Application of Square Wave Anodic Stripping Voltammetry for Determination of Traces of Ti(I) at Carbon Electrodes In Situ Modified with Bi Films

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Abstract
Bismuth films deposited in situ at glassy carbon and carbon film electrodes were tested for the determination of traces of Tl(I) separately and together with Zn(II) and Pb (II), in acetate buffer solution pH 3.7, using square wave anodic stripping voltammetry. Electrochemical impedance spectra in the presence of Tl(I) showed differences between the electrode substrates. The sensitivity to Tl does not depend on the presence of other ions, and was better at carbon film electrodes, although the 2 nmol L^{-1} detection limit was independent of electrode substrate. Application to the measurement of Tl(I) in commercial berry juice is demonstrated.

Keywords: Bismuth film, Carbon film electrodes, Trace metal determination, Stripping voltammetry, Electrochemical impedance spectroscopy

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Thallium is a metal that is most used in the electronic and pharmaceutical industries. Since it forms toxic compounds it is important to monitor it in industrial residues and in quality control in the pharmaceutical industry.

Bismuth film electrodes (BiFEs) have become an attractive subject for electroanalytical research during the last decade as a substitute for mercury film electrodes in stripping voltammetry. This is due to bismuth's low toxicity and, as a film on a solid electrode substrate, similar electrochemical properties to mercury films, in terms of potential window and ability to electrodeposit other substances on its surface by formation of intermetallic compounds or fused alloys [1–8].

Bi is deposited on carbon substrates either under in situ or ex situ conditions depending on the target analyte or the aim of analysis, such as glassy carbon (GC), carbon fibre, screen-printed, carbon paste, electrically heated carbon paste, boron-doped diamond, carbon film (CF), carbon-polymer composite electrodes [1,5,8–10], and even carbon nanotube modified electrodes [11–14].

Anodic stripping voltammetry at BiFE has been used mostly for heavy metal determination, in particular Cd and Pb [4,5,8]. However, other metal ions, such as Tl(I) [8,15–17], In(III), Cu(II) and Hg(II) [5,8,9] were also determined using square wave anodic stripping voltammetry (SWASV). The sensitivity depends on the BiF deposition conditions, electrode substrate, electrolyte medium, and deposition time [4,5,8].

In this work, bismuth films have been electrochemically in situ deposited onto GC and CF electrodes. Electrodes modified with BiF were applied to the determination of the heavy metals Tl, Zn, and Pb in acetate buffer (ABS) pH 3.74, by SWASV separately and together. Tl(I) was determined at CF modified with BiF for the first time and the results were compared with those at a GC-BiF electrode. After characterization of the electrode processes, the BiFE was used for the determination of thallium in juice samples.

The response to Tl(I), Zn(II), and Pb(II) was investigated first separately in acetate buffer solution pH 3.74 in the presence of Bi(III) and then with all metal ions together. BiF was deposited in situ at GCE or CFE under optimised conditions (see Experimental). As seen from the results in Fig. 1A, the peaks were well defined and a linear response to Tl(I) at GCE was obtained from 0.5 to 120 nmol L^{-1}. The other metal ions, Zn(II) and Pb(II), were also determined separately. A similar sensitivity was obtained for Pb(II) but with a different linear range, from 15 to 430 nmol L^{-1}. A significantly higher concentration range was obtained for Zn(II) from 0.5 to 5.0 $\mu\text{mol L}^{-1}$ at GCE.

The Inset of Figure 1A shows the calibration curve calculated from the stripping voltammogram in Figure 1A.

Calibration data for all metals are given in Table 1. The lowest sensitivity was for Zn(II) and the limit of detection (*LOD*) was much higher than that of Tl(I) and Pb(II). This is due to hydrogen evolution already occurring at the potential used for Zn deposition, −1.4 V vs. Ag/AgCl. The highest sensitivity and the lowest *LOD* was found for Tl(I), promising for its successful determination at BiFE. Moreover, Tl(I) presents two linear ranges, one for lower and other for higher concentrations; in [17] this was attributed to the formation of different microscopic phases. Two range calibration curves were also found at porous Bi film electrodes for Pb(II) and Cd(II) with a higher slope at higher concentrarions due to the ability to explore the deeper layers of the porous electroactive surface at high metal ion concentrations [18]. It is likely that similar effects are occurring here; there is evidence of surface roughness from impedance spectra (see below).

Analysing the results from Tl(I) mixed together with the other metal ions, Zn(II) and Pb(II), similar results were obtained as for separate metal ions. The sensitivity

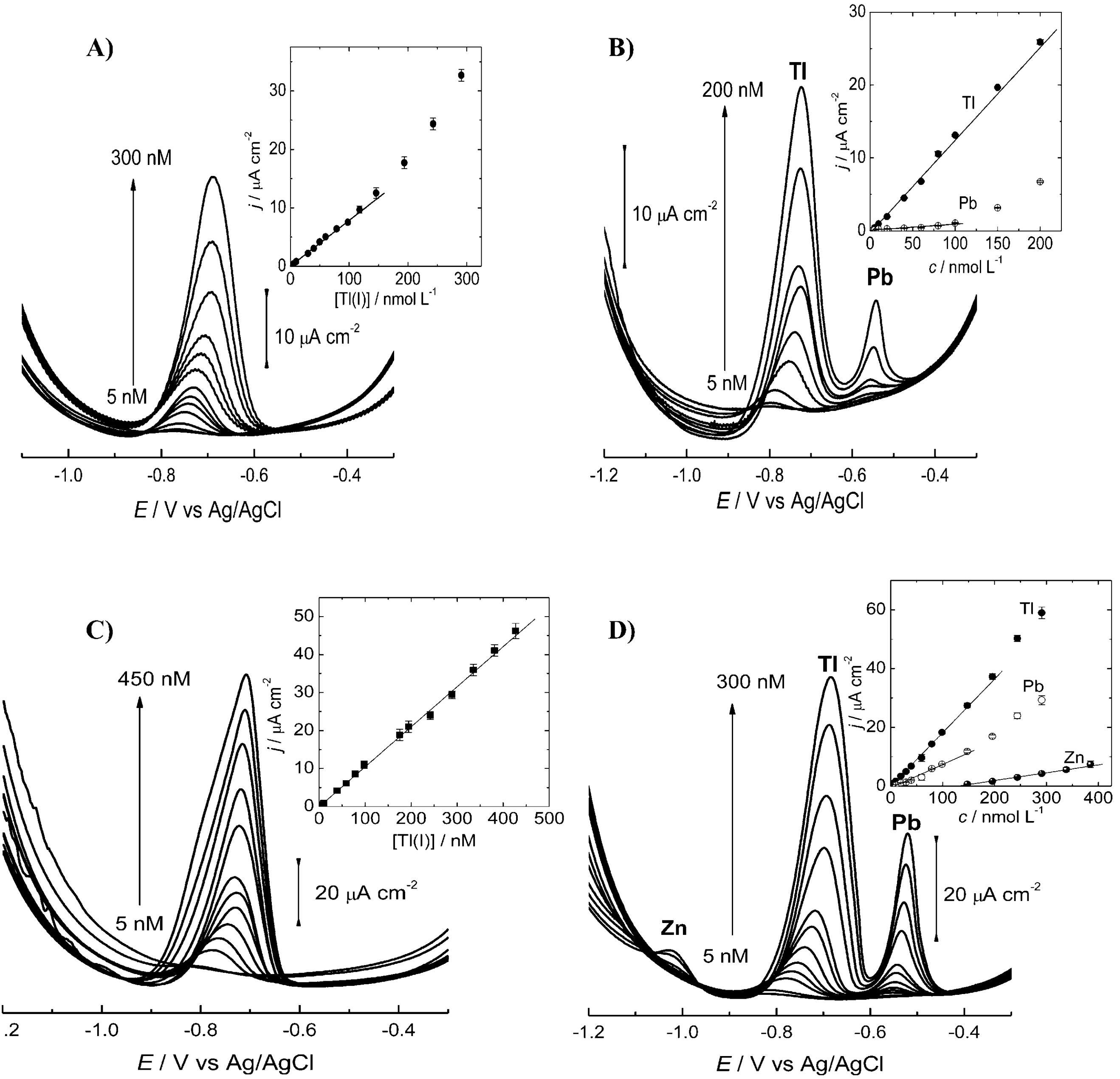

Fig. 1. SWASVs at GCE (A,B) and CFE (C,D) for Tl(I) 5; 10; 30; 40; 50; 60; 80; 100; 120; 150; 200; 250; and 300 nmol L^{-1} (A); Tl(I) and Pb(II) 5; 10; 20; 40; 60; 80; 100; 150; and 200 nmol L^{-1}, each, (B); Tl(I) 5; 10; 40; 60; 80; 100; 180; 200; 250; 300; 350, 400; and 450 nmol L^{-1} (C); and Tl(I) and Pb(II) 5; 10; 20; 30; 40; 60; 80; 100; 150; 200; 250, and 300 nmol L^{-1}, each, and Zn 150; 200; 250; 300; 350; and 400 nmol L^{-1} (D) in the presence of 2 μmol L^{-1} of Bi(III) in 0.1 mol L^{-1} of acetate buffer pH 3.74. Insets present calibration curves.

Table 1. Calibration parameters of Zn, Tl, Pb, at GCE and CFE modified with Bi film. Data calculated from Figure 1. Standard deviations are given for $n=3$.

Metal ion	Sensitivity ($\mu A\,cm^{-2}\,nmol^{-1}\,L$)	Correlation coefficient (R^2)	*LOD* ($nmol\,L^{-1}$)
GCE Individual calibration			
Zn	0.009 ± 0.001	0.994	37.4 ± 0.9
Tl	0.124 ± 0.008	0.998	2.16 ± 0.15
Pb	0.078 ± 0.002	0.996	9.08 ± 0.08
GCE Simultaneous calibration			
Tl	0.127 ± 0.001	0.998	1.91 ± 0.09
Pb	0.008 ± 0.001	0.994	4.01 ± 0.11
CFE Individual calibration			
Tl	0.106 ± 0.002	0.998	2.04 ± 0.12
CFE Simultaneous calibration			
Zn	0.027 ± 0.001	0.994	28.4 ± 0.07
Tl	0.183 ± 0.008	0.998	2.07 ± 0.08
Pb	0.080 ± 0.002	0.997	7.99 ± 0.10

to Zn(II) was far too low to be useful to determine it together with Tl(I) and Pb(II). Tl(I) and Pb(II) can be easily determined simultaneously as seen in Figure 1B. The sensitivity was much higher to Tl(I) than to Pb(II), as when separate; the response to Pb decreased in the presence of Tl(I), showing that Tl(I) interferes with lead determination, probably due to competitive co-deposition together with Bi at low Pb concentrations.

Calibration curves are plotted in the Inset of Figure 1B and the data are presented in Table 1. The first linear range for Tl(I) was from 5 to 200 $nmol\,L^{-1}$ and for Pb(II) from 5 to 100 $nmol\,L^{-1}$; the second slope for Tl(I) was higher, similarly as for Tl(I) determined separately. The sensitivity to Tl(I) at lower concentrations was 0.102 $\mu A\,cm^{-2}\,nmol^{-1}\,L$, close to that obtained in separate determinations, and the LOD was slightly lower than that from the separate determination, 1.91 $nmol\,L^{-1}$.

A similar response to Tl(I) by itself was found at CFE; SW stripping voltammograms are shown in Figure 1C and present the same type of profile as at GCE. The linear range was longer than at GCE, up to 450 $nmol\,L^{-1}$, with a similar *LOD*, 2.04 $nmol\,L^{-1}$. The calibration curve (Figure 1C, Inset) had the same correlation coefficient ($R^2=0.998$) but a lower sensitivity than at GCE, 0.106 ± 0.002 $\mu A\,cm^{-2}\,nmol^{-1}\,L$.

Determining Tl(I) together with Zn(II) and Pb(II) gave better-defined SWASV peaks (Figure 1D) and there was a response to lower concentrations of Zn(II) compared to GCE modified with BiF. The linear range, up to 200 $nmol\,L^{-1}$ (Figure 1D, Inset), was lower for Tl(I) than for separate determination. The other calibration parameters are given in Table 1. The sensitivity to Tl(I) of 0.183 $\mu A\,cm^{-2}\,nmol^{-1}\,L$ was higher than that in [10] which was 0.102 $\mu A\,cm^{-2}\,nmol^{-1}\,L$ after the same deposition time (120 s), but lower than in [17], obtained at Bi nanopowder: 1.252 $\mu A\,L\,\mu g^{-1}$ (value from logarithmic scale) after a deposition time of 180 s.

As at GCE/BiF, the sensitivity to Pb(II) was lower than to Tl(I), see Table 1 and Figure 1D, Inset, showing again that Tl(I) interferes with Pb(II) determination. On the other hand, Pb(II) helps the formation of Bi-Pb-Tl alloy similarly to in [19], where this phenomenon was observed for Bi-Pb-Cd alloys.

Electrochemical impedance spectra (not shown) were recorded at GCE and CFE in blank ABS pH 3.74; in the presence of 2 $\mu mol\,L^{-1}$ Bi(III), and after further addition of 200 $nmol\,L^{-1}$ Tl(I). Spectra were recorded at: i) −1.2 V, where deposition of Bi(III) and pre-concentration of Tl(I) was performed, ii) −0.75 V, where stripping of Tl(I) occurs; and iii) −0.2 V, where BiF was stripped from the electrode surface. The spectra showed a big influence of electrode substrate (at CFE impedance values were higher than at GCE) and of electrode modification with BiF and with Bi-Tl. At −1.2 V the spectra evidenced both hydrogen evolution and metal deposition, the former more evident at GCE than at CFE; subsequent stripping of Tl was faster at CFE than at GCE, confirming the superior properties of CFE compared to GCE. Nevertheless, after stripping of bismuth, the CFE still needed additional cleaning prior to use for the next determination.

Tl(I) is rarely present in natural samples in sufficient amounts for it to be possible to be determined directly; therefore, a commercial berry juice sample was chosen for its determination using a CFE. As expected, no metal-peaks were observed in diluted juice with acetate buffer pH 3.74 in the presence of 2 $\mu mol\,L^{-1}$ Bi(III). Therefore, a known amount of Tl(I) was added to the diluted juice sample and analysed by SWASV using the calibration curve obtained from a model solution with the three metal ions. Voltammograms in commercial berry juice with an added amount of Tl(I) (40 $nmol\,L^{-1}$) in the presence and absence of Pb(II) are presented in Figure 2. As seen, Pb(II) practically does not interfere with Tl(I) determination. The results obtained showed that the recovery for Tl(I) was 105 % with *RSD* ($n=3$) 0.5 %. These results demonstrate that there is no matrix effect from solid particles in the natural sample on Tl(I) determination and no additional pre-treatment of sample is needed for determination Tl(I) in similar drinks.

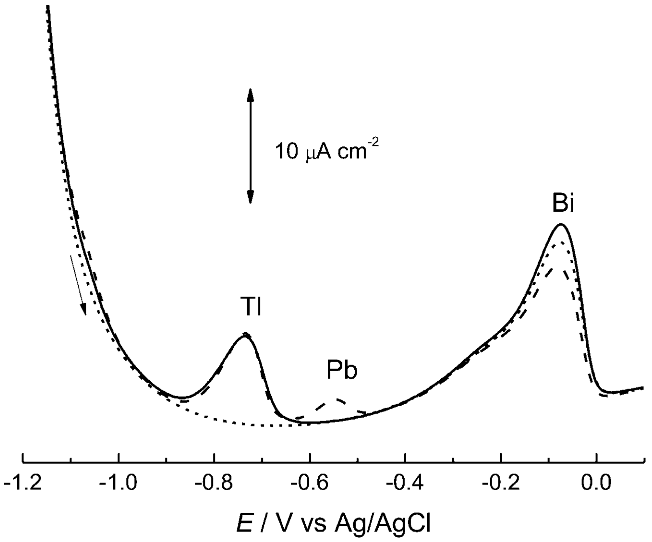

Fig. 2. SWASVs at CFE in acetate buffer pH 3.74 with addition of 2 μmol L^{-1} of Bi(III) and 100 μmol L^{-1} of commercial berry juice (dotted line) in the presence of 40 nmol L^{-1} of Tl(I) (solid line) and 40 nmol L^{-1} Tl(I) and Pb(II) (dashed line). SWASV conditions: $t_{dep} = 120$ s, $E_{dep} = -1.4$ V vs. Ag/AgCl, $f = 25$ Hz, $\Delta E = 2$ mV, amplitude 25 mV, $t_{eq} = 15$ s.

In conclusion, bismuth films were deposited in situ at GCE and CFE and tested for the determination of Tl separately and together with Zn and Pb in ABS pH 3.74 using SWASV. It was shown that it is possible to determine Tl individually and simultaneously with the other metal ions at in situ deposited BiF at both electrode substrates. The sensitivity to Tl does not depend on the presence of the other ions; it was better at CFE although the *LOD* did not depend on the electrode substrate. Impedance spectra showed different behaviour after Bi-Tl co-deposition at each electrode substrate. Determination of Tl(I) added to commercial juice showed that there was no matrix effect and with 105 % recovery. Deeper studies of SWASV in the presence of cadmium and the other metal ions are in progress. More detailed electrochemical impedance studies will also be performed, and the sensor will be applied to the analysis of waste water.

Experimental

$Bi(NO_3)_3$, $Pb(NO_3)_3$, $ZnCl_2$ and TlCl were obtained from Sigma (Germany). Na_2CH_3COO and CH_3COOH (Riedel–de Haën, Germany) were used to prepare 0.1 mol L^{-1} acetate buffer solution pH 3.74. Chemical reagents were all of analytical grade and were used without further purification.

Stock solutions of the metal ions were diluted as required before measurements in acetate buffer solution and stored at room temperature. All solutions were prepared with water purified in a Millipore Milli-Q system (resistivity ≥18 MΩ cm).

All voltammetric measurements were carried out in a 10 mL total capacity glass cell at 25 ± 1 °C, using the GC or CF working electrode, Ag/AgCl 3 M KCl as a reference, and Pt wire as auxiliary electrode. SWASV was performed with an μAutolab Type II (Metrohm-Autolab, Netherlands) potentiostat/galvanostat coupled to a personal computer and controlled with GPES 4.9 software. Geometric areas of the electrodes were 0.018 and 0.20 cm^2 for GC and CF electrodes, respectively.

Electrochemical impedance measurements were carried out in the same electrochemical cell with a PC-controlled Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical, UK). A sinusoidal voltage perturbation of amplitude 10 mV was superimposed on the applied potential, scanning from 65 kHz to 0.1 Hz with 10 points per frequency decade. Fitting to equivalent electrical circuits was performed with ZView 3.0 software.

Preparation of the carbon film electrodes from 2 Ω carbon film electrical resistors is described elsewhere [20–22]. The glassy carbon electrode was polished with diamond spray of 3 and 1 μm particle size (Kemet, UK) using a polishing cloth (Kemet, UK). Each polishing step followed by 1 min sonication in deionized water. Electrodes were pretreated in acetate buffer solution by potential cycling from −1.5 to +1.5 V vs. Ag/AgCl 10 times before first use.

Bi films were deposited in situ with the other metals from a solution containing 2 μmol L^{-1} Bi(III), and other metal ions, as needed, in acetate buffer solution pH 3.74. The following conditions were applied for the in situ deposition and for SWASV: pulse amplitude of 25 mV, frequency of 40 Hz, step potential 2 mV, accumulation time 120 s, equilibration time 5 s, and potential sweep from −1.4 to +0 V vs. Ag/AgCl.

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