

# Stripping voltammetry with a bismuth electrode as an alternative to mercury electrode - a contribution to green chemistry

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Received July 20, 2023; Revised August 21, 2023; Accepted August 28, 2023

**Abstract** Stripping voltammetry can be used to measure trace metals simultaneously at low concentrations. The experimental equipment is inexpensive, especially compared to spectroscopic methods such as atomic emission spectroscopy. In the past, mercury has been used as a drop or film electrode. However, due to its high toxicity, an alternative has to be found. Experiments using non-toxic bismuth as an electrode are described. A chemist is familiar with the chemical principles used, such as pre-concentration of the metal ions of interest at a suitable electrode and subsequent stripping of the metal. Therefore, the teaching of the principles of stripping voltammetry would be a straightforward task.

**Keywords:** Voltammetric stripping, square wave voltammetry, differential pulse voltammetry, bismuth electrode

**Cite This Article:** A. Habekost, "Stripping voltammetry with a bismuth electrode as an alternative to mercury electrode - a contribution to green chemistry." *World Journal of Chemical Education*, vol. 11, no. 3 (2023): 92-96. doi: 10.12691/wjce-11-3-12.

## 1. Introduction

Stripping voltammetry is an electrochemical technique used to measure the concentration of a trace metal in a sample solution. It is a highly sensitive and selective technique and is capable of detecting trace amounts of metals in complex samples. It is widely used for the analysis of heavy metals and other trace elements in environmental, biological and industrial applications.

The electrochemical principle is easy to understand: A potential is applied to a working electrode in the presence of the sample solution, resulting in the reduction of metal ions on the electrode surface. The reduction reaction produces a current proportional to the concentration of metal ions in the solution. The longer the reduction time the higher the metal concentration on the electrode. After the reduction or pre-concentration step, the potential is changed and scanned to higher potentials. This causes the reduced metal ions to be oxidized back to their original form, resulting in a current flowing in the opposite direction. The concentration of the metal ion in the solution is proportional to the magnitude of this current flow.

The metal can be identified by the oxidation potential (relative to the reference electrode used) and its concentration in the solution can be determined by analyzing the integral of the oxidation current peaks.

In the past, anodic stripping voltammetry ("polarography") used a hanging mercury droplet or mercury film electrodes that formed amalgams with the

metals being analyzed [1,2], but the use of mercury and mercury salts is now obsolete due to its high toxicity.

The advantage of bismuth as electrode in stripping voltammetry is its ability to form cold-melt alloys with various heavy metals [3].

Wang et al [4] have shown that bismuth coated carbon screen-printed electrodes (SPE) provide reliable quantification of several heavy metals by stripping voltammetry. The bismuth film was prepared using a Bi(III) solution at a deposition potential of -0.8 V for 4 min. The metal (lead) solution was pre-concentrated by applying -1.0 V for 120 s while stirring the solution the lead was oxidized at -0.35 V. The authors show a linear range over 10-100 ppb after 4 min of deposition with a limit of detection (LOD) of 0.3 ppb.

There are two main ways of preparing the electrode: By means of electrodeposition (or other methods such as the sparking of bismuth) on a substrate prior to the pre-concentration of the metal ion to be analyzed, or by the addition of a bismuth salt and synchronous reduction with the metal [5].

Bismuth electrode stripping voltammetry has been used to detect a wide range of metal ions. These include heavy metals such as lead and cadmium as well as essential trace elements such as zinc and copper. Hocevar et al [6] analyzed lead and cadmium through bismuth films deposited on various surfaces such as platinum, gold, glassy carbon and carbon. The authors found that the optimum conditions for the detection of lead and cadmium are between pH 4 and 5 and that the peak potential differs

slightly depending on the conducting salts used. A carbon surface gives the best result.

Bonfil and Kirowa-Eisner [7] used a silver electrode to measure lead and cadmium simultaneously, determined by subtractive anodic stripping voltammetry (ASV, with and without deposition) under subpotential deposition conditions, forming monolayers of the metals studied. This means that no bulk deposition is achieved. The authors show that the supporting electrolyte has a strong influence on the ASV signals. The LOD was 50 pmol for lead and 1 nmol for cadmium. Demetriades et al [8] used disposable and inexpensive pencil lead graphite as a substrate for bismuth films. The films were prepared in situ by simultaneous deposition of bismuth and the metals of interest. The LOD is 0.3  $\mu\text{g/L}$  for cadmium and 0.4  $\mu\text{g/L}$  for zinc and lead. The authors also found that coating the electrode with Nafion increased sensitivity and prevented contamination of the electrode. Chen et al [9] used bismuth coated porous carbon electrodes for the detection of heavy metal ions. Porosity was achieved by adding  $\text{CaCO}_3$  to graphite and then dissolving the  $\text{CaCO}_3$ . Bi(III) was deposited on the electrode together with the heavy metal ions. The LOD was 0.03  $\mu\text{g/L}$  for lead and 0.34  $\mu\text{g/L}$  for cadmium. The authors showed that various cations and anions did not interfere with the detection of lead and cadmium, with the exception of copper ions, which may compete with bismuth for active surface sites. Paloma-Merín et al [10] used a commercial screen-printed electrode based on sputtered bismuth as the working electrode for the detection of cadmium and lead. The authors measured LODs of 11.8 ng/mL and 6.1 ng/mL, respectively, in a 0.1 M HCl solution. The results were compared to ICP-MS measurements. Electrochemical impedance spectroscopy (EIS) shows that the use of HCl results in increasing the roughness of the Bi electrode.

Maria-Hormigos et al [11] determined lead and cadmium concentrations down to 0.27  $\mu\text{g/L}$  and 0.10  $\mu\text{g/L}$  respectively by modifying bismuth with polystyrene sulphate (PSS) and carbon nanopowder using  $\text{Bi}_2\text{O}_3$  and bismuth (III) solution. Polystyrene sulphate is water soluble and acts as an accumulator because of the interaction with metal cations due to its negative sulphate group. PSS also facilitates the uptake of Bi species by acting as a dispersant for the carbon nanoparticles used.

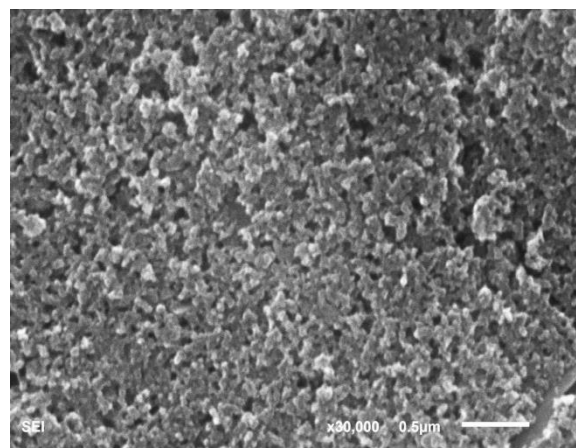
## 2. Experiments

### 2.1. Instruments and chemicals

All electrochemical measurements, including EIS measurements, were recorded using a STAT-I-400 EIS potentiostat (Metrohm/DropSens). DropView control software was used.

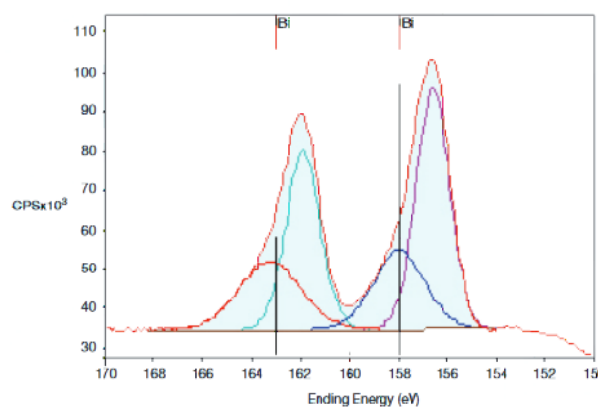
Bismuth and carbon working electrodes were used as screen-printed electrodes (Bi- and C-SPE (screen-printed electrode), all SPEs from Metrohm/DropSens), lead nitrate (1P5X.1, Carl Roth, Germany), cadmium acetate-dihydrate (KK06.1, Carl Roth, Germany), bismuth nitrate-penta-hydrate (2554.4, Carl Roth, Germany).

An SEM image of the commercial Bi-SPE is shown in Figure 1. In the carbon substrate, the white Bi domains are homogeneously distributed.



**Figure 1.** SEM image of a Bi-SPE (courtesy of Metrohm/DropSens). The white particles are agglomerates of Bi on carbon substrate.

Figure 2 shows the XPS spectrum of the electrode after the electrochemical reduction of  $\text{Bi}_2\text{O}_3$  in an alkaline solution.



**Figure 2.** XPS of electrochemically reduced  $\text{Bi}_2\text{O}_3$  in an alkaline solution at -1.4 V for 300 s with formation of Bi. The formation of Bi can be identified by the shoulders at 163 eV and 158 eV ( $4f_{5/2}$  and  $4f_{7/2}$ ). With kind permission from Metrohm/DropSens.

Typically, two types of voltammetric measurements are used.

#### a) Square wave voltammetry (SWV)

SWV is a type of electrochemical technique used to measure the concentration of an analyte in a solution. It is a highly sensitive method that is widely in use in the field of electroanalysis. After deposition, a voltage is applied to an electrochemical cell containing the analyte of interest. The waveform consists of a series of square-wave pulses (sawtooth) which are superimposed on a linear sweep of the voltage. The SWV applies a potential of height  $E_{\text{amp}}$  which varies according to the potential step  $E_{\text{inc}}$  and the duration  $t_2 - t_1$ . The current is measured at the end of the direct ( $t_1$ ) and reverse ( $t_2$ ) pulses and the signal is obtained as the intensity of the resulting differential current. This technique offers excellent sensitivity by high rejection of capacitive (= non-faradaic or charging of the Helmholtz double layer) background current, resulting in a high signal-to-noise ratio. This is due to the faster time constant of the capacitive current compared to the faradaic

current (which causes the redox reaction at the surface) [12].

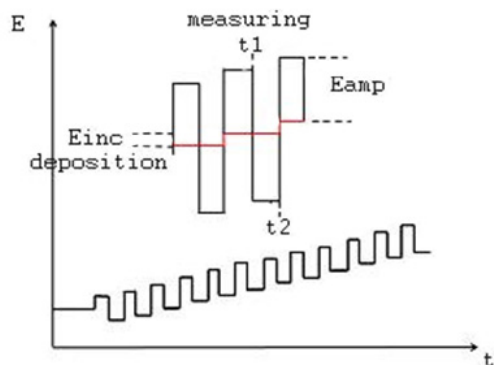


Figure 3. SWVs potential curve with variable parameters.

### b) Differential pulse voltammetry (DPV)

The DPV applies a potential of height  $E_{\text{pulse}}$  which varies according to the potential step  $E_{\text{step}}$  and the duration  $t_{\text{pulse}}$ . As the name suggests, in DPV currents are measured just before each potential change ( $i_1$ ) and at the end of the applied pulse ( $i_2$ ). Unlike SWV, the time between two pulses ( $dt$ ) is much longer than the pulse duration ( $t_{\text{pulse}}$ ). As in SWV the current difference is plotted as a function of potential. The capacitive background in DPV can also be reduced in this way.

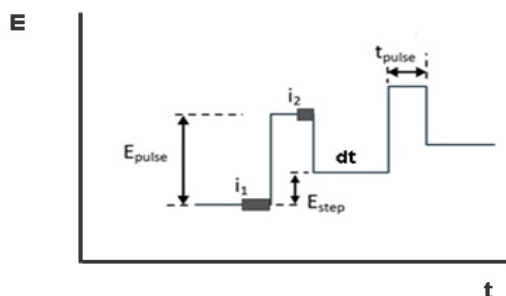


Figure 4. DPVs potential curve with variable parameters.

The analytical power of both methods is comparable.

## 3. Results

Metrohm/DropSens proposed an electrochemical formation of Bi-SPE by applying -1.4 V for 300 s in an alkaline solution to form a Bi film on the electrode.

The SWV (Figure 5) of an acidic (HCl)  $\text{Cd}^{2+}$  solution and the EIS spectrum (Figure 6) show the difference between unformatted and electrochemically formatted Bi-SPE. In contrast to the Metrohm/DropSens proposal, we do not find a significant effect of the formation. This is due to the fact that the deposition process not only concentrates the metal under investigation, but also reduces the  $\text{Bi}_2\text{O}_3$  deposited on the carbon substrate in the commercial electrode.

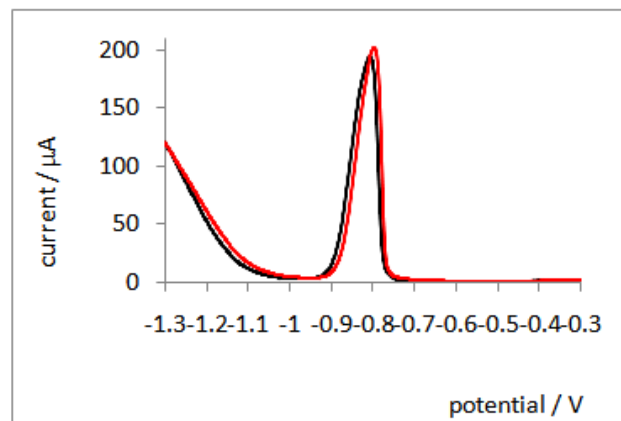


Figure 5. SWV of formatted (red) and unformatted (black) Bi-SPE. Formation with NaOH solution at -1.2 V for 120 s. SWV-Parameters:  $E_{\text{amp}} = 0.05$  V, frequency = 5 Hz,  $E_{\text{cond}} = 0.5$  V, 30 s,  $E_{\text{dep}} = -1.3$  V, 120 s.

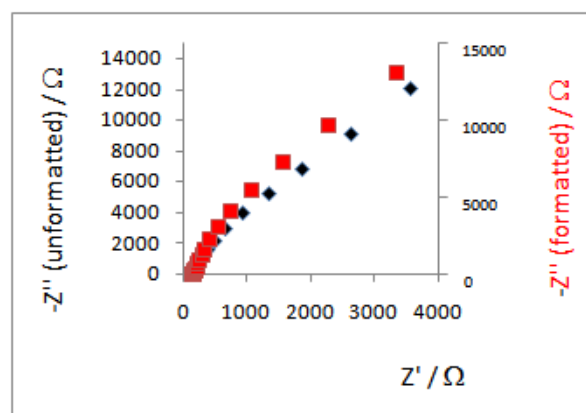


Figure 6. EIS spectra of unformed (black) and formed Bi-SPE (red). Only at high frequencies is the impedance of the formed Bi-SPE slightly lower.

Figure 7 shows the result of the flowing oxidation charge for different deposition times (left side), Figure 7 the estimation of the surface coverage (right side).

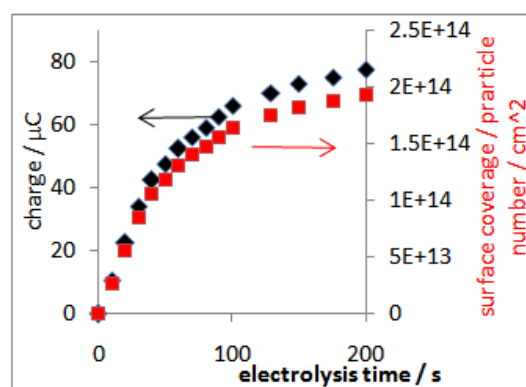
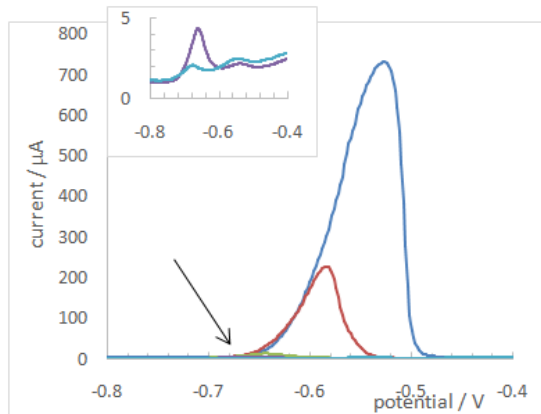


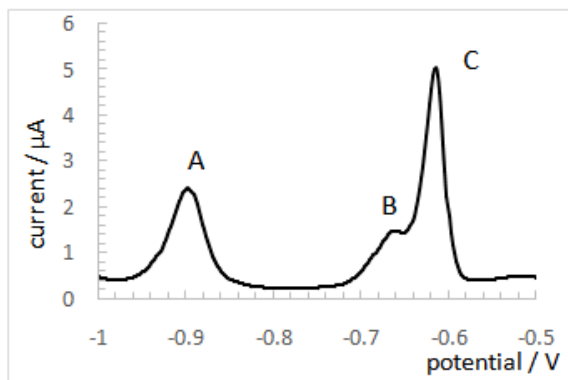
Figure 7. Black: Charge of the oxidation of  $\text{Cd}^{2+}$  as a function of the deposition time ( $c(\text{Cd}^{2+}) = 0.1$  ppm). Red: Estimated surface coverage =  $Q/(F \cdot A)$  in particles /  $\text{cm}^2$ , with surface area  $A = 2.5$   $\text{cm}^2$ ,  $F$ : Faraday constant.

The SWV curves for selected lead concentrations are shown in Figure 7, the SWV of a mixture of cadmium, lead and tin (same concentration) is shown in Figure 8.



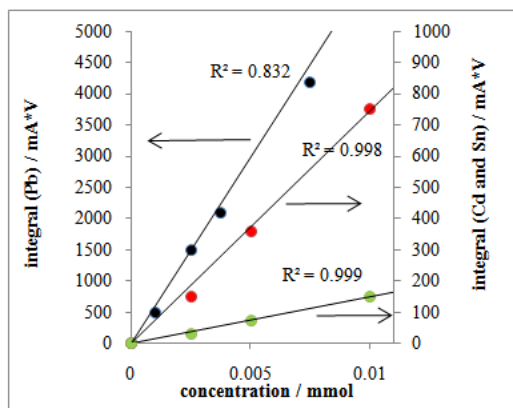
**Figure 8.** SWV of lead at different concentration. Parameters:  $E_{amp}=0.05$  V,  $E_{step} 0.002$  V, frequency= 5 Hz,  $E_{cond}: 0.5$  V, 30 s,  $E_{dep}: -1.2$  V, 120 s.

Due to the slight difference between the standard potentials of lead and tin (-0.13 V and -0.14V), the tin signal appears as a shoulder to the lead signal. The difference between the tabulated and measured standard potentials is due to the different references (normal  $H_2$  vs. Ag/AgCl) and the overpotential of the metal deposition on bismuth.



**Figure 9.** SWV of  $Cd^{2+}$  (A),  $Sn^{2+}$  (B) and  $Pb^{2+}$  (C) (all concentrations  $10^{-5}$  mol/L). Parameters:  $E_{amp}=0.01$  V,  $E_{step} 0.002$  V, frequency= 1 Hz,  $E_{cond}: 0.5$  V, 30 s,  $E_{dep}: -1.2$  V, 120 s.

The different concentration dependence of lead, cadmium and tin is shown in Figure 10, and the limit of detection (LOD) for lead, cadmium and tin is given in Table 1.

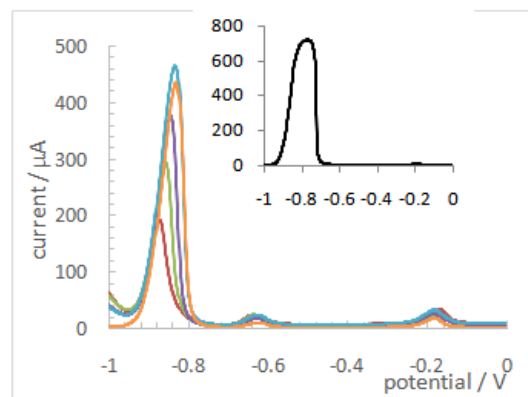


**Figure 10.** Concentration dependence of lead (black circles), cadmium (red circles) and tin (green circles).  $R^2$ : coefficient of determination.

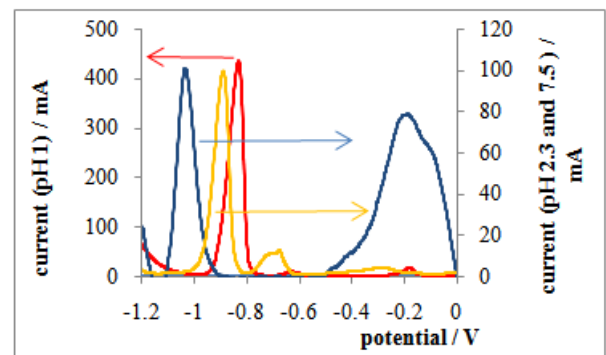
**Table 1. Limit of detection (LOD)**

	Cd	Pb	Sn
LOD (mol)	$< 10^{-11}$	$< 10^{-12}$	$< 10^{-11}$
LOD (mol/L)	$< 2 \times 10^{-8}$	$< 10^{-8}$	$< 10^{-7}$
LOD (g/L)	$< 4 \mu\text{g/L}$	$< 3 \mu\text{g/L}$	$< 10 \mu\text{g/L}$

Figure 11 shows an analytical application of stripping voltammetry: Wood metal (an alloy of Cd (12.5%), Pb (25%), Sn (12.5%), Bi (50%)). The intensity distribution does not reflect the chemical composition of the alloy, although the signals of the four different metals (Cd, Sn (only as a shoulder), Pb and Bi) are present. This becomes particularly evident after stirring the alloy in HCl for one day (inset, Figure 11): Only the cadmium peak appears significantly.



**Figure 11.** SWV of Wood metal after different sampling times. With increasing leaching time, the cadmium current increases, but the other peaks are independent (inset: After one day).

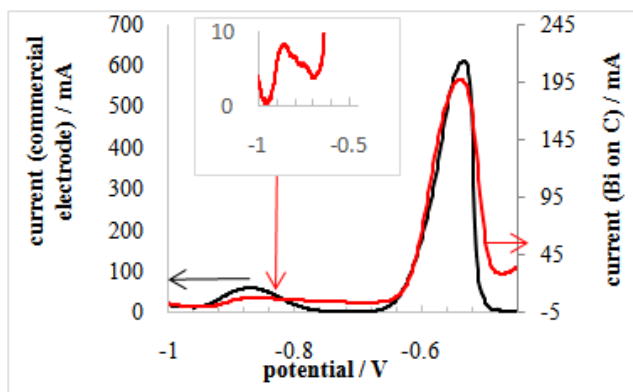


**Figure 12.** SWV of Wood metal at different pH: pH 7.5 (blue line), pH 2.3 (orange line), pH 1 (red line).

Figure 12 shows the pH dependence of the SWV of wood metal. As pH increases, the signals move to lower potentials. Pb, Sn and Bi currents decrease and are less measurable than cadmium. We think this is due to the leaching of wood's metal: Pb, Sn and Bi may be more stable in the alloy than cadmium.

To construct a home-made Bi electrode, a carbon SPE was used and the Bi was deposited onto the electrode by electrolyzing an acidic (HCl)  $Bi(NO_3)_3$  solution at -1V for 120 s. In this solution,  $BiOCl_2$ , a white solid, is formed. However, after a short period of cathodic deposition, the solution becomes quite clear. Figure 13 shows the comparison between commercial Bi-SPE (black line) and Bi coated C-SPE (red line) for Cd and Pb. Note the different y-axis. The intensity of the signals is about three times lower for the homemade electrode and the peaks are

rather larger. This means that the detection limit of the homemade electrode is much lower than the commercial Bi electrode.



**Figure 13.** Cd/Pb SWVs compared between commercial (black line) and homemade (red line) Bi-electrodes. Note the different y-axis.

In summary, a bismuth electrode is a green alternative to mercury for the analysis of heavy metals such as cadmium, lead and tin. The detection limit is in the order of nanomoles. This is comparable to the LOD of mercury or mercury coated SPE, around  $1 \mu\text{g/L}$  [13]. The methods of deposition and analysis described can be easily understood by undergraduate students. The method described can therefore be easily integrated into an electrochemistry course. For safety, the harmful cadmium can be replaced by zinc.

## Acknowledgement

The author would like to thank the Chemical Industry Fund for its support.

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