

1ANTIMONY- BASED ELECTRODES FOR ANALYTICAL 2DETERMINATIONS

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27 **Abstract**

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29 This review summarizes analytical determinations carried out using antimony film
30 electrodes (SbFEs), an environmentally safe option that constitutes an alternative not only
31 to the most conventional Hg-based electrodes but also to Bi-based electrodes. SbFEs offer
32 some interesting characteristics such as favorably negative overvoltage of hydrogen
33 evolution, wide operational potential window, convenient operation in acidic solutions of
34 pH 2 or lower and a very small Sb stripping signal. The substrate on which the Sb was
35 plated is used to classify the types of SbFEs. Moreover, we detail the method of coating the
36 substrate with Sb as well as the Sb modifiers. We present tables with the most important
37 information from the accessible literature.

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41 Keywords: Analytical determination; Antimony film, Antimony-coating method; Antimony
42 modified glassy carbon electrode (SbGCE); Antimony modified carbon paste electrode
43 (SbCPE); Antimony modified screen-printed electrode (SbSPE); Environment-friendly
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50**1. INTRODUCTION**

51 Stripping techniques are particularly suitable for trace and species analysis due to their high
52 sensitivity and selectivity, their capacity to multielement determination and their simple but
53 complete instrumentation and their relative low cost, being particularly suitable for the
54 determination of trace heavy metal ions in environmental samples [1]. The performance of
55 the stripping techniques is strongly influenced by the working electrode material. Mercury-
56 based electrodes have been extensively used not only for inorganic compounds
57 determination, such as for heavy metal analysis, but also for the determination of many
58 organic compounds, since they are very reproducible and have a wide cathodic window [2].
59 However, in the last years the potential toxicity of mercury vapors and mercury salts, and
60 the European Regulations on banning exports and safe storage of metallic mercury have led
61 to the development of alternative electrodes that exhibit an analogous electrochemical
62 behavior but lower toxicity. In 2001 bismuth film electrodes (BiFE) were introduced by
63 Wang *et al.* as substitutes of mercury electrodes demonstrating their applicability for heavy
64 metals analysis [3]. Since their presentation, bismuth-based electrodes became a valuable,
65 attractive and widely used alternative to common mercury-based electrodes for
66 electroanalytical purposes being environment friendly and offering the features closest to
67 those of mercury [4-6]. With the aim of developing new electrode materials, in 2007
68 Hocevar and coworkers introduced the antimony film electrodes (SbFEs) for the
69 determination of metal ions. SbFEs feature some interesting characteristics such as
70 favorably negative overvoltage of hydrogen evolution, wide operational potential window,
71 convenient operation in acidic solutions of pH 2 or lower (which is superior to that reported
72 for BiFEs) and a very small stripping signal for antimony itself under some conditions
73 [7,8]. Moreover, although antimony does not belong to the group of “green elements”, its
74 toxicity is markedly lower than that of mercury.

75 As in the case of Bi electrodes and among other considerations, two important aspects have
76 to be taken into account in the preparation of a Sb electrode: i) The substrate on which the
77 Sb will be plated; and ii) the selected antimony-coating method.

78Sb can be plated on different supports being the carbon substrate in its diverse forms
79(carbon paste, glassy carbon, screen-printed carbon ink...) the most important support for
80the preparation of the Sb film, revealing a clear advantage over the metal electrode
81materials [9], although gold and platinum disk electrode as well as boron doped diamond
82(BDD) were also used.

83Regarding on Sb-coating methods, they are similar to those used for the preparation of
84BiFEs [10]: (i) *In-situ* plating method: the electrode is immersed directly into the sample
85solution containing Sb(III) ions and antimony is electrochemically deposited on the
86electrode surface during the analysis; (ii) *ex-situ* plating or preplated method: the electrode
87is immersed into a Sb(III) solution and, after the application of an appropriate potential,
88Sb(III) ions are reduced to metallic Sb and electroplated on the electrode surface; later, the
89SbFE is rinsed carefully with ultra-pure water and then immersed into the sample solution;
90(iii) the “bulk” method: the modification with Sb takes place during the preparation of the
91electrode and involves the preparation of a mixture of carbon paste and antimony precursor
92(Sb_2O_3); Sb precursor is later electrochemically reduced to metallic Sb at a selected
93potential; and (iv) the sputtering method: the thin film of antimony is obtained by the
94antimony sputtering on a silicon substrate.

95Fig. 1 shows the SEM images of a bare (commercial) screen-printed carbon electrode
96(SPCE), as an example of carbon support for the preparation of the Sb electrodes, and
97different antimony-coated screen-printed electrodes (SbSPE). The scanning electron
98micrograph of the bare SPCE (Fig. 1A) shows a uniform carbon surface compared to the
99other SbSPE surfaces (Fig. 1 B-D). The SEM image of an *in-situ* SbSPCE (Fig. 1B) shows
100that its surface is different from that of the *ex-situ* SbSPCE (Fig. 1C), in which the Sb
101particles are bigger, brighter and more randomly dispersed than those observed on the *in-*
102*situ* approach. The surface morphology of $\text{Sb}_{\text{sputtered}}$ SPE (Fig. 1D) was the most different
103from the rest of SbSPE. The main differences are that the substrate of this electrode is
104ceramic instead of carbon and that the Sb was sputtered directly on it, showing Sb particles
105of different sizes which are bigger and more compact than those observed on the *ex-situ*
106SbSPCE.

107The possibility of preparation of Sb electrodes in a great variety of supports and suitable
108substrate electrodes combined with the different methods for coating the substrate with Sb
109significantly extends the scope and applicability of the antimony-based electrodes to
110different environmental challenges.

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112**2. ANTIMONY FILM ELECTRODES**

113Despite both the quantity of substrates available and the different coating methods, in most
114cases the antimony film is plated on a carbon substrate via *in-situ* or *ex-situ* leading to an
115antimony working electrode that is placed in a typical electrochemical cell together with a
116platinum counter electrode and a conventional silver / silver chloride reference electrode.
117Particularly, the screen-printed electrode approach usually integrates in a same strip a
118carbon working electrode, whose surface is modified with antimony, a carbon counter
119electrode, and a silver or silver / silver chloride reference electrode. However, the antimony
120screen-printed working electrode can also be placed in a conventional electrochemical cell.
121For this review, SbFEs were categorized in four groups in agreement with the substrate on
122which the Sb was plated. Moreover, the method of coating the substrate with Sb and the Sb
123modifiers were also itemized.

124The four considered categories are:

- 125(1) Antimony modified glassy carbon electrode (SbGCE)
- 126(2) Antimony modified carbon paste electrode (SbCPE)
- 127(3) Antimony modified screen-printed electrode (SbSPE)
- 128(4) Miscellaneous

129**2.1. Antimony modified glassy carbon electrode (SbGCE)**

130A major part of the investigations related to the applicability of a SbFE was performed
131using the glassy carbon electrode (GCE) as a substrate for the antimony film. The
132significant applications of antimony modified glassy carbon electrode (SbGCE) are
133reported in Table 1. As it can be seen, in a significant percentage of the studies the
134antimony was coated on the glassy carbon substrate by means of the *in-situ* approach. Prior
135to the formation of the Sb film via *in-situ*, the GCE should be polished using a suspension
136of alumina particles of 50-300 nm diameter rinsed with purified water and methanol or

ethanol for 5 min in an ultrasonic bath, and dried. In stripping measurements with *in-situ* SbGCE, Sb(III) ions are directly added into the sample solution containing usually hydrochloric acid (pH 2.0), in the concentration range 0.3–2 ppm being 1 ppm the most common, and Sb is codeposited onto the bare glassy carbon electrode together with the target metal /metals [7, 9, 12-13, 15-17, 23-24, 30-31]. The potential and the time of deposition are defined by the own analytical determination. Most of the authors, before each stripping measurement, perform a cleaning step by keeping the working electrode at usually 0.3 V during 30 s. In other cases, a (1-5 %) Nafion solution [14, 28] was placed on the surface of the GCE prior to the modification with Sb, or the Sb was plated on a GCE through the poly p-aminobenzene sulfonic acid poly (p-ABSA) film [20] resulting in the formation of the NSbFE and Sb/poly(p-ABSA)FE, respectively. In other studies the addition of tartrate to the measurement solution is also considered, on the one hand a saturated solution of hydrogen potassium tartrate (pH 3.6) is used as a complexing supporting electrolyte [19] to prevent the precipitation of SbOCl that may otherwise occur in diluted hydrochloric acid media [32]. On the other hand, in mildly alkaline solution (pH 9.0), potassium sodium tartrate is added to stabilize the Sb(III) [22]. The main use of the *in-situ* SbGCE is the determination of heavy metals, especially Pb(II), Cd(II) and Zn(II), in water samples, vegetables or even urine by voltammetric and chronopotentiometric techniques [7, 9, 24, 30-31, 14, 19-20, 28]. Characteristic voltammetric stripping signals resulting from simultaneous measurements at increasing concentrations of Pb(II) and Cd(II) using an *in-situ* SbGCE are illustrated in Fig. 2. In addition, a sequential injection-SWASV method was applied for the simultaneous determination of Pb(II) and Cd(II) opening up the possibilities for full automation of the measuring process [15-17]. The *in-situ* SbGCE were also successfully used for the determination of In(III) and Tl(I) in water samples yielding well-defined and separated stripping peaks for these ions [13, 19], as well as for the monitoring of trace levels of Hg(II) in the presence of Cu(II) [23]. Further, *in-situ* SbGCE were also suitable for the determination of trace amounts of Sn(II) in canned fruit juices [12]. Also, *in-situ* SbGCE in combination with adsorptive cathodic stripping regime allows the measurement of trace levels of Ni(II) using DMG as complexing agent [22]. Another *in-situ* approach is based on the simultaneous plating of bismuth and antimony into a GCE. Bi–SbFE exhibited much better response to Cd(II) than the BiFE or SbFE alone [21].

Moreover, in these studies the possible interferences related to the presence of some metal ions and the influence of bioactive molecules, such as ascorbic acid and dopamine on the analyte stripping voltammetric response of the antimony film electrodes were also examined.

Ex-situ plated procedure is specially appropriated in such applications in which the *in-situ* approach is not suitable, e.g. at relatively high pH, where the Sb(III) hydrolysis occurs; when Sb(III) ions can not be added to the medium (in environmental or in-vivo measurements); or in metal complexation studies, where the presence of Sb(III) ions in the medium can completely disturb the speciation of the system [6, 8]. Prior to the formation of the Sb film via *ex-situ*, the GCE should be polished and rinsed as it is mentioned above for the *in-situ* approach. After being dried, the GCE was immersed into the plating solution usually containing 0.01 M HCl (pH 2.0) and 10-100 ppm Sb (III). Although, in a study in which the antimony concentration for the film formation is optimized [29], the highest sensitivity of Cd(II) and Pb(II) by DPASV was found at 4 and 8 ppm of Sb(III), respectively. During the electrodeposition step a deposition potential in the range -0.5 V to 1.20 V was applied during a deposition time of 45-150 s under stirring conditions [8, 11, 18, 26-27, 29]. GCE surface can be also modified with 5 % Nafion solution prior to the modification with Sb [27]. As can be seen in Table 1, the studies using an *ex-situ* SbGCE focus on both the determination of heavy metal ions [8, 27, 29], and the measurements of organic compounds such as dopamine and ascorbic acid [11], pantoprazole [26] and sulfasalazine [18], in which *ex-situ* SbGCE reveals a better electroanalytical performance than *ex-situ* BiGCE and bare GCE. Related to the metal ion determination, Pb(II) and Cd(II) were selected, in these studies, as model metal ions and their determination is carried out in water samples usually by ASV. Nevertheless, some authors point out that for this purpose the AdSV using pyrogallol red (PGR) as adsorbing and complexing ligand is more sensitive than the ASV method [27].

Finally, a SbGCE based on a Sb₂S₃-Nafion nanocomposites cast on a GCE works as an *Escherichia coli* DNA biosensor using methylene blue as the electrochemical indicator [25].

2.2. Antimony modified carbon paste electrode (SbCPE)

As seen above, antimony film electrodes were successfully introduced into electroanalytical

199 applications using a glassy carbon electrode as a substrate for the preparation of the film.
 200 Nevertheless, similarly as bismuth film modified carbon paste electrode [33], the use of
 201 carbon paste as alternative substrate for the antimony film was also examined. In
 202 comparison with glassy carbon electrodes, carbon paste electrodes have the additional
 203 advantage of an easy surface renewal. Taking into account that carbon paste electrodes can
 204 also be bulk-modified, other studied approaches of SbCPE are based on a carbon paste
 205 bulk-modified with antimony powder (Sb-CPE) [34-35] and with Sb_2O_3 powder (Sb_2O_3 -
 206 CPE) [36]. The different applications of antimony modified carbon paste electrodes
 207 (SbCPE) available in the literature are summarized in Table 2. Regardless of the Sb-coating
 208 method, first of all is necessary to prepare the bare carbon paste electrode. Typically, the
 209 carbon paste mixture is prepared by intimately hand mixing of two components: 0.5 g
 210 graphite powder and 0.3 mL highly viscous silicone oil, which are homogenized to obtain a
 211 mixture that is subsequently packed into an appropriate electrode holder providing a carbon
 212 paste electrode support for the preparation of the antimony film [34-45]. The carbon paste
 213 surface can be mechanically renewed when necessary, extruding ca. 0.5 mm of the paste
 214 out of the electrode holder and smoothed with a filter paper. In the case of a Sb-CPE and a
 215 Sb_2O_3 -CPE, an appropriate amount of antimony powder (usually 17 % (w/w)) and Sb_2O_3
 216 powder (3 % (w/w)) are also added to the mixture of both components resulting in a bulk-
 217 modified carbon paste electrode, which does not require the subsequent plating of the film.
 218 Regarding the bare CPE, once again, the *in-situ* approach is the most common method of
 219 Sb-coating film. Sb(III) ions are added to the cell in a concentration range 0.5-1 ppm
 220 together with the desired concentration of target metal / metals in usually 0.01 M HCl
 221 solution (pH 2.0), by the application of a deposition potential during a deposition time,
 222 which depends on the nature of the analysis. Then Sb is codeposited onto the bare carbon
 223 paste electrode [9, 34, 37-42, 44]. Normally, before each measurement a pre-conditioning
 224 step at the potential range of 0.1-0.3 V was applied for 30-60 s. Once more, the principal
 225 use of this electrode is the determination of heavy metals, especially Pb(II) and Cd(II), in
 226 water samples by voltammetric and chronopotentiometric stripping techniques [9, 34, 37-
 227 38, 44]. The *in-situ* SbCPE exhibited well-developed and separated stripping signals for
 228 both Cd(II) and Pb(II) with improved sensitivity of approximately 35% for Cd(II) and
 229 105% for Pb(II) in comparison with the glassy carbon counterpart (SbGCE) (Fig. 3). In

addition, *in-situ* SbCPE exhibited attractive electroanalytical characteristics for simultaneous chronopotentiometric stripping measurements of In(III), Tl(I) and Zn(II) at pH 2 [39], as well as for the voltammetric determination of Hg(II) [40] and Bi(III) [41] in the presence of Cd(II), which functioned as an apparent catalyst, and for the voltammetric determination of Cu(II), in which *in-situ* SbCPE exhibited even more attractive electroanalytical behaviour than the corresponding *in-situ* BiCPE [42]. Another convenient method for the preparation of the Sb film over the CPE surface is via *ex-situ*, in which Sb deposition was carried out using 10 mM antimony trichloride solution (in 0.02 M HCl) at a deposition potential of -0.6 V for 100 s and then, the *ex-situ* SbCPE is relocated to the sample solution and applied to the determination of Cd(II), Pb(II) and Cu(II) in water samples; whereas for the analysis of Hg(II), Au was deposited along with Sb to make the Sb–Au nanocomposite modified CPE [45]. Furthermore, CPE can be also modified *ex-situ* by drop coating of different materials such as SbNP-MWCNT nanocomposite or Sb_{microsphere}-MWCNT. The application to the analysis of Pb(II) and Cd(II) indicates that the size of the Sb particles on the coating layer influenced the oxidation current signals of Pb and Cd, decreasing in the order $I_{\text{Sb-nanoparticle}} > I_{\text{Sb-film}} > I_{\text{Sb-microsphere}}$ [44]. Another *in-situ* or *ex-situ* approach is based on the simultaneous codeposition of Bi(III) and Sb(III) on the carbon paste surface, in which the determination of Cd(II) and Pb(II) was also successfully attempted resulting in a higher current response in comparison with electrodes electroplated by individual metals [43].

2.3. Antimony modified screen-printed electrode (SbSPE)

Nowadays, the screen-printing technology is well-established for the production of thick-film electrochemical transducers. This technology allows the mass production of numerous highly-reproducible single-use screen-printed electrodes (SPEs) with an accessible and low-cost character. The coupling of these disposable SPEs with stripping techniques presents an attractive alternative to more conventional electrode supports for analytical determinations [6, 46]. Table 3 summarizes the studies carried out on SbSPE. SPEs can be produced in the own research group laboratories that possess screen-printed machines by printing different inks on various types of plastic or ceramic holdings. However, currently an increasing number of types of SPE can be commercially purchased from different firms specialized in the design and mass production of instruments for electrochemical purposes

261(e.g., Dropsens, PalmSens Electrochemical Sensor Interface, Pine Research
 262Instrumentation, eDAQ, Metrohm, Micrux Technologies, etc). Similarly to other supports,
 263the working electrode of the SPE device can be modified via the usual Sb-coating methods.
 264Commonly, carbon is the preferred material for the working electrode surface for the
 265modification with Sb via *in-situ* or *ex-situ* [10, 49, 51-52], although the working carbon
 266layer can also be modified with novel material such as 4 % (w/w) of MWCNTs and 4 %
 267(w/w) of [Bmim]BF₄ that were added into the graphite carbon ink [48]. For the “bulk”
 268modification approach Sb₂O₃, SnO₂/Sb₂O₅, or Sb^{III}(C₂O₄)OH were used as a metal precursor
 269which is loaded with graphite at different loadings during SPE fabrication [47, 50]. As can
 270be seen in Table 3, almost all studies, which use a SbSPE, focus again on quantification of
 271heavy metal ions in different water samples by means of stripping techniques [10, 52, 47-
 27250]. Nevertheless, SbSPE prepared on-line and installed as part of a sequential injection
 273system, was also used as an electrochemical detector to determine azo dyes in food samples
 274[51]. Related to the metal determination, in the *in-situ* approach the Sb film was obtained
 275by the application of the corresponding deposition potential and time, depending on the
 276metal analysis, by co-electrodepositing together with the analyte / analytes 1 ppm Sb(III) in
 277hydrochloric acid solution (pH 1.53) in the case of Hg(II) determination [48]; and 0.5 ppm
 278Sb(III) in acetate buffer solution (pH 4.5) in the case of the simultaneous determination of
 279Pb(II) and Cu(II), and Cd(II), Pb(II) and Cu(II) [10]. Characteristic stripping signals
 280resulting from simultaneous measurements at increasing concentrations of Pb(II), Cd(II)
 281and Cu(II) using an *in-situ* SbSPCE are illustrated in Fig. 4. Bi(III) and Sb(III) can be also
 282simultaneously *in-situ* plated to the SPCE surface from a solution containing a total
 283concentration of Bi(III) and Sb(III) of 1.5 ppm in 0.1 M acetate buffer (pH 4.5), showing an
 284enhanced signal towards Pb(II) compared to BiSPE, SbSPE and Bi-SbGCE [49]. Also, the
 285determination of traces of Ni(II) in the presence of dimethylglyoxime by AdSV was
 286achieved using an *ex-situ* SbSPCE, demonstrating the suitability of this approach for
 287measurements of this metal. In this case, Sb film was *ex-situ* plated on the SPCE surface
 288using 50 ppm Sb(III) in 0.01 M HCl solution (pH 2.0) at a deposition potential of -0.5 V for
 289300 s [52]. The determination of Cd(II) and Pb(II) was also attempted using different bulk-
 290modified SPE [47, 50], being the Sb^{III}(C₂O₄)OH-SPE the one which produced the highest
 291sensitivity for both considered metal ions. In all Sb-coating approaches, before each

measurement a cleaning step is recommended in order to eliminate analyte traces from the electrode surface.

2.4. Miscellaneous

Table 4 presents antimony-based electrode contributions in which the substrate for the deposition of the Sb film is different from a glassy carbon, carbon paste or screen-printed support. One of the approaches to prepare a SbFE is based on an antimony nanoparticle modified boron doped diamond (Sb-BDD) electrode, in which Sb film was performed *in-situ* with the analytes, from a solution of 1 ppm Sb(III) in 0.1 M HCl (pH 1). The use of Sb to modify BDD electrodes improved simultaneous detection of Cd(II) and Pb(II) [54]. Another process of preparation of a SbFE consists in the *in-situ* deposition of Sb film on both a carbon fiber surface [57] and a pencil core rod [59]. This modification process takes place in 0.01 M HCl (pH 2) solution with 1 ppm Sb(III) for the Sb film microelectrode (SbFME) or 0.5 ppm for the Sb film pencil core electrode together with the considered analytes. Electrochemical characteristics of the SbFME are similar to those found at the SbGCE and SbCPE, however the SbFME revealed higher current densities/responses for tested heavy metal ions [57]. Sb film pencil core electrode was applied to the simultaneous determination of Pb(II) and Cd(II) achieving much lower LOD than that of Bi film pencil core electrode [59]. Although carbon substrates are the most common support for the deposition of the Sb film, other approaches considered Au as a substrate in which Sb is coated via *in-situ* [9], or a suspension of polystyrene spheres (0.3 % (w/w)) spread over an Au surface in which Sb is *ex-situ* electrodeposited resulting in a macroporous SbFAuE [56]. *In-situ* SbFAuE was applied to the stripping determination of Pb(II), Cd(II) and Zn(II). In comparison to a SbFE prepared on the GC surface which displays well-defined peaks for all three considered analytes, the signals for Pb(II) and Cd(II) recorded with the SbFE prepared on the Au substrate electrode are significantly lower and poorly developed and no signal for Zn(II) is shown due to the high hydrogen evolution contribution [9]. In contrast, macroporous SbFAuE allows the simultaneous determination of Pb(II) and Cd(II) with sensitivities more than three times higher than using a non-porous SbFE [56]. Another approach to achieve the determination of Ni(II) with dimethylglyoxime as complexing agent is based on the use of a sputtered SbFE. It should be pointed out that whereas no stripping signals were obtained on *ex-situ* SbGCE, well-shaped stripping peaks for Ni(II)

were obtained on sputtered SbFE [55]. The stripping determination of trace Pb(II) and Cd(II) in water was also performed by a copper-based Cu-Sb/Sb composite film electrode consisting of a copper-antimony alloy transitional layer and an outer electrodeposited antimony film that was fabricated on a Cu substrate [58]. Finally, the determination of sulfide in wastewater samples was also carried out using a Sb-based electrode, i.e., a SPE modified with $[Sb^VO(CHL)_2]Hex$, which shows a good working stability in contrast to $[Sb^VO(CHL)_2]Hex-CME$ with no significant loss of their initial activity for more than 100 runs [53].

3. CONCLUSIONS AND FUTURE TRENDS

This work summarizes the analytical determinations available in the literature that are performed using different types of Sb-based electrodes. The good results achieved in most of the reported studies together with their low toxicity make the Sb-based electrodes a suitable alternative not only to the most conventional electrodes such as Hg-based electrodes but also to Bi-based electrodes. For example, the limitations observed for the determination of Cu(II) using an *in-situ* BiFE due to the competition of the electrodeposited Cu(II) and the Bi(II) for surface sites [3] were overcome using an *in-situ* SbSPCE [10]. The compiled contributions were categorized in four different groups in agreement with the support in which the Sb can be coated: glassy carbon electrodes, carbon paste electrodes, screen-printed electrodes and miscellaneous. In each category the advantages and limitations of the considered Sb approaches were discussed. It can be concluded that regardless of the support selected for the Sb film formation, the carbon substrate is the preferred support for the preparation of the Sb film, and the *in-situ* approach is the main Sb-coating method used being more minority the *ex-situ*, “bulk” and sputtered approaches. However, as detailed above, some Sb modified supports such as the introduction of different modifiers in the classical carbon paste mixture or new modified inks in the case of the SPE were also successfully tested.

As can be seen from the presented tables, SbFE were largely applied to the determination of heavy metal ions, particularly of Cd(II) and Pb(II) although other metals such as Cu(II), Zn(II), Hg(II), Tl(I), In(III), Ni(II), Sn(II) and Bi(III) were also studied with large linearity ranges. In most of the studies the obtained LODs and LOQs were very good, at levels of

353ppb, and similar or even slightly lower than those achieved using Hg or Bi-based
354electrodes. Moreover, SbFE was also successfully applied to the analysis of organic
355compounds such as dopamine, ascorbic acid, pantoprazole, sulfasalazine, allura red and
356tartrazine.

357The future trends for Sb-based electrodes should be aimed at enhancing their analytical
358applications to more complex problems. This improvement could be achieved by expanding
359their application to other inorganic and organic analytes in samples of biological or
360environmental interest, and also reinforcing the pioneering results obtained with some Sb-
361based electrodes.

362SbFEs constitute an environmentally safe option that in combination with the relatively low
363cost of the stripping techniques in comparison with other available techniques make them a
364suitable implement for analytical determinations.

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Caption to figures

Figure 1. Scanning electron micrographs: (A) Commercial screen printed carbon electrode (SPCE); (B) antimony film coated *in-situ* on a commercial SPCE; (C) antimony film coated *ex-situ* on a commercial SPCE; (D) commercial antimony sputtered screen-printed electrode. Resolution of 1 μ m, magnification of 5,000x and accelerating potential of 15.0 kV were used. Reproduced with permission from [10].

Figure 2. SWASV measurements at increasing concentrations of Cd(II) and Pb(II) from 20 to 140 ppb obtained at an *in-situ* prepared antimony film glassy carbon electrode (*in-situ* SbGCE) at 0.01 M HCl (pH 2) containing 1 ppm Sb(III). The inset shows the resulting calibration plots. Deposition at -1.2 V for 120 s, equilibration period of 15 s, and cleaning step of 30 s at 0.1 V. Reproduced with permission from [7].

Figure 3. SWASV measurements at increasing concentrations of Cd(II) and Pb(II) from 5 to 50 ppb obtained at an *in-situ* prepared antimony film carbon paste electrode (*in-situ* SbCPE) at 0.01 M HCl (pH 2) containing 0.5 ppm Sb(III). The inset shows the resulting calibration plots. Deposition at -1.2V for 120 s, equilibration step of 15 s, and cleaning step of 30 s at 0.1V. Reproduced with permission from [37].

Figure 4. DPASV measurements at increasing concentrations of Cd(II), Pb(II) and Cu(II) from 1.0×10^{-7} to 2.0×10^{-6} M on an *in-situ* antimony screen-printed carbon electrode (*in-situ* SbSPCE) at acetate buffer solution (pH 4.5) containing 0.5 ppm Sb(III). Deposition at -1.2 V for 120 s, equilibration step of 30 s, and cleaning step of 15 s at 0.5V.

Figure 1

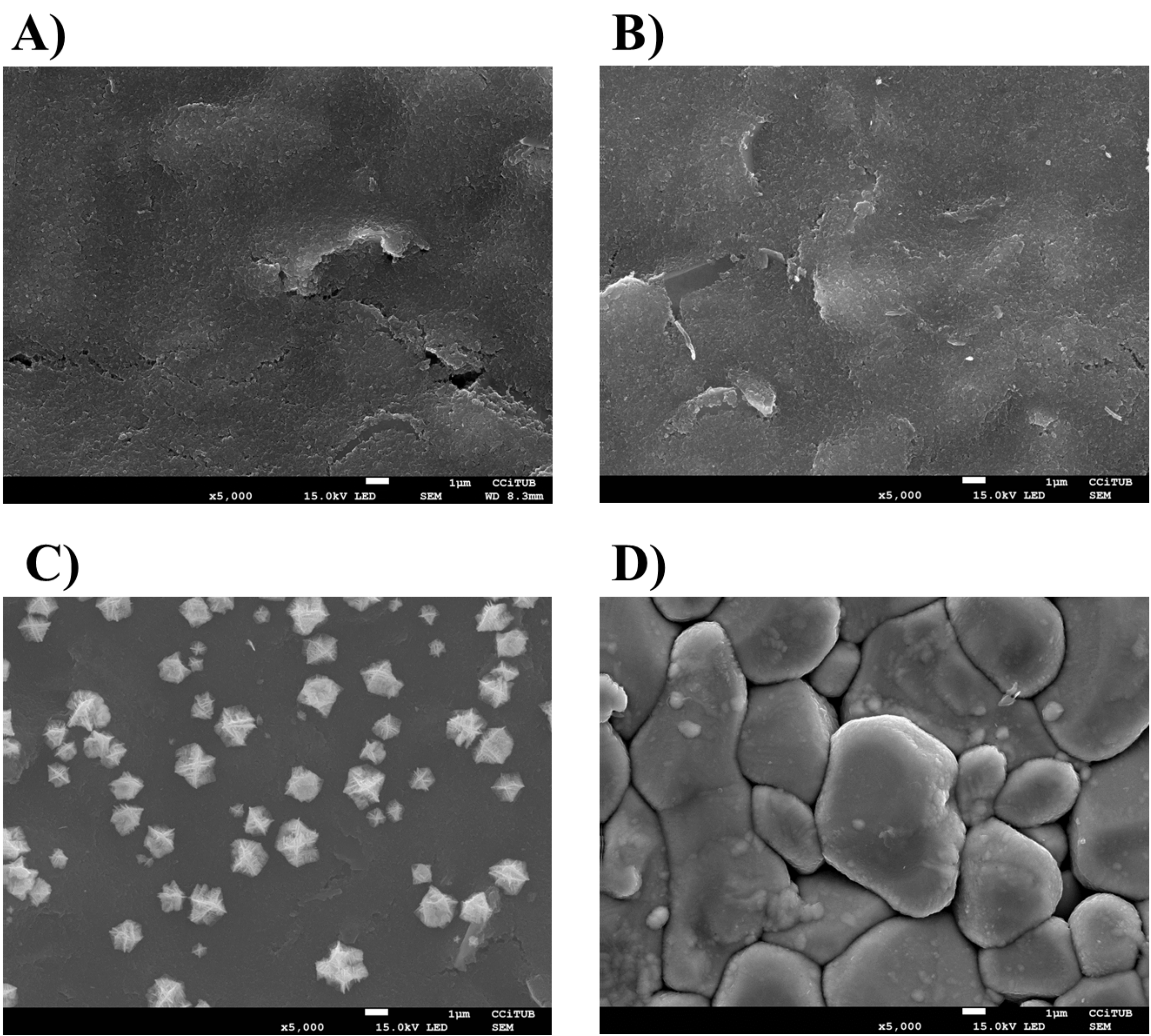


Figure 2

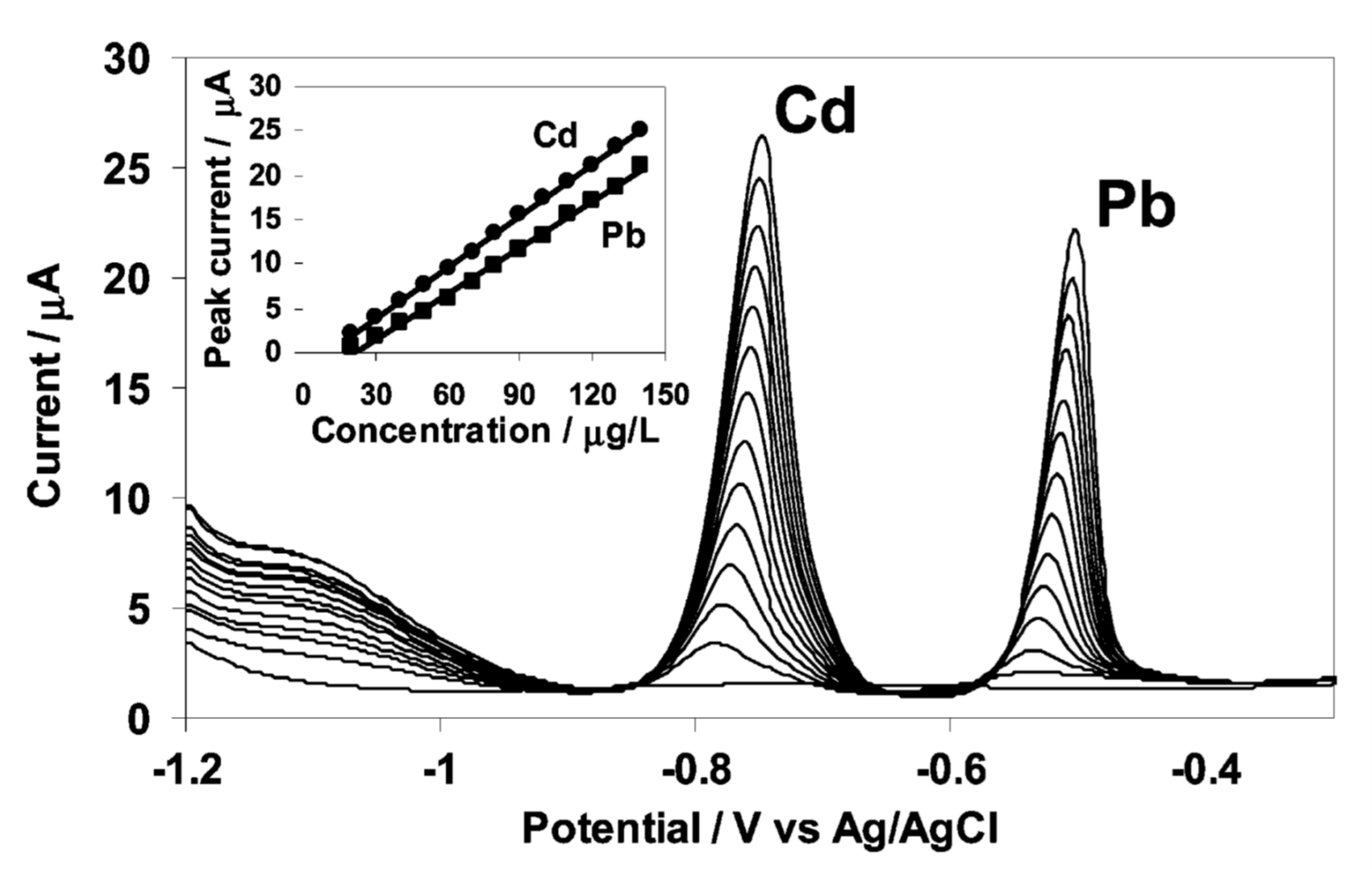


Figure 3

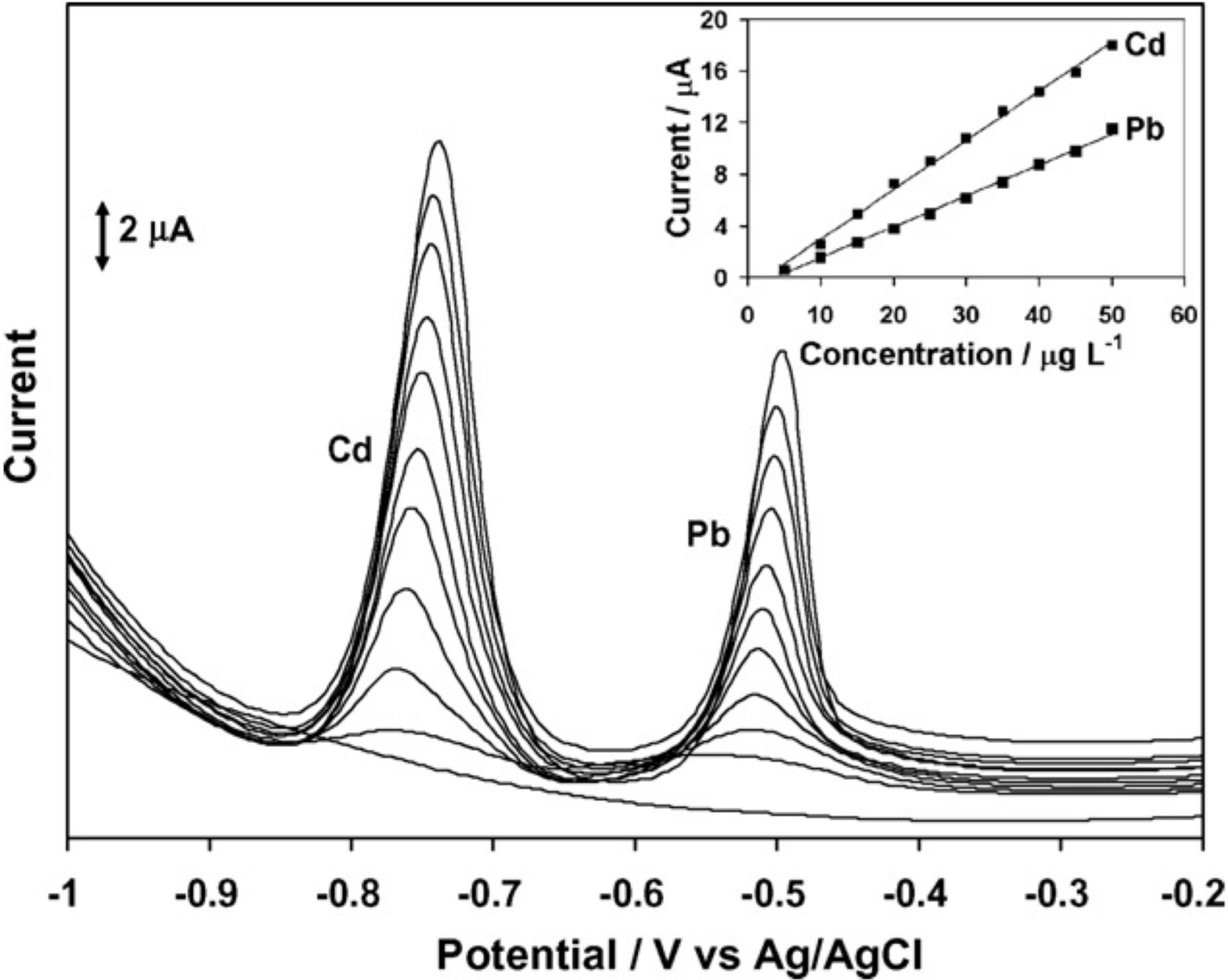


Figure 4

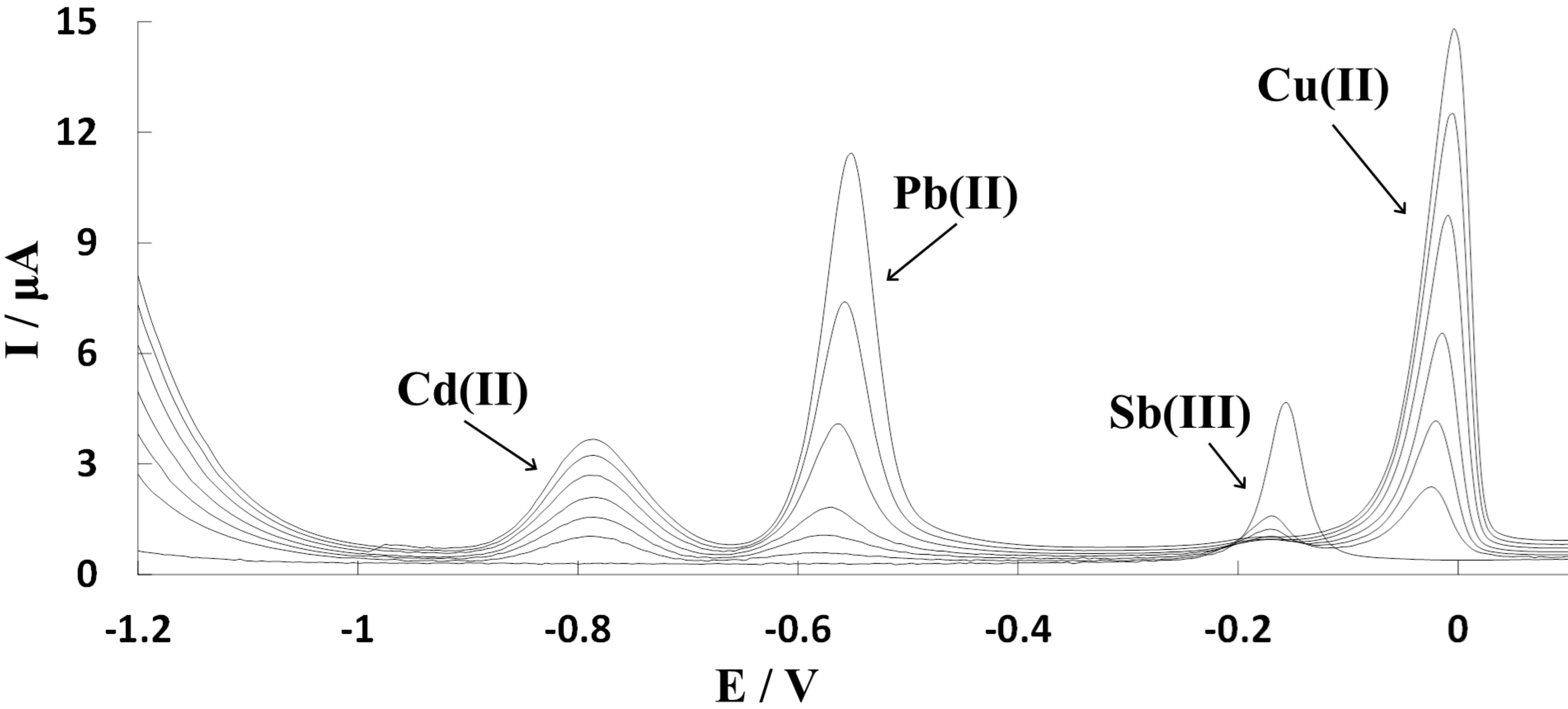


Table 1. Antimony modified glassy carbon electrode (SbGCE).

ASV: anodic stripping voltammetry, SCP: stripping chronopotentiometry, SbFE: antimony film electrode, DPV: differential pulse voltammetry, GCE: glassy carbon electrode, BiFE: bismuth film electrode, AdSV: adsorptive stripping voltammetry, NSbFE: nafion antimony film electrode, NMFE: nafion mercury film electrode, NBiFE: nafion bismuth film electrode, SIA: sequential injection analysis, SWV: square wave voltammetry, Bi-SbFE: bismuth and antimony film electrode, AdSCP: adsorptive stripping chronopotentiometry, DMG: dimethylglyoxime, Sb-CdFE: antimony and cadmium film electrode, CV: cyclic voltammetry, CPE: carbon paste electrode, EIS: electrochemical impedance spectroscopy, AA: ascorbic acid, DA: dopamine, LOD: limit of detection.

Ref.	Coating method	Analyte	Technique	Sample	Detec. limit (ppb)	Linear range (ppb)	Additional information
[7]	<i>In-situ</i> with Sb(III)	Pb, Cd	ASV SCP	---	0.9 (Pb, t_d = 120 s) 0.7 (Cd, t_d = 120 s)	20-140 (Pb, Cd)	<ul style="list-style-type: none"> SbFE is reported for the first time as a possible alternative for electrochemical stripping analysis of trace heavy metals SbFE revealed favorable electroanalytical performance similar to that of bismuth- and mercury-based electrodes SbFE offers a remarkable performance in more acidic solutions ($pH \leq 2$)
[11]	<i>Ex-situ</i> with Sb(III)	Ascorbic acid (AA) Dopamine (DA)	DPV	AA tablets DA injections	6.7×10^{-7} M (AA) 1.5×10^{-7} M (DA)	2.6×10^{-6} - 1.2×10^{-3} M (AA) 6.8×10^{-7} - 1.33×10^{-2} M (AA)	<ul style="list-style-type: none"> The potential difference of oxidation peaks of DA and AA at the SbFE was 316 mV, which is much larger than that (136 mV) at the bare GCE The simultaneous determination of DA and AA was possible using the SbFE
[12]	<i>In-situ</i> with Sb(III)	Sn(II)	ASV	Canned fruit juices	0.5, t_d = 120 s	10-120	<ul style="list-style-type: none"> BiFE and SbFE are feasible for the voltammetric determination of trace amounts of Sn(II) ion The presence of cetyltrimethylammonium bromide (CTAB) in the sample highly enhances the response of the electrodes

[8]	<i>Ex-situ</i> with Sb(III)	Pb, Cd	ASV	---	0.3 (Pb, t_d = 60 s) 1.1 (Cd, t_d = 60 s)	25-80	<ul style="list-style-type: none"> • BiFE and SbFE present very similar performance characteristics
[13]	<i>In-situ</i> with Sb(III)	In, Tl(I)	ASV	River water Tap water	8 (In, t_d = 120 s) 2 (Tl, t_d = 120 s)	20-100	<ul style="list-style-type: none"> • <i>Ex-situ</i> SbFE revealed favorable electroanalytical performance similar to that of the <i>in-situ</i> prepared SbFE and comparable to bismuth- and mercury- based electrodes • SbFE was also preliminary tested for measuring low levels of Ni(II) using AdSV • SbFE yielded well-defined and separated from each other stripping peaks for In and Tl(I), while the peaks were completely overlapped with <i>in-situ</i> BiFE • The peaks determined with SbFE show much better resolution as compared with unmodified GCE
[14]	<i>In-situ</i> with Sb(III)	Pb, Cd	ASV	Vegetable Water sample	0.15 (Pb, t_d = 300 s) 0.3 (Cd, t_d = 300 s)	2-50	<ul style="list-style-type: none"> • 1 % Nafion solution was placed on the surface of the GCE prior to the modification with Sb • Compared with SbFE, the electrochemical signals on the NSbFE were improved about 70% for Pb and 50% for Cd • In comparison with the NMFE, signals for Pb and Cd at the NSbFE remarkably enhanced, and the resolution between Pb and Cd was also improved. • The electrochemical response of Cd at the NSbFE was the same as that at NBiFE, however, the sensitivity for Pb was improved • In the presence of 5 ppm gelatin, the peak heights at the NSbFE for Pb and Cd enhanced

[15]	<i>In-situ</i> with Sb(III)	Pb, Cd	ASV	Tap water [16-17]	<i>SbFE-batch</i>	<i>SbFE-batch</i>	<ul style="list-style-type: none"> • ASV-SIA/SbFE reduces the risk of sample contamination, requires smaller volumes of solution, eliminates majority of the subjective errors that may arise in the measurement, and opens up the possibilities for full automation of the measuring process • KCl and KBr had a favorable effect on the shape and intensity of the oxidation peaks of Cd and Pb • The presence of KSCN in the sample solution allowed a multitarget analysis, i.e., additional detection of Zn(II), Mn(II) or Cr(III) besides of Cd(II) and Pb(II) • BiFE and SbFE have shown similar performances • SbFE is presented for the first time for direct cathodic voltammetric measurement of an organic compound • The SbFE revealed superior electroanalytical performance than <i>ex-situ</i> BiFE and bare GCE • SbFE was prepared <i>in-situ</i> in a new supporting electrolyte, a saturated solution of hydrogen potassium tartrate in which Sb(III) ions were complexed by tartrate • The use of this electrolyte eliminates the risk of SbCl₃ hydrolysis in acidic media • In this medium (less acidic than HCl), the potential window is wider and the voltammetric
[16]			ASV-SIA		1.5 (Pb, t_d = 120 s)	4.7-120 (Pb)	
[17]					1.7 (Cd, t_d = 120 s)	5.2-100 (Cd)	
					<i>SbFE-SIA</i>	<i>SbFE-SIA</i>	
					1.2 (Pb, t_d = 100 s)	4-100 (Pb)	
					1.4 (Cd, t_d = 100 s)	5-120 (Cd)	
[18]	<i>Ex-situ</i> with Sb(III)	Sulfasalazine	SWV	Pharmaceutical tablets	7.8×10^{-7} M	3×10^{-6} - 2.5×10^{-4} M	
[19]	<i>In-situ</i> with Sb(III)	Cd, Pb, Zn, Tl(1), In, Cu(II)	ASV	Rainwater	1.5 (Pb, t_d = 120 s)	5-100 (Pb)	
					0.06 (Pb, t_d = 360 s)	2-100 (Cd)	
					0.7 (Cd, t_d = 120 s)	2-100 (Tl)	
					1.0 (Tl, t_d = 120 s)	20-200 (Zn)	
					3.8 (Zn, t_d = 120 s)	10-100 (In)	
					1.4 (In, t_d = 120 s)	2-50 (Cu)	
					0.5 (Cu, t_d = 120 s)		

[20]	<i>In-situ</i> with Sb(III)	Pb	ASV	Tap water	0.1, $t_d = 240$ s	0.5-150	signals are well-developed, especially in the case of Zn(II)
							<ul style="list-style-type: none"> • Zn(II), Cd(II) and Pb(II) or Zn(II), Tl(I) and Pb(II) can be detected simultaneously • The simultaneous determination of Tl(I) and Cd(II), Cd(II) and In(III), or Tl(I) and In(III) is not possible due to the strong overlapping of their voltammetric signals • Sb was plated on a GCE through the poly p-aminobenzene sulfonic acid poly (p-ABSA) film • The poly(p-ABSA) film can protect the antimony surface against abrasion, adsorption of surface-active compounds and enhance the sensitivity of antimony film for determining heavy metals • Compared with the commonly used SbFEs and BiFEs the Sb/poly(p-ABSA)FE, offers a remarkable performance in more acidic solutions ($\text{pH} \leq 2.0$)
[21]	<i>In-situ</i> with Bi(III) and Sb(III)	Cd	ASV	Tap water	0.15, $t_d = 210$ s	1-220	<ul style="list-style-type: none"> • Bi-SbFE is reported for the first time as a possible alternative for electrochemical stripping analysis of trace heavy metals • Bi-SbFE revealed better electroanalytical performance than the BiFE and SbFE

[22]	<i>In-situ</i> with Sb(III)	Ni(II)	AdSV AdSCP	---	0.11, $t_d = 60$ s	2-20	<ul style="list-style-type: none"> • Tartrate has proven to be an appropriate complexing agent preventing hydrolysis of Sb(III) in the ammonia buffer solution (pH 9.0) • Dimethylglyoxime (DMG) was used as complexing agent • <i>In-situ</i> SbFE revealed superior performance over its <i>ex-situ</i> prepared analogue and, furthermore, exhibited auspicious electroanalytical performance also under AdSCP conditions
[23]	<i>In-situ</i> with Sb(III)	Hg(II)	ASV	Real water	0.39, $t_d = 300$ s	2.5-80	<ul style="list-style-type: none"> • The presence of Cu(II) for measuring trace concentration levels of Hg(II) is evaluated • This procedure revealed an improved electroanalytical performance of the SbFE versus SbFE without added Cu(II), and also versus Sb-CdFE and BiFE, exhibiting comparable results to some gold-based electrodes
[9]	<i>In-situ</i> with Sb(III)	Pb Cd Zn	ASV CV	Tap water River water	>1 (Pb, Cd, Zn, $t_d = 240$ s)	---	<ul style="list-style-type: none"> • Five different substrate electrodes were examined: three carbon-based electrodes, i.e. carbon fibre microelectrode, GCE and CPE electrode, and two metal electrodes, i.e. Au and Pt disc electrode • A clear advantage of the carbon based substrates over the metal electrode materials is revealed • The functioning of the <i>in-situ</i> formed SbFE in six different acidic media is inspected • The electrode cleaning step is of essential importance due to the formation of Sb

							hydroxides/oxides that remain adsorbed at the substrate electrode surface after the anodic stripping step is completed
[24]	<i>In-situ</i> with Sb(III)	Pb Cd Zn	ASV	---	---	---	<ul style="list-style-type: none"> • Mechanism and kinetics of anodic stripping electrode processes of Zn(II), Cd(II) and Pb(II) at BiFE, SbFE and bare GCE have been studied • Mechanisms and kinetics of the three metal ions are different and depend significantly on the electrode substrate • Kinetics of electrode reactions can be estimated by means of quasireversible maximum and the peak potential separation between the forward and backward components of the potential-corrected SW voltammograms • The electrode reactions at BiFE are faster than at SbFE. The kinetics of all studied analytes is rather fast and comparable at BiFE, whereas at SbFE the kinetics of Zn(II) is significantly slower compared to Cd(II) and Pb(II)
[25]	Sb ₂ S ₃ -Nafion nanocompo sites	Escherichia Coli DNA	CV EIS		2.4 x 10 ⁻¹³ M	1.0 x 10 ⁻¹² -1.0 x 10 ⁻⁷ M	<ul style="list-style-type: none"> • Sb₂S₃-Nafion was obtained by mixing rod-like Sb₂S₃ and Nafion in alcohol solution • The Sb₂S₃-Nafion nanocomposites were cast on a GCE to fabricate a Sb₂S₃-Nafion/GCE • The sulfonic groups on Nafion were transferred to sulfonyl chloride groups by PCl₅, and the obtained sulfonyl chloride groups were applied to the covalent immobilization of Escherichia Coli gene related oligonucleotides

							<ul style="list-style-type: none"> • Methylene blue (MB) was used as the electrochemical indicator
[26]	<i>Ex-situ</i> with Sb(III)	Pantoprazole	SWV	Pharmaceutical tablets	9.1 x 10 ⁻⁷ M	9.0 × 10 ⁻⁶ -2.0 × 10 ⁻⁴ M	<ul style="list-style-type: none"> • Determination of pantoprazole was based on the electrochemical reduction of its sulfoxide group • SbFE exhibited favorable operation capability when compared to BiFE and bare GCE
[27]	<i>Ex-situ</i> with Sb(III)	Pb, Cd	AdSV	Certified water	2-mm diameter GCE 0.4 (Pb, t _d = 100 s) 0.5 (Cd, t _d = 100 s) 3-mm diameter GCE 0.9 (Pb, t _d = 100 s) 1 (Cd, t _d = 100 s)	0.9-12 (Pb, Cd)	<ul style="list-style-type: none"> • 5 % Nafion solution was placed on the surface of the GCE prior to the modification with Sb • Pyrogallol red is used as adsorbing and complexing ligand in a solution of acetate buffer • Using NSbFE deposited <i>ex-situ</i>, AdSV is more sensitive than the ASV method
[28]	<i>In-situ</i> with Sb(III)	Pb, Cd	ASV	---	Without AA and DA 0.05 (Pb, Cd, t _d = 120 s) With AA or DA 0.015 (Pb, Cd, t _d = 120 s)	Without AA and DA 10-150 With AA or DA See Fig. 7 in [28]	<ul style="list-style-type: none"> • 5 % Nafion solution was placed on the surface of the GCE prior to the modification with Sb • The influence of AA and DA on the stripping voltammetric response of SbFE was evaluated • Nafion film prevented the biomolecular fouling effect • NSbFE exhibited higher sensitivity for electrochemical stripping analysis of Cd and Pb in the presence of AA or DA, whereas unmodified SbFE showed no separation of ASV peaks for the metals

[29]	<i>Ex-situ</i> with Sb(III)	Pb,Cd	ASV	Tap water	0.6 (Pb, t_d = 140 s) 0.17 (Cd, t_d = 130 s)	2.28-559.4 (Pb) 6.63-331.6 (Cd)	<ul style="list-style-type: none"> • The electrochemical responses of Pb and Cd were improved in comparison with bare GCE (LOD of Pb and Cd is 1.67 and 0.86 ppb on bare GCE, respectively) • Suitable operation in acidic solution in the presence of dissolved oxygen • Well defined peaks of Pb and Cd were obtained
[30]	<i>In-situ</i> with Sb(III)	Pb,Cd	ASV	Surface water	0.99 (Pb, t_d = 180 s) 1.21 (Cd, t_d = 180 s)	10-100 (Pb, Cd)	<ul style="list-style-type: none"> • Well defined peaks of Pb and Cd were obtained
[31]	<i>In-situ</i> with Sb(III)	Pb,Cd	ASV	Urine (Pb)	0.47 (Pb, t_d = 180 s) 0.78 (Cd, t_d = 180 s)	0-100 (Pb, Cd)	<ul style="list-style-type: none"> • Cetyltrimethylammonium bromide (CTAB) was used as sensitizer • Well defined peaks of Pb and Cd were obtained

Table 2. Antimony modified carbon paste electrode (SbCPE).

ASV: anodic stripping voltammetry, SbCPE: antimony carbon paste electrode, Sb-CPE: carbon paste electrode bulk-modified with Sb powder, SbGPE: antimony glassy carbon electrode, BiCPE: bismuth carbon paste electrode, MCPE: mercury carbon paste electrode, SCP: stripping chronopotentiometry, Bi-CPE: carbon paste electrode bulk-modified with Bi powder, Sb₂O₃-CPE: carbon paste electrode bulk-modified with Sb₂O₃, Bi₂O₃-CPE: carbon paste electrode bulk-modified with Bi₂O₃, CV: cyclic voltammetry, SbNP-MWCNT: multiwalled carbon nanotubes modified with antimony nanoparticles.

Ref.	Coating method	Analyte	Technique	Sample	Detec. limit (ppb)	Linear range (ppb)	Additional information
[34]	<i>In-situ</i> with Sb(III) Sb powder	Pb, Cd	ASV	---	---	---	<ul style="list-style-type: none"> • Initial studies with SbCPE and Sb-CPE are presented • SbCPE and Sb-CPE are more flexible than SbGCE thanks to the use of carbon paste-based substrates which can be easily regenerated and their properties controlled via the actual carbon paste composition • See more detailed information in Ref [35]
[37]	<i>In-situ</i> with Sb(III)	Pb, Cd	ASV	Lake water	0.2 (Pb, t_d = 120 s) 0.8 (Cd, t_d = 120 s)	5-50 (Cd, Pb)	<ul style="list-style-type: none"> • The SbCPE exhibited well-developed and separated stripping signals for both Cd and Pb, and with improved sensitivity in comparison with the SbGCE • In comparison with BiCPE and MCPE, the SbCPE exhibited superior electroanalytical performance at pH 2 • SbCPE and MCPE exhibit comparable performance for measuring trace concentration levels of Zn(II) at pH 2, whereas its detection with BiCPE was practically impossible
[38]	<i>In-situ</i> with	Pd, Cd	SCP	---	---	10-100 (Cd, Pb)	<ul style="list-style-type: none"> • Sb(III) ions are first presented as chemical

Sb(III)

[39]	<i>In-situ</i> with Sb(III)	In, Tl(I), Zn	SCP	---	1.4 (Tl, t_d = 120 s)	10-100 (In, Tl)	<p>oxidants in stripping potentiometry, exhibiting considerably moderate and selective oxidizing capabilities</p> <ul style="list-style-type: none"> • Stripping peaks were also obtained for In(III), Tl(I) as Zn(II) • The use of complexing media containing higher concentrations of chloride or bromide ions is especially recommended • SbCPE exhibited attractive electroanalytical characteristics for simultaneous measurements of In(III), Tl(I) and Zn(II) at pH 2 • SCP measurement yielded considerably more favorable responses for all three examined metal ions than ASV • In comparison with BiCPE and MCPE, the SbCPE exhibited advantageous electroanalytical performance: at the BiCPE the measurement of Zn(II) was practically impossible due to hydrogen evolution, whereas MCPE exhibited a poorly developed signal for Tl(I)
					2.4 (In, t_d = 120 s) --- (Zn)	--- (Zn)	
[35]	Sb powder	Pb, Cd	ASV SCP	Tap water	0.9 (Pb, t_d = 120 s) 1.4 (Cd, t_d = 120 s)	20-120 (Cd, Pb)	<ul style="list-style-type: none"> • A new Sb electrode based on a carbon paste bulk-modified with Sb powder (Sb-CPE) is presented • CPE with 17% of antimony powder was selected • Sb-CPE displays higher voltammetric signals for both tested metals compared to Bi-CPE but lower signal for Cd(II) in comparison with SbCPE

[40]	<i>In-situ</i> with Sb(III)	Hg(II)	ASV	River water	1.3, $t_d = 150$ s	10-100	<ul style="list-style-type: none"> • Voltammetric measurements can be made in a wide potential window in highly acidic medium • The presence of Cd(II), which functioned as an apparent catalyst, allows to separate peaks of Hg(II) and Sb(III) • SbCPE proved to be more competent than analogous bismuth-based electrodes
[41]	<i>In-situ</i> with Sb(III)	Bi(III)	ASV	River water	1.55, $t_d = 160$ s	10-110	<ul style="list-style-type: none"> • Voltammetric measurements are carried out in highly acidic medium in which antimony peak is negligible • Bi peak increased drastically in the presence of Cd(II) which functioned as an apparent catalyst
[36]	Sb ₂ O ₃ powder	Pb Cd	ASV SCP	Tap water	ASV 0.7 (Pb, $t_d = 90$ s) 1.0 (Cd, $t_d = 90$ s) SCP 1.0 (Pb, $t_d = 90$ s) 1.0 (Cd, $t_d = 90$ s)	10-100 (Pb, Cd)	<ul style="list-style-type: none"> • CPE with 3% (w/w) of Sb₂O₃ powder was tested • The signals obtained at the Sb₂O₃-CPE were well-developed and comparable in both height and shape to those obtained at the Bi₂O₃-CPE • In contrast to SbCPE, the Sb₂O₃-CPE performed well in mild acidic media (with pH about 4.5), as well as in more acidic solutions of diluted HCl (with pH 1-2)
[42]	<i>In-situ</i> with Sb(III)	Cu(II)	ASV	River water	1) 1.45, $t_d = 120$ s 2) 1.10, $t_d = 60$ s	1) 0-120 2) 0-100	<ul style="list-style-type: none"> • Two new voltammetric procedures were elaborated: 1) Cu(II) was accumulated from a medium of 0.01 M HCl, and 2) Pyrocatechol Violet was used as a chelating ligand • When compared with analogous bismuth-based electrodes, SbCPE exhibited even more attractive electroanalytical behavior
[9]	<i>In-situ</i> with Sb(III)	Pb Cd Zn	ASV CV	Tap water River	>1 (Pb, Cd, Zn, $t_d = 240$ s)	---	<ul style="list-style-type: none"> • See comments in Table 1

[43]	<i>In-situ</i> or <i>ex-situ</i> with Bi(III) and Sb(III)	Pb Cd	ASV	water ---	<i>In-situ</i> 0.9 (Pb, t_d = 300 s) 0.8 (Cd, t_d = 300 s) <i>Ex-situ</i> 1.4 (Pb, t_d = 300 s) 1.1 (Cd, t_d = 300 s)	10-70	<ul style="list-style-type: none"> • An optimum concentration ratio $c(\text{Sb})/[c(\text{Sb}) + c(\text{Bi})]$ was around 0.7 when <i>in-situ</i> electrodeposition was applied and around 0.8 at <i>ex-situ</i> plating • Compared with electrodes electroplated by individual metals, current responses obtained within reoxidation of both metal ions tested were favorably higher when related with measurements at codeposited films
[44]	<i>In-situ</i> with Sb(III) <i>Ex-situ</i> drop with SbNP- MWCNT	Pb Cd	ASV	Wheat flour material	0.65 (Pb, t_d = 120 s) 0.77 (Cd, t_d = 120 s)	10-60	<ul style="list-style-type: none"> • SbNP-MWCNT nanocomposite electrode based on the carbon paste substrate was optimized • An enhancement in the current signal was achieved in comparison with those obtained with <i>in-situ</i> SbCPE and Sb_{microsphere}-MWCNT composite CPE • High surface area and the enhancement of mass transport at the SbNP-MWCNT electrode resulted in a high signal-to-noise ratio
[45]	<i>Ex-situ</i> with Sb(III) <i>Ex-situ</i> with Sb(III) and Au(III)	Cd Pb Cu(II) Hg(II)	ASV	Lake water Ground water	2.65 (Pb, t_d = 300 s) 2.32 (Cd, t_d = 300 s) 9.73 (Cu, t_d = 300 s) 0.052 (Hg, t_d = 300 s)	See inset Figure 5 in [45] (Pb, Cd) 25-150 (Cu) 0.5-2 (Hg)	<ul style="list-style-type: none"> • SbCPE was used for the analysis of Cd, Pb and Cu, whereas for the analysis of Hg, gold was deposited along with Sb to make the Sb–Au nanocomposite modified CPE • Cd and Pb ions were determined simultaneously • Cu was determined separately and the pH of the solution was the most crucial factor and was optimized to a value of 6

Table 3. Antimony modified screen-printed electrode (SbSPE).

ASV: anodic stripping voltammetry, Sb₂O₃-SPE: screen-printed electrode bulk-modified with Sb₂O₃, Bi₂O₃-SPE: screen-printed electrode bulk-modified with Bi₂O₃, SPSbFE/MWCNT: multiwalled carbon nanotubes modified screen-printed antimony film electrode, SPSbFE/IL: ionic liquid [Bmim]BF₄-modified screen-printed antimony film electrode, Bi-SbSPE: bismuth and antimony screen-printed electrode, BiSPE: bismuth screen-printed electrode, SbSPE: antimony screen-printed electrode, Bi-SbGCE: bismuth and antimony glassy carbon electrode, Sb^{III}(C₂O₄)OH-SPE: screen-printed electrode bulk-modified with Sb^{III}(C₂O₄)OH, SnO₂/Sb₂O₅-SPE: screen-printed electrode bulk-modified with SnO₂/Sb₂O₅, LOD: limit of detection, SbSPCE: antimony screen-printed carbon electrode, BiFE: bismuth film electrode, BiSPCE: bismuth screen-printed carbon electrode, SIA: sequential injection analysis, HPLC: High-performance liquid chromatography, DPV: differential pulse voltammetry, AdSV: adsorptive stripping voltammetry, DMG: dimethylglyoxime, Bi_{sputtered}SPE: sputtered bismuth screen-printed electrode.

Ref.	Coating method	Analyte	Technique	Sample	Detec. limit (ppb)	Linear range (ppb)	Additional information
[47]	Bulk-modified with Sb ₂ O ₃	Pb, Cd	ASV	---	20 (Cd, t _d = 600 s)	20-100 (Cd)	<ul style="list-style-type: none">• The best composition established is 0.9-1.0 % (w/w) in the carbon ink• Sb₂O₃-SPE displays higher quantification limit for Cd than Bi₂O₃-SPE at the same conditions• Pb cannot be determined on the Sb₂O₃-SPE by the possibly formation of some stable intermetallic compound
[48]	<i>In-situ</i> with Sb(III)	Hg(II)	ASV	Tap water Wastewater	<i>SPSbFE/IL</i> : 0.36, t _d = 120 s	<i>SPSbFE/IL</i> : 20-140	<ul style="list-style-type: none">• MWCNTs-modified screen-printed antimony film electrode (SPSbFE/MWCNT) and ionic liquid [Bmim]BF₄-modified screen-printed antimony film electrode (SPSbFE/IL) were developed• SPSbFE/IL provides the largest stripping current for Hg(II)• The SPSbFE/MWCNT offers more sensitive responses to Pb than the bare one
[49]	<i>In-situ</i> with	Pb	ASV	River water	0.07, t _d = 240 s	0.1-90	<ul style="list-style-type: none">• Bi-SbSPE shows an enhanced signal towards

	Bi(III) and Sb(III)							Pb compared to BiSPE, SbSPE and Bi-SbGCE <ul style="list-style-type: none"> • There is a synergistic effect existing among Bi(III) and Sb(III) when the simultaneous deposition/stripping take place • Some new types of electroplated and precursor-modified screen-printed antimony and tin electrodes were developed • A comprehensive comparison of the new sensors was performed against the benchmark electroplated and precursor-modified screen-printed Bi electrodes. • Provided LOD values are similar to those obtained on BiSPE for Cd (2.3 ppb) and Pb (1.2 ppb) • Sb^{III}(C₂O₄)OH-SPE together with BiSPE, produced the highest sensitivity for both Cd and Pb.
[50]	<i>In-situ</i> with Sb(III) Bulk-modified with Sb ₂ O ₃ , SnO ₂ /Sb ₂ O ₅ , and Sb ^{III} (C ₂ O ₄)OH	Pb, Cd	ASV	Mineral water	<i>SbSPE</i> : 1.0 (Pb, t _d = 240 s) 2.7 (Cd, t _d = 240 s) <i>Sb₂O₃-SPE</i> : 0.9 (Pb, t _d = 240 s) 2.5 (Cd, t _d = 240 s) <i>SnO₂/Sb₂O₅-SPE</i> : 1.1 (Pb, t _d = 240 s) 1.8 (Cd, t _d = 240 s) Sb ^{III} (C ₂ O ₄)OH-SPE 1.1 (Pb, t _d = 240 s) 3.5 (Cd, t _d = 240 s)	5-45 (Pb) 10-90 (Cd)		
[10]	<i>In-situ</i> with Sb(III)	Cd, Pb, Cu(II)	ASV	Groundwater	E _d = -1.2 V 5.0 (Pb, t _d = 120 s) 3.4 (Cd, t _d = 120 s) 1.6 (Cu, t _d = 120 s) E _d = -0.7 V 4.8 (Pb, t _d = 120 s)	E _d = -1.2 V 16.8-62.6 (Pb) 11.5-72.4 (Cd) 5.3-99.8 (Cu) E _d = -0.7 V	<ul style="list-style-type: none"> • <i>In-situ</i> SbSPCE is proposed as a valuable alternative to <i>in-situ</i> BiFEs, since no competition between the electrodeposited Cu and Sb for surface sites was noticed • An E_d of -0.7 V and -1.2 V for the simultaneous detection of Pb and Cu(II) and Cd, Pb and Cu(II), respectively provide the best 	

					0.28 (Cu, t_d = 120 s)	16.1-55.5 (Pb) 0.95-54.8(Cu)	voltammetric response
[51]	<i>Ex-situ</i> with Sb(III)	Allura red (AR), Tartrazine (T)	DPV-SIA	Candies Gelatin Corn flour based Isotonic drink Wastewater	0.3 μ M (AR, T)	1.0-5.0 μ M (AR, T)	<ul style="list-style-type: none"> • Cu(II) LODs obtained in this work are significantly lower than those provided by <i>in-situ</i> BiSPCE • SbSPE used as an electrochemical detector to determine azo dyes in food samples • SbSPE could be easily renewed on-line without affecting the analytical parameters • DPV-SIA provided determinations comparable to those obtained by HPLC reference method • <i>Ex-situ</i> SbSPCE behaves much better (lower LOD and higher sensitivity) than both <i>ex-situ</i> BiSPCE and Bi_{sputtered}SPE for Ni(II) determination • Dimethylglyoxime (DMG) was used as complexing agent at pH 9.2 • The <i>ex-situ</i> protocol avoids the Sb(III) hydrolysis occurring at relatively high pH
[52]	<i>Ex-situ</i> with Sb(III)	Ni(II)	AdSV		0.9, t_d = 120 s	3.1-197	

Table 4. Miscellaneous.

[Sb^VO(CHL)₂]Hex-SPE: screen-printed electrode bulk-modified with [Sb^VO(CHL)₂]Hex, CV: cyclic voltammetry, ASV: anodic stripping voltammetry, SbBDD: antimony nanoparticle modified boron doped diamond, BDD: boron doped diamond, AdSV: adsorptive stripping voltammetry, DMG: dimethylglyoxime, SbFE: antimony film electrode, Macroporus SbFAuE: macroporous antimony film electrodes, SbFME: antimony film microelectrode, SbGCE: antimony glassy carbon electrode, SbCPE: antimony carbon paste electrode, BiFME: bismuth film microelectrode, SbFAuE: antimony film gold electrode, GCE: glassy carbon electrode, CPE: carbon paste electrode, LOD: limit of detection.

Ref.	Electrode	Analyte	Technique	Sample	Detec. limit (ppb)	Linear range (ppb)	Additional information
[53]	[Sb ^V O(CHL) ₂]Hex-printed electrodes	Sulfide	CV	wastewater	5 µM	0.01-0.7 mM	<ul style="list-style-type: none"> The fabrication of SPEs with a mixture of 5% (w/w) [Sb^VO(CHL)₂]Hex/graphite powder in 1.5% (w/v) ethyl cellulose in 2-butoxyethyl acetate, as well as their behavior as electrocatalysts toward the oxidation of sulfide are described [Sb^VO(CHL)₂]Hex-SPE showed good working stability in contrast to [Sb^VO(CHL)₂]Hex-chemically modified electrodes
[54]	Sb nanoparticles modified BDD (SbBDD)	Pb Cd	ASV	---	Pb <i>Bare BDD</i> 41.8, <i>t</i> _d = 120 s <i>SbBDD</i> 18.5, <i>t</i> _d = 120 s Cd <i>Bare BDD</i> 150, <i>t</i> _d = 120 s <i>SbBDD</i>	Pb Pb+Cd 50-500 (<i>Bare BDD, SbBDD</i>) Cd 250-500 (<i>Bare BDD, SbBDD</i>)	<ul style="list-style-type: none"> Sb deposition was performed <i>in-situ</i> The detection of Pb and Cd as individual analytes was not improved by the presence of Sb, particularly evident in the case of Cd Pb inhibited the detection of Cd during simultaneous additions at the bare BDD electrode, whereas in the presence of Sb, both peaks were readily discernable and quantifiable

					150, $t_d=120$ s		
					Pb and Cd		
					<i>Bare BDD</i>		
					25.7 (Pb, $t_d=120$ s)		
					<i>SbBDD</i>		
					25.4 (Pb, $t_d=120$ s)		
					38.1 (Cd, $t_d=120$ s)		
[55]	Sputtered SbFE	Ni(II)	AdSV	---	0.2, $t_d=60$ s	0-30	<ul style="list-style-type: none"> The electrode was microfabricated by coating a silicon chip with a thin antimony-film by means of sputtering and the active area of the electrode was defined by photolithography Dimethylglyoxime (DMG) was used as complexing agent at pH 9.2 Well-formed Ni stripping peaks were obtained on sputtered SbFE, whereas no stripping signals were obtained on <i>ex-situ</i> SbGCE
[56]	Macroporous SbFAuE	Pb Cd	ASV	---	<i>Porous SbFE</i> 0.5 (Pb, $t_d=100$ s) 0.7 (Cd, $t_d=100$ s) <i>Non-porous SbFE</i> 1.8 (Pb, $t_d=100$ s) 2.8 (Cd, $t_d=100$ s)	20-120 (Pb, Cd)	<ul style="list-style-type: none"> Colloidal crystal templating has been used to electrochemically deposit three-dimensional macroporous antimony films A suspension of polystyrene spheres (0.3 % (w/w)) was spread over of a gold electrode. Antimony is then infiltrated in the polystyrene opal by <i>ex-situ</i> electrodeposition The sensitivity of the porous SbFE was more than three times higher for both metals than non-porous SbFE
[57]	SbF micro-	Pb	ASV	Natural	3.1(Pb, $t_d=120$ s)	20-100 (Pb, Cd)	<ul style="list-style-type: none"> Sb deposition was performed <i>in-situ</i>

	electrode (SbFME)	Cd Cu(II)		water (Cu)	1.9 (Cd, t_d = 120 s) 1.0 (Cu, t_d = 120 s)	5-150 (Cu)	<ul style="list-style-type: none"> • Electrochemical characteristics of the SbFME are similar to those found at the SbGCE and SbCPE, however SbFME revealed higher current densities/responses for tested heavy metal ions • In comparison with the BiFME, the SbFME exhibited favorably lower hydrogen evolution and associated wider applicable potential window, and rather lower response for Pb
[58]	Cu-Sb/Sb composite film electrode	Pb Cd	ASV	---	0.08 (Pb) 0.25 (Cd)	1-100 (Pb, Cd)	<ul style="list-style-type: none"> • The electrode was first prepared to obtain a copper-antimony alloy layer on the surface of a copper substrate. Then, an Sb film was plated on the alloy layer by electrolytic deposition potentiostatically • The prepared Cu-Sb/Sb composite film electrode possesses low cost, long term stability, low toxicity, high sensitivity and good reproducibility • See comments in Table 1
[9]	<i>In-situ</i> SbFAuE	Pb Cd Zn	ASV CV	Tap water	>1 (Pb, Cd, Zn, t_d = 240 s)	---	
[59]	SbF pencil core electrode	Pb Cd	ASV	River water Tap water	0.13 (Pb, t_d = 180 s) 0.49 (Pb, t_d = 300 s) 0.075 (Cd, t_d = 180 s) 0.048 (Cd, t_d = 300 s)	4-10, 15-65 (Pb, Cd, t_d = 180 s) 4-10, 15-50 (Pb, Cd, t_d = 300 s)	<ul style="list-style-type: none"> • A pencil core rod was used as the substrate for SbFE • Sb deposition was performed <i>in-situ</i> • SbF pencil core electrode shows a lower LOD than that of BiF pencil core electrode