II) by DPASV and SWASV [42].

A second piece of work utilized chemically synthesized Bi₂O₃ and (BiO)₂CO₃ in order to modify a graphite-epoxy composite electrode that has been found applicable to the SWASV detection of trace metals [43]. It was found that modification with Bi₂O₃ resulted in lower limits of detection.

Table I: Applications of bismuth, antimony and tin precursor-modified electrodes in voltammetric analysis (DPASV: differential pulse anodic stripping voltammetry; SWASV: square wave anodic stripping voltammetry).

Modifier	Substrate	Film formation	Analytes	Detection technique	Sample	LOD ($\mu\text{g L}^{-1}$)	Notes	Ref
Bi_2O_3	carbon paste	<i>in situ</i>	Cd(II), Pb(II)	DPASV	drinking water, mineral water, urine	–	limited linearity for Cd(II)	23
Bi_2O_3	carbon paste	<i>in situ</i>	Cd(II), Pb(II), Zn(II)	DPASV	tapwater	1 (Pb(II)), 2 (Cd(II)), 50 (Zn(II))	addition of Ga(III) to alleviate Cu(II) interference on Zn(II) operation in strong acidic media	24
NH_4BiF_4	carbon paste	<i>in situ</i>	Pb(II), Cd(II)	SWASV	–	1.2 (Pb(II)), 9.8 (Cd(II))	operation in strong acidic media	25
BiF_3	carbon paste	<i>in situ</i>	Cd(II), Pb(II)	SWASV	sewage sludge	1 (Pb(II)), 0.7 (Cd(II))		26
hydrolysis product of SbCl_3	carbon paste	<i>in situ</i>	Pb(II), Cd(II), Sn(II), Tl(I), Zn(II), In(III)	SWASV	–	19 (Zn(II)), 72 (In(II)), 53 (Sn(II)), 35 (Tl(I)), 5 (Cd(II)), 5 (Pb(II))	modifier is a mixture of SbOCl , SbO(OH) and Sb_2O_3 operation in strong acidic media	27
SbF_3	carbon paste	<i>in situ</i>	Cd(II), Pb(II)	SWASV	–	–	operation in strong acidic media	28
Bi_2O_3 , Sb_2O_3	screen-printed graphite ink	<i>in situ</i>	Cd(II), Pb(II)	DPASV	urine, drinking water (Bi_2O_3 -modified electrode)	Bi_2O_3 -modified electrode: 10 (Pb(II)), 10 (Cd(II)) Sb_2O_3 -modified electrode: 20 (Cd(II))	Bi_2O_3 -modified electrode better than Sb_2O_3 -modified electrode	31

Modifier	Substrate	Film formation	Analytes	Detection technique	Sample	LOD ($\mu\text{g L}^{-1}$)	Notes	Ref
Bi_2O_3	screen-printed Bi_2O_3 on screen-printed carbon paste	<i>ex situ</i> (in 0.1 M KOH)	Cd(II), Pb(II)	SWASV	river water	2.3 (Pb(II)), 1.5 (Cd(II))	interference by Cu(II) comparison of <i>in situ</i> and	32
Bi_2O_3	screen-printed graphite ink	<i>in situ</i>	Cd(II), Pb(II)	stripping chronopotentiometry	waste water, soil	8 (Pb(II)), 16 (Cd(II))	no possibility of simultaneous determination interference by Cu(II)	33
Bi_2O_3	screen-printed graphite ink	<i>in situ</i>	Cd(II), Pb(II), Zn(II)	SWASV	river water	5 (Pb(II)), 2.5 (Cd(II))		34
Bi_2O_3	screen-printed graphite ink	<i>in situ</i>	Zn(II)	SWASV	seawater	33 (buffer), 50 (seawater)		35
Bi_2O_3	screen-printed graphite ink	<i>in situ</i> , <i>ex situ</i> (in 0.1 M KOH)	Cd(II), Pb(II)	DPASV	–	1.1 (Pb(II)), 2.1 (Cd(II))	comparison of <i>in situ</i> , <i>ex situ</i> reduction modes	36
Bi_2O_3 , $\text{Bi}_2\text{O}_3\cdot 2\text{TiO}_2$, ($\text{Bi}_2(\text{Al}_2\text{O}_4)_3\cdot x\text{H}_2\text{O}$)	in screen-printed graphite ink	<i>in situ</i>	Pb(II)	SWASV	tapwater	0.6	comparison of precursors (bismuth aluminate best)	37
Bi_2O_3 , $\text{Bi}_2\text{O}_3\cdot 2\text{TiO}_2$, ($2\text{Bi}_2\text{O}_3\cdot 3\text{ZrO}_2$), Bi citrate	screen-printed graphite ink	<i>in situ</i>	Pb(II), Cd(II)	DPASV	lake water	0.9 (Pb(II)), 1.1 (Cd(II))	comparison of precursors (bismuth citrate best)	38

Modifier	Substrate	Film formation	Analytes	Detection technique	Sample	LOD ($\mu\text{g L}^{-1}$)	Notes	Ref
Bi_2O_3 , ($\text{Bi}_2(\text{Al}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$, ($2\text{Bi}_2\text{O}_3 \cdot 3\text{ZrO}_2$), Bi citrate	screen-printed graphite ink	<i>in situ</i>	Tl(I)	DPASV	lake water	0.9–1.6	comparison of precursors	39
BiPO_4	screen-printed graphite ink/Nafion	<i>ex situ</i>	Cd(II), Pb(II), Zn(II)	SWASV	–	8 nM (Zn(II)), 4 nM (Cd(II)), 2 nM (Pb(II))	BiPO_4 chemically synthesized on the electrode (surface modification)	40
Bi_2O_3 , Sb_2O_3 , ($\text{Sb}(\text{C}_2\text{O}_4)\text{OH}$), $\text{SnO}_2/\text{Sb}_2\text{O}_5$	screen-printed graphite ink	<i>in situ</i>	Cd(II), Pb(II)	DPASV	mineral water	0.9–1.2 (Pb(II)), 1.7–3.5 (Cd(II))	comparison of precursors	41
$\text{Bi}(\text{NO}_3)_3$	epoxy composite	<i>in situ</i>	Pb(II), Cd(II)	DPASV, SWASV	–	11.81 (Pb(II)), 7.23 (Cd(II))		42
Bi_2O_3 , $(\text{BiO})_2\text{CO}_3$	epoxy composite	<i>ex situ</i> (<i>acetate</i> <i>buffer</i>)	Cd(II), Pb(II), Zn(II)	SWASV	–	0.52 (Pb(II)), 0.26 (Cd(II)), 2.23 (Zn(II))	the modifiers were chemically synthesized	43

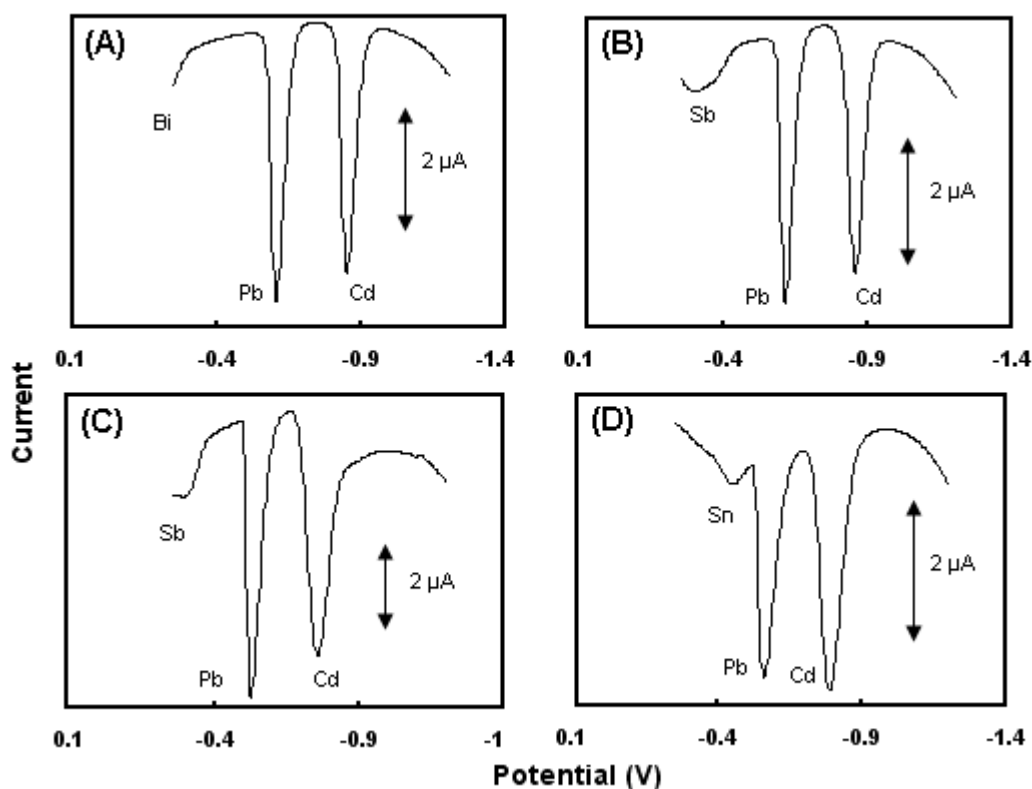


Fig. 1: DPASV responses in a solution containing $25 \mu\text{g L}^{-1}$ Pb(II) and $50 \mu\text{g L}^{-1}$ Cd(II) at screen-printed sensors modified with 4% (w/w) (A) Bi_2O_3 , (B) Sb_2O_3 , (C) $\text{Sb}(\text{C}_2\text{O}_4)\text{OH}$, (D) $\text{SnO}_2/\text{Sb}_2\text{O}_5$. Legend: supporting electrolyte: 0.1 M acetate buffer (pH 4.5); preconcentration time, $t_{\text{dep}}=240$ s; preconcentration potential, $E_{\text{dep}}=-1.4$ V; scan rate, $v=10$ $\text{mV}\cdot\text{s}^{-1}$; pulse height, $E_{\text{p}}=20$ mV; pulse duration, $t_{\text{p}}=50$ ms.

Conclusions

This review has demonstrated that the field of electrodes modified with bismuth, antimony and tin precursor compounds is active area of research. Although far less popular than their electroplated thin-film counterparts, these sensors present extended scope for rapid field voltammetric screening of trace metals. The advantages of the *in situ* formation of the metal film are obvious, especially for on-site analysis where experimental simplicity, speed and convenience are critical. Therefore, the vast majority of published work in this field makes use of *in situ* precursor reduction. Although the earlier (and even some recent) applications utilized carbon paste as the support material for both fundamental studies and analytical applications; the current trend being the development of modified screen-printed electrodes.

Screen-printing enables the on-chip fabrication of reference and counter electrodes so that complete cell-on-a-chip disposable sensors can be realized with scope for mass production. Regarding precursor compounds, these are currently dominated by bismuth compounds, in particular Bi₂O₃. This is expected since bismuth was the first “green” mercury substitute and also offers a wider polarization range than tin or antimony. However, the relevant literature suggests that antimony precursor compounds frequently perform better than their bismuth analogues in acidic media. So far, not enough experimental data are available to assess the analytical utility of tin precursor compounds. Possible applications of such electrodes to determine electrochemically reducible organic compounds should still be investigated.

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