Bismuth as an Electrode Material in the Simultaneous
Determination of Pb (II) and Cd (II) in
Poplar (Populus) Leaves by SWASV

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Abstract
In this work we tested the performance of the bismuth film electrode in the detection
and simultaneous determination of toxic metals on real samples in a complex matrix, by
square wave anodic stripping voltammetry. The studied samples were white poplar
leaves gathered in “2ª Circular”, which is an area of major traffic intensity of the city of
Lisbon. The determined metals were Pb (II) and Cd (II). After being dried, the white
poplar leaves were submitted to an acid digestion process assisted by microwave
technology. A complete optimization study of the voltammetric parameters was made in
order to simultaneously determine the metals as well as to decrease the detection limits
and improve the method’s repeatability and sensitivity. The working electrode consisted
in a bismuth film deposited on a vitreous carbon disc surface. The Ag/AgCl system was
used as the reference electrode and a platinum wire as the auxiliary electrode. The
concentrations (in mg of metal/kg of dry matter - leaves) obtained for Pb (II) and Cd (II)
were of 3.0 and 1.7, respectively. Also, detection limits of $1.80 \times 10^{-8}$ mol L$^{-1}$ for Pb (II)
and $6.90 \times 10^{-9}$ mol L$^{-1}$ for Cd (II) were estimated. In addition, a well shaped
voltammogram obtained in the analysis of real samples opens excellent perspectives for
the use of the bismuth electrode as an alternative to toxic metals such as mercury.

Keywords: bismuth electrode, toxic metals, stripping voltammetry, poplar leaves.

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Introduction

The development and implementation of methods and procedures in order to detect and determine toxic metals in environmental samples is, at present, an issue of major importance, regarding the negative impact and consequences brought by these agents to human health, environment and biological systems in general [1-4].

In this regard, Anodic Stripping Voltammetry, ASV, shows to be a powerful electroanalytical technique, namely due to its high sensitivity, repeatability, low detection limits, low cost of equipment, as well as to its possibility of performing in-situ field analysis [5-7].

Another significant advantage of this technique lies in its ability to simultaneously determine several metals, at trace level.

When ASV is-applied to the determination of toxic metals, it essentially involves two steps [8].

The pre-concentration or pre-deposition step which consists in reducing the metallic ions present in the sample solution onto the surface of a working electrode, by means of the application of an adequate cathodic potential, $E_{dep}$, for a certain period, $t_{dep}$. The mass transport in this step may be enhanced by means of solution magnetic stirring or by using a rotating electrode [9, 10].

The next step is the redissolution or determination step, where the metals deposited in the previous step are re-oxidized back into the solution by means of the application of an anodic potential sweep. If the potential is scanned in a potential-time square wave form, then the technique can be, in general terms, designated by Square Wave Anodic Stripping Voltammetry, SWASV [11, 12].

The resultant voltammogram (current-potential plot in peak shape) recorded during this step provides the analytical information of interest. The stripping current, $I_p$, due to the oxidation of a given metal, is proportional to its concentration at the electrode, and therefore to its concentration in the sample solution. Peak potentials, $E_p$, are characteristic of each metal, and therefore serve to identify the metals in the sample.

In terms of the working electrode materials, it can be seen that mercury, more frequently [13-16], but also gold [17, 18] or carbon (in its several forms) [19-24] have been the most used. Recently, however, bismuth has acquired a prominent stand in this context of electroanalysis [25-30]. This observation is due to the fact that in general terms bismuth exhibits an electroanalytical performance that compares favorably with the other referred electrode materials. Also, the low toxicity for bismuth is a major advantage, namely when compared with mercury, which is a very toxic element.

Like most of the analytical techniques, SWASV, can also be affected by some interferences, which can influence the quality of the final results. The most important one is the presence of organic substances in the sample matrix [31]. These substances can be adsorbed onto the electrode surface and therefore make difficult or inhibit the pre-concentration of the metals and their re-oxidation in the subsequent step. Also, complexation of metal cations in solution may occur, leading to a change in their concentration.
The procedure used in this work in order to decompose the organic matter present in the studied samples (poplar leaves), thus minimizing the errors affecting the final results, consisted on a wet digestion of the samples, using adequate oxidizing agents and heating the mixture. This heating was performed using microwave radiation [32-34]. Microwave heating presents significant advantages when compared to conventional heating (hot plate or sand bath), where part of the energy is lost heating the walls of the vessel containing the mixture. Thus, the heating process becomes significantly slower, limiting the digestion temperatures that can be achieved, and affecting thus the overall effectiveness of the process.

In the present work we explore the potentialities of bismuth, as an electrode material, in the determination of Pb (II) and Cd (II) in real samples with complex matrix, by SWASV. Following this objective, we performed a complete study on the optimization of the voltammetric parameters that characterize SWASV (deposition potential, deposition time, square wave frequency, square wave amplitude and potential step), in order to simultaneously detect both metals, decrease total analysis time and method detection limit and also to increase the method’s sensitivity and repeatability.

**Experimental**

**Reagents and solutions**

The supporting electrolyte used in both test and real sample solutions was HNO₃ 0.1 mol L⁻¹, pH=1, prepared from a Merck HNO₃ 65% solution.

For the preparation of the bismuth electrode (deposition of a bismuth film on the surface of an adequate substrate) a 5 × 10⁻⁵ mol L⁻¹ in Bi⁺³ solution, from a Bi(NO₃)₃ Atomic Absorption Standard Solution from Merck, with a concentration of 1000 mg L⁻¹, in Bi⁺³, was used.

The Pb (II) and Cd (II) solutions used in the optimization study of the voltammetric parameters were prepared from Cd(NO₃)₂ and Pb(NO₃)₂ Atomic Absorption Standard Solutions from Merck, with a concentration of 1000 mg L⁻¹, in both metals.

Ultra pure water from Millipore, with a resistivity ≥ 18.2 MΩ, was always used in the preparation of all solutions as well as in glassware washing and electrode rinsing.

**Instrumentation**

For the voltammetric assays we used an AUTOLAB PGSTAT 10 potenziostat, with AUTOLAB GPES, version 4.6 software.

Microwave digestion of the samples was performed with an open vessel microwave digestor, CEM STAR SYSTEM 2.

The working electrode consisted on a bismuth film, BiFE, deposited onto the surface of a 3 mm diameter vitreous carbon disc, sealed with Teflon.
Before each assay the vitreous carbon disc was always polished with 0.02 µm
grit alumina powder in order to remove any residues from the surface of the
bismuth film deposition substrate. Abundant washing with ultra pure water
followed this step.
As reference electrode we used the system Ag/AgCl (sat. KCl 3 mol L⁻¹). The
counter electrode consisted on a spiral platinum wire, sealed with glass.
The electrochemical cell used was a conventional cell, capable of working with
volumes up to 50 mL, covered with a Teflon lid.
For solution stirring we used a standard magnetic stirrer.

**Procedure**

**Sample pre-treatment**
As mentioned before, the sample was submitted to a microwave digestion
program in order to eliminate the organic matter present in the sample complex
matrix, thus minimizing the errors affecting the electroanalytical performance of
the BiFE.
Before the digestion procedure the leaves were dried in an oven, for 96 h, at 65
°C, followed by grinding until a fine dust was obtained.
A mass of ca. 2 g of this powder, accurately weighed to ± 10⁻⁵ g, was then
submitted to the digestion procedure.
The oxidizing agents used in the digestion of the leaves were nitric acid and
hydrogen peroxide, according to a digestion program described elsewhere
[JCBS]
The residue resulting from the digestion procedure was then dissolved with 20
mL of a HNO₃ 0.5 mol L⁻¹ warm solution, filtered and diluted to a final volume
of 100 mL.

**Voltammetric parameters optimization**
The SWASV parameters optimized were: Deposition Potential (Eₜₐₜ), Deposition
Time (tₜₐₜ), Square Wave Frequency (f), Square Wave Amplitude (Eₛₘₜ) and
Potential Step (ΔE).
The concentration of Pb (II) and Cd (II) used in the voltammetric parameters
optimization study was 1 × 10⁻⁷ mol L⁻¹ for each metal.
Note that in each optimization assay as well as in real sample analysis, we used,
in the pre-concentration step, a co-deposition procedure, in which de bismuth
film is co-deposited with the metals present in solution.
After the reoxidation step, the bismuth film is removed and the vitreous carbon is
electrochemically cleaned by means of the application of an adequate potential
(+0.2 V).
In the subsequent cycle the bismuth film is, again, co-deposited with the metals.

**Results and discussion**
The results obtained from the parameters optimization assays, where it was
studied their influence in each metal peak current, are shown in the plots of Fig.
1. We only present the results for $E_{\text{dep}}$, $t_{\text{dep}}$, and $f$, due to their relevance in method’s figures of merit. The assays for the remaining parameters ($E_{sw}$ and $\Delta E$) were performed in a similar manner and the same criteria were assumed when choosing their optimized values.

![Figure 1](image)

**Figure 1.** Voltammetric parameters: a) deposition potential; b) deposition time; c) square wave frequency.

In Fig. 1 a) we can see that for both metals peak current increases as $E_{\text{dep}}$ becomes more negative. This behavior is due to the fact that Pb (II) and Cd (II) are positively charged ions which are thus preferentially reduced at more negative potentials. The limiting current [35] for Pb (II) and Cd (II) is reached at -1.2 V. We took -1.0 V as the optimum value for $E_{\text{dep}}$, considering the simultaneous determination of the studied metals in conditions of significant sensitivity and repeatability. The results on Fig. 1 b) show that peak current for both metals increases with deposition time, since the amount of metal deposited is higher for higher deposition times. At about 175 s a deviation from linearity can be observed due to bismuth film saturation for higher deposition times, rendering impossible a further increase of $I_p$ [36]. Therefore, in order to prevent saturation and to reduce total analysis time, a deposition time of 60 s was chosen as the optimum value. With the optimum values of -1.0 V and 60 s for $E_{\text{dep}}$ and $t_{\text{dep}}$, respectively, we proceeded with square wave frequency optimization. In Fig. 1 c) we can see that, for both metals, the relation between peak current and frequency is linear. However, frequency values above 150 Hz, invariable produced an increase in background noise and a decrease in the voltammogram shape and definition. We thus decided to take 100 Hz as the optimum value for square wave frequency [8]. Table 1 summarizes the values obtained for each voltammetric parameter as well as further experimental conditions for SWASV assays.
With the optimized conditions summarized in Table 1, the calibration of the BiFE (establishment of the linear range between peak current and metal concentration) followed. Calibration plots are shown in Fig. 2.

Table 1. Experimental condition for SWASV assays.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-deposition potential</td>
<td>-1.0 V</td>
</tr>
<tr>
<td>Co-deposition time</td>
<td>60 s</td>
</tr>
<tr>
<td>Conditioning potential</td>
<td>+ 0.2 V</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>30 s</td>
</tr>
<tr>
<td>Square wave frequency</td>
<td>100 Hz</td>
</tr>
<tr>
<td>Square wave amplitude</td>
<td>25 mV</td>
</tr>
<tr>
<td>Potential step</td>
<td>2 mV</td>
</tr>
<tr>
<td>Bismuth concentration</td>
<td>$5 \times 10^5$ mol L$^{-1}$</td>
</tr>
<tr>
<td>Nitric acid concentration</td>
<td>0.1 mol L$^{-1}$</td>
</tr>
<tr>
<td>Stirring</td>
<td>1000 rpm</td>
</tr>
</tbody>
</table>

Figure 2. Calibration plots for: a) lead, and b) cadmium, with BiFE.

In Table 2 we can see the linear concentration range for Pb (II) and Cd (II). Note that, in both cases, and for higher concentrations, a deviation from linearity was observed due to the BiFE’s saturation.

Table 2. Linear concentration range for cadmium and lead with BiFE.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Linear concentration range (mol.L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (II)</td>
<td>$6 \times 10^{-9}$ - $3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>$3 \times 10^{-8}$ - $3 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
After establishing the linear range between peak current and concentration we estimated the limit of detection, $L_d$, for BiFE in the determination of Pb (II) and Cd (II) [37]. The results are shown in Table 3.

**Table 3.** Values of $L_d$ for the determination of cadmium and lead with BiFE.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$L_d$ (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (II)</td>
<td>$1.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>$6.9 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Next the analysis of real samples was performed. The amount of Pb (II) and Cd (II) in poplar leaves was determined through the standard addition method [38], using a standard solution with adequate concentrations of Pb (II) and Cd (II). Fig. 3 shows the voltammograms resulting from the voltammetric assay performed on the poplar leaves sample. The base voltammogram corresponds to the sample signal and the other curves result from the 1$^{st}$ to the 4$^{th}$ addition of standard solution, to 25 mL of sample solution. The insertion in Fig. 3 depicts standard addition calibration plots for Cd (II) and Pb (II).

![Voltammograms and calibration lines](image)

**Figure 3.** Voltammograms and calibration lines (inserted) obtained in the analysis of cadmium and lead in poplar leaves with BiFE.

The concentrations obtained for Cd (II) and Pb (II) in poplar leaves, by SWASV, using the BiFE are shown in Table 4. The values are expressed in mg of metal/kg of dry matter (leaves), as these units are usually used in environmental analysis.
Table 4. Concentration obtained for cadmium and lead in poplar leaves.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg / kg dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (II)</td>
<td>3.0</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>1.7</td>
</tr>
</tbody>
</table>

As mentioned above the assays performed on the leaves samples consisted, firstly, in measuring the metal’s signal in the sample, and after the volume additions of the standard solution. The current intensity values considered for each standard addition resulted from the average of five replicates. Table 5 shows the results obtained in the determination of Pb (II) and Cd (II) in the studied sample. The precision of the method is evaluated by means of the standard deviation calculation.

The resulting coefficient of variation (\(s_d / \bar{I_p} \times 100\)) is about 1.6% for the two metals, showing the good overall precision of the method. This significant precision is partially due to the digestion program optimized by us in order to decompose any organic matter present in the sample, thus, minimizing errors arising from the presence of these components.

The coefficient of variation obtained for the analysis of Cd (II) and Pb (II) in poplar leaves with BiFE, coincides with that obtained for MFE when applied to the determination of these metals in the same real sample [39]. Note that MFE can be taken as a reference since it is, perhaps, the most frequently used electrode material, in SWASV of toxic metals.

Regarding the limit of detection estimated for both electrodes, we can see that BiFE can also be compared to MFE [40].

The \(L_d\), estimated for Pb (II) using BiFE (1.8 \(\times\) 10\(^{-8}\) mol L\(^{-1}\)), is identical to that estimated when MFE is used (9.1 \(\times\) 10\(^{-9}\) mol L\(^{-1}\)). In the case of Cd (II) the \(L_d\) estimated with MFE (6.9 \(\times\) 10\(^{-10}\) mol L\(^{-1}\)) is about ten times lower than the one estimated with BiFE (6.9 \(\times\) 10\(^{-9}\) mol L\(^{-1}\)). However, we find most relevant the low detection limits achieved with BiFE.

Conclusions

The analysis of the obtained results allows us to conclude that the BIFE has a favorable electroanalytical performance in comparison with MFE taken as the reference for this type of work. This conclusion is supported both by the comparable values of method precision associated to BIFE and MFE and the observed detection limits. These immediately lead us to foresee the possibility of using BiFE to analyze toxic metals at trace level. On the other hand, the excellent voltammograms’ definition together with the excellent correlation between metal peak current and concentration also support the same conclusion. This evidence is partly related to the sample’s pre-treatment, including the acid digestion step to ensure full decomposition of its content in organic matter. This microwave digestion process shows to be extremely effective towards minimizing the
interferences typically associated with this type of compounds in SWASV assays.

Table 5. Evaluation of the precision of the SWASV method using the BiFE.

<table>
<thead>
<tr>
<th>Standard addition</th>
<th>Replicate</th>
<th>Peak current ( I_p )/µA</th>
<th>Average peak current ( \bar{I}_p )/µA</th>
<th>Standard deviation ( sd(I_p) )/µA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{Pb}^{2+} )</td>
<td>( \text{Cd}^{2+} )</td>
<td>( \text{Pb}^{2+} )</td>
</tr>
<tr>
<td>Sample</td>
<td>1</td>
<td>18.75</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>18.26</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18.08</td>
<td>0.50</td>
<td>18.32</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.00</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>18.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>1\text{st}</td>
<td>1</td>
<td>38.50</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>Standard addition</td>
<td>2</td>
<td>38.20</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>38.00</td>
<td>0.90</td>
<td>38.07</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>37.90</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37.77</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>2\text{nd}</td>
<td>1</td>
<td>64.09</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>Standard addition</td>
<td>2</td>
<td>65.55</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>63.37</td>
<td>1.25</td>
<td>64.10</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>64.00</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>63.50</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>3\text{rd}</td>
<td>1</td>
<td>85.48</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>Standard addition</td>
<td>2</td>
<td>85.06</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>84.73</td>
<td>1.84</td>
<td>85.35</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>87.00</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>84.50</td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>4\text{th}</td>
<td>1</td>
<td>100.30</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Standard addition</td>
<td>2</td>
<td>100.60</td>
<td>2.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>106.00</td>
<td>2.60</td>
<td>101.28</td>
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<tr>
<td></td>
<td>4</td>
<td>100.00</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>99.50</td>
<td>2.45</td>
<td></td>
</tr>
</tbody>
</table>

A reference is due to a significant disadvantage of BiFE relative to MFE related to the difficulties in analyzing some metals which are traditionally determined by MFE because their reoxidation potentials are more positive than the potential at which bismuth itself reoxidizes. This is the case for copper and antimony among others.

As a final remark, if some conditions are met, not very specific but mostly related to the type and concentration of the metals under study, the results
obtained with BiFE are in complete agreement with those from MFE with an obvious advantage in human and environmental health terms, considering that bismuth is far less toxic than mercury.

References


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