Determination of Free Metal Ion Concentrations Using Screen-Printed Electrodes and AGNES with the Charge as Response Function

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Abstract
AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has been implemented with screen-printed electrodes (SPE) for the determination of the free concentration of Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$. For SPE, the stripped charge is a suitable response function which does not require the second stage of AGNES to be under diffusion limited conditions. This property can be used in the avoiding of the interference of Pb on [Cd$^{2+}$] determination. The proportionality factor between stripped charge and concentration of amalgamated metal depends on the volume of mercury and opens the way to a future calibrationless strategy. Zn and Cd complexation with oxalate at various pH-values confirms the suitability of the developed methodology, which compares favourable with the standard one based on the Hanging Mercury Drop Electrode.

Keywords: AGNES, Screen-printed electrodes, Speciation, Oxalate, Zinc, Cadmium, Lead

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1 Introduction

The knowledge of the free ion concentrations of metals like Zn, Cd or Pb is key to predict the bio-uptake of trace elements. Consequently, in order to determine the free metal ion concentrations in natural samples, many analytical techniques like diffusive gradients in thin-films (DGT) [1] or Donnan Membrane Technique (DMT) [2] have been developed. These methods agree well with speciation models (WHAM or MINTEQ) [3,4], but need of complementary equipments which, at least at present and in the near future, cannot be moved into the field for in situ measurements of natural waters. Electrochemical techniques such as commercial ion selective electrodes (ISE) are of particular relevance for trace metal studies [5,6], but in their commercial versions lack the required sensitivity and cannot measure Zn. More recently, Galceran and coworkers [7] proposed a new electroanalytical technique typically implemented with the hanging mercury drop electrode (HMDE), the Absence of Gradient and Nernstian Equilibrium Stripping method (AGNES). In AGNES conditions, the stripping stage leads to a measured current just proportional to the free metal ion concentration in the solution. AGNES with HMDE has been used, amongst other applications, to determine free Zn$^{2+}$ concentration in sea [8] and river [9] waters. Obviously, the HMDE is poorly adapted for in situ studies. Consequently, we have undertaken the application of AGNES with thin film mercury screen-printed electrodes (SPE). These sensors represent an ideal alternative to the use of HMDE as i) they are very cheap to produce, ii) can be easily modified in order to enhance its selectivity and/or sensitivity and iii) due to their small size, they could be deployed in situ and, thus, avoid problems of contamination [10–12].

The aim of this paper is to describe how AGNES can be implemented with SPE. To this end, the specific SPE characteristics and the required experimental conditions of AGNES technique will be explored. The application of AGNES with SPE in calibration curves performed in synthetic solutions containing Zn$^{2+}$, Cd$^{2+}$ and/or Pb$^{2+}$ will allow a discussion on the proportionality factors. Finally, the determination of free ion concentrations in synthetic solutions containing a complexing ligand will confirm (via comparison with MINTEQ and with results of the HMDE) the suitability of this implementation of AGNES with SPE.

2 Material and Methods

2.1 Equipment and Reagents

Polystyrene support for serigraphy was obtained from Sericol. Commercial ink (electrodag PF-407A) was purchased from Acheson Colloids. Acetic acid (Trace select), sodium acetate trihydrate (Trace select) and potassium oxalate were obtained from Fluka. Nitric acid (69–70%,
Baker Instra-Analysed for trace metal analysis), sodium hydroxide (Baker Analysed), hydrochloric acid (Baker Instra-Analysed for trace metal analysis) and mercury(II) nitrate (atomic absorption standard) were obtained from J.T. Baker. Potassium thiocyanate (Reagentplus, 99.995%) and mesitylene were obtained from Aldrich. The stock solutions of Cd, Pb and Zn were obtained from Merck.

Working solutions were diluted by using milli-Q water (resistivity of 18 MΩ cm). Acetate buffer solution (0.2 M, pH 4.6) was prepared by mixing appropriate amounts of CH₃COOH and CH₃COONa.

Voltammetric measurements were performed with an Eco Chemie Autolab PGSTAT 10 potentiostat attached to a Metrohm 663 VA Stand and to a computer by means of the GPES 4.9 (Eco Chemie) software package. The working electrode was the SPE or a Metrohm multimode mercury drop electrode, the auxiliary electrode was a glassy carbon electrode and the reference electrode was Ag/AgCl/KCl(3 M), encased in a 0.1 M KNO₃ jacket.

A glass combined electrode (Orion 9103) and Cd ion-selective electrode (Crison, model 9658) were attached to an Orion Research 720A ion analyzer and introduced in the cell to control de pH and the Cd²⁺ concentration, respectively.

A glass jacketed cell provided by Metrohm was used in all measurements. The vessel was thermostated at 25.0°C.

2.2 Preparation of SPE

The electrodes were manually screen-printed on 1 mm-thick polystyrene plates by using a commercial ink to produce an array of 8 electrodes [10]. After a drying step (1 hour at room temperature) and a curing step (1 hour in an oven at 60°C), an insulator layer (polystyrene dissolved in an adequate volume of mesitylene) was spread manually over the conductive track, leaving a working disk area of 9.6 mm² and an electrical contact.

A thin layer of mercury was then deposited onto the electrode surface. The electrode working surface was conditioned by applying 4 cycles of cyclic voltammetry (CV) using the following conditions: potential range from −0.1 V to +0.8 V, scan rate 100 mV/s, step potential 2.4 mV. This step is necessary to obtain a stable baseline. This conditioning was performed in a 0.2 mol L⁻¹ acetate buffer solution containing 1.66×10⁻³ M Hg(NO₃)₂. The Hg film was then deposited at −1.0 V in the same solution, with stirring until the charge associated to the deposited mercury (Qₜₜₒₜ) reached 25mC (unless stated otherwise). To avoid the oxidation of the mercury, a potential of −0.1 V is applied when AGNES potential program (“2 pulses”) has been suggested [14] and applied to different systems such as humic acids [15–17] or wine [18]. Regardless of the number of pulses, at the end of the deposition stage, Nernstian equilibrium is reached and there is no gradient in the concentration profiles at each side of the electrode surface. Nernst equation allows to calculate the ratio of concentrations at each side of the mercury electrode, or gain Y, as:

\[ Y = \frac{[M^0]}{[M^{n+}]} = \exp[-nF/RT \cdot (E_1 - E^*)] \] (1)

where \( n \) is the number of exchanged electrons, \( F \) is the faraday constant, \( R \) the gas constant and \( T \) the temperature.

The aim of the second stage of AGNES is to measure the concentration of reduced metal M⁺ inside the mercury amalgam. For that purpose, in its typical implementation, the amalgamated metal is reoxidated applying \( E_2 \), a much more positive potential than \( E_1 \), during a time \( t_2 \), so that the stripping proceeds under diffusion limited conditions. Due to the lineal properties of the diffusion of the metal inside the amalgam [7], the measured faradaic current \( I \) (obtained by subtraction of a suitable blank from the measured stripping current in diffusion limited conditions) is proportional to \([M^0] \):

\[ I = \eta \cdot [M^0] \] (2)

where \( \eta \) is a proportionality factor, which depends on the elapsed time along the stripping stage and on the characteristics of the diffusion of M⁰ inside the amalgam (shape and size of the mercury electrode and diffusion coefficient). The combination of Equations 1 and 2 yields the proportionality between the faradaic current and the free metal concentration:

\[ I = \eta \cdot [M^0] = \eta \cdot Y \cdot [M^{n+}] = h \cdot [M^{n+}] \] (3)

Different amounts of mercury deposited on the SPE have been tried and the ones reported here provide a good sensibility, stability and repeatability. Higher sensitivities can be reached by electrodepositing larger amounts of mercury (see Section 3.4).

2.3 The Charge as Response Function of AGNES

AGNES is an electroanalytical technique consisting of two conceptual stages: a deposition (first) stage (along which the metal ion M⁺⁺ from the solution is reduced to M⁺ which accumulates in the amalgam) and a stripping (second) stage. The main idea of AGNES is the attainment of a special situation of equilibrium by the end of the deposition stage. This equilibrium can, in the simplest implementation of AGNES, be achieved by applying a potential \( E_1 \), just a few millivolts more negative than the standard formal potential of the couple \( E^* \), for a sufficiently long time \( t_1 \). A more elaborate potential program (“2 pulses”) has been suggested [14] and applied to different systems such as humic acids [15–17] or wine [18]. Regardless of the number of pulses, at the end of the deposition stage, Nernstian equilibrium is reached and there is no gradient in the concentration profiles at each side of the electrode surface. Nernst equation allows to calculate the ratio of concentrations at each side of the mercury electrode, or gain Y, as:

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\[ I = \eta \cdot [M^0] = \eta \cdot Y \cdot [M^{n+}] = h \cdot [M^{n+}] \] (3)
is a proportionality factor which can be determined experimentally by carrying out a calibration.

As detailed in Section 3.1, diffusion limited conditions for the stripping stage cannot be achieved with SPE, so that Equation 3 no longer holds with a constant \( \eta \) for a given time. Alternatively to the standard use of current as response function of AGNES, recent work [13] suggested the use of the stripped (faradaic) charge (\( Q \)). This charge (which corresponds to the total reoxidation of \( M^0 \)) can be easily computed by integration of the faradaic current:

\[
Q = \int_0^\infty I dt_2 \approx \Delta t \left( \sum_{i=1}^{n_{\text{max}}} I_i \right)
\]

(4)

provided that the experimental stripping time (say \( n_{\text{max}} \Delta t \), if we work with a constant interval time and \( n_{\text{max}} \) sampled points) is long enough.

The suitability of the charge as response function of AGNES can follow an alternative derivation to that presented in [13]. This derivation stems from noticing that the charge is proportional to the number of moles of \( M^0 \), which can be computed from its reached concentration and the volume of the mercury amalgam (\( V_{\text{Hg}} \)):

\[
Q = nFV_{\text{Hg}} [M^0] = \eta_0 [M^0]
\]

(5)

where we have denoted by \( \eta_0 \) the new factor of proportionality between charge and reduced metal concentration. Thus,

\[
\eta_0 = nFV_{\text{Hg}}
\]

(6)

One key advantage of the charge as response function is that we can relax the condition of diffusion limited conditions for the second stage of AGNES (as this diffusion limited condition has not been used in the derivation of \( \eta_0 \) (Eq. 5)). Thus, the charge is used in this work as response function of AGNES. Indeed, the charge can also be related to the free metal concentration in the bulk of the solution using the preconcentration gain \( Y \):

\[
Q = \eta_0 [M^0] = \eta_0 Y [M^{\ast}] = h_0 [M^{\ast}]
\]

(7)

Once \( \eta_0 \) (or the new proportionality factor \( h_0 \)) has been determined from calibration plots, the faradaic \( Q \) of the sample can be used to obtain \( [M^{\ast}] \).

2.4 Procedure

AGNES experiments were performed in 0.1 M KNO\(_3\), to fix the ionic strength. Solutions were purged with oxygen-free nitrogen before the application of a sequential combination of chronamperometric methods. Different \( E_1 \) values were selected to reach fixed preconcentration gains. All experiments were performed with mechanical stirring during the deposition stage in order to enhance the effectiveness of the mass transport. \( E_2 \) was computed to reach gains sufficiently low as to practically strip all the metal deposited in the mercury amalgam during the first stage of AGNES (\( Y_1 = 10^{-8} \) for Zn and \( Y_1 = 0.1 \) for Cd and Pb). The measured response is the stripped charge (\( Q \)) along a sufficiently long time \( t_2 \) to be under full depletion regime (less than 50 ms for SPE and less 10 s for HMDE) and can be computed using Equation 4. These times \( t_2 \) are enough, in all cases, to extinguish the faradaic current during the second stage of AGNES and, thus, to ensure the complete reoxidation of the deposited metal. In order to remove other contributions different from the faradaic one (such as the capacitative, \( O_2 \) and other nonanalyte charges), we subtract the shifted blank [8], which consists of applying, to the solution containing the metal, a potential program shifted to a range in which there is no analyte deposition or reoxidation. Usually, the shifted blank deposition potential \( E_{1,sb} \) (for Zn and Pb) corresponds to a very low gain (\( Y_{1,sb} = 0.01 \)) and the stripping potential \( E_{2,sb} \) is applied keeping the same potential jump as in the metal measurement (\( E_{1,sb} - E_{2,sb} = E_1 - E_2 \)). Cd requires a special treatment as discussed in Section 3.5.

3 Results and Discussion

3.1 The Current at a Fixed Stripping Time Cannot be Used as Response Function

When working with HMDE, the standard response in AGNES has been the stripping current under diffusion limited conditions at a fixed \( t_2 \) [7]. The plot of the normalised faradaic currents \( \eta(t_2) = I(t_2)/(Y[M^{\ast}]) \) vs. \( t_2 \) under diffusion limited conditions collapses in just one curve (for a fixed electrode) with a kind of cottrellian-like decay [13]. However, the behaviours of the SPE and HMDE currents found in the present work are very different. Figure 1 shows the normalised faradaic currents along the stripping time (\( t_2 \)) when AGNES was performed in a Zn solution of \( 2.5 \times 10^{-7} \) M in KNO\(_3\), 0.1 M, using a SPE and different depositions gains (\( Y_1 = 100, 200, 500 \) and 1000) under intended diffusion limited conditions (\( Y_1 = 10^{-8} \)). The normalised SPE currents present a peaked shape and differ greatly depending on the applied preconcentration gain. The use of Equations 2 and 3 requires a collapse in a Figure such as Figure 1, so the SPE current cannot be taken as AGNES analytical signal. We conclude that the currents in SPE are not under diffusion limited conditions, even though we apply \( Y_1 = 10^{-8} \). As detailed in [13] anomalous currents also appear in HMDE when the ratio [M\(^0\)] over ionic strength is very large, so we checked here whether an increase in the ionic strength could change the SPE peaked behaviour into the cottrellian-like one. Increasing the ionic strength up to 1 M did not correct the abnormal SPE current. We speculate that there is perhaps a delayed application of the nominal stripping potential (\( E_2 \)) probably due to a relatively large resistance and capacitance of the SPE.
As mentioned before, an alternative response function for AGNES is the stripped faradaic charge which can be computed by subtracting the shifted blank charge \( Q_{sb} \) from the charge of the main measurement. This is the strategy used in the remainder of this work. Further work is needed to establish under which conditions the electro-odic adsorption of organic matter can introduce a difference between the capacitive charges of the main measurement and the shifted blank.

3.2 Calibrations of Zn with SPE

Once established the analytical response to use with SPE, we look for suitable settings for the rest of the experimental conditions of the AGNES technique in order to measure three different metals in aqueous solutions: Zn, Pb and Cd.

First of all, we study the impact of the deposition potential \( E_1 \) and the deposition time \( t_1 \). The deposition time required to reach AGNES conditions depends directly on the chosen gain and, therefore, on the potential \( E_1 \) (see Equation 1). \( E_1 \) should be as less negative as possible in order to have a small gain \( Y_1 \) and, thus, shorter \( t_1 \). But, on the other hand, it is also interesting to have larger \( Y_1 \) and, then, longer \( t_1 \), in order to improve the sensitivity of the technique and to obtain measurable currents even with very low metal concentrations. So, it is necessary to find a compromise between higher and lower values of the gain. We have analysed the stripped charge for different deposition times (from 25 to 1500 s) and for three different gains \((Y_1=500, 1000 \text{ and } 5000)\) with SPE in a solution of \([\text{Zn}^{2+}]=2.0 \times 10^{-6} \text{ M}\) and \([\text{KNO}_3]=0.1 \text{ M}\). Figure 2 shows the recorded charges and, as expected, larger values of the gain require longer times to reach stabilization of the analytical signal: for \( Y_1=5000, 800 \text{ s are needed to reach AGNES conditions (see square markers), whereas for } Y_1=500 \text{ (see triangles), equilibrium is reached at the first assayed } t_1. \) To be on the safe side, we have usually applied a gain of 500 and a deposition time of 400 s.

These results reflect an important advantage of SPE over HMDE: for a fixed desired gain, the deposition times \( t_1 \) needed to reach the equilibrium are considerably shorter when screen-printed electrodes are used. With HMDE and the simplest potential program, the suggested practical rule is \( t_1 = 7Y_1 \) \([19]\), while with SPE much shorter \( t_1 \) times are enough (Figure 2).

With these settings, we have carried out different calibrations in \( \text{KNO}_3 \) for \( \text{Zn}^{2+} \), which show the expected linearity between charge and free metal concentration. The slope of the plots \( Q \) vs free metal provides \( h_Q \) which, divided by the gain, yields \( \eta_3 \) with Equation 5, whose value is 0.320 C/M for Zn.

3.3 Specificities of Cd and Pb Determination

When the settings which worked for Zn \((Y_1=500, t_1=400 \text{ s}, Y_2=10^{-3})\) are applied with Cd, the measured charge along the stripping stage is not constant, but usually keeps increasing with deposition time. The reason of this fact can be found looking with more detail at the potential program: when we preconcentrate Cd, in the first stage, we also accumulate Pb; and, when, during the second stage of AGNES, we apply the reoxidation gain...
Turning our attention to Pb, a stripping potential under diffusion limited conditions implies an $E_{1,\text{sb}}$ value (ca. +0.02 V) which is enough to start the reoxidation of the mercury deposited on the SPE. This problem can be solved by moving the stripping potential to more negative values (e.g. $Y_1=0.1$), as diffusion limited conditions are not required. These conditions have been applied in a calibration of Pb with SPE in which a good linearity between the response function ($Q-Q_\text{u}$) and the free metal concentration is found. The obtained $\eta_Q$ value is 0.318 C/M (Figure 4).

### 3.4 $\eta_Q$-Values are Proportional to the Mercury Volume

We undertook experiments to check the expected proportionality of $\eta_Q$ with the volume of mercury deposited on the surface of a SPE predicted by Equation 6. Calibrations with a solution of Zn in 0.1 M KNO$_3$ were carried out with three mercury film thicknesses (80, 200 and 400 nm) on a SPE with a working surface area of 9.6 mm$^2$. The experimental $\eta_Q$ values increase with the mercury volume (Figure 5), but the value of $\eta_Q$ for the larger thickness is slightly less than expected. We speculate that part of the deposited Hg can fall down from the surface after its deposition, which is more likely for thicker films (which correspond to bigger droplets). So, despite higher $Q_{\text{Hg}}$ would lead to better sensitivities (higher $\eta_Q$ values), in this work we preferred to deposit $Q_{\text{Hg}}=25$ mC (i.e. a thickness of 200 nm) to avoid mercury losses.

Table 1 shows the average of $\eta_Q$-values found in calibrations of Zn, Cd and Pb with SPE. The difference between metals seems not relevant, as there is an intrinsic variability of the $\eta_Q$-values obtained with different SPE’s (i.e. from the calibrations done on different days with different $t$ and $\sigma$ values (e.g. $Zn^{2+}$ and $Cd^{2+}$). This dramatic change of the stripping potential could not have been done if the current was the response function, but, as we are using the charge as response function, there is no need that the stripping proceeds under diffusion limited conditions. The same precautions have been taken into account when applying the shifted blank, whose potential program must be shifted to a range in which there is neither Cd nor Pb deposition or reoxidation ($Y_{1,\text{sb}}=0.1$, $E_{1,\text{sb}}=-0.28$ V, $t_{1,\text{sb}}=50$ s). With these new settings, we have analyzed the stripped charge, with different $t_1$ in the same Cd and Pb solution above mentioned (see circles in Figure 3). As expected from the behaviour of Zn in Figure 2, the equilibrium is now reached very soon.

To confirm the validity of the new potential program, a calibration of Cd with SPE in KNO$_3$ 0.1 M was carried out. A good linearity between charge and concentration was obtained ($r^2=1.000$) with an $\eta_Q$ value of 0.287 C/M.
newly prepared films). This variability between days is accounted for via the initial calibration of the recently prepared SPE.

In order to compare these results obtained with SPE, we have also carried out similar calibrations of Zn$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ using HMDE. The experimental settings have been $Y_1 = 20$ and $t_1 = 140$ s under diffusion limited conditions for Zn and Pb and $Y_2 = 0.1$ for Cd and the obtained results are shown in Table 1. A good linearity of the calibration is obtained ($r^2 > 0.997$). The lower $\eta_O$ values obtained with SPE with respect to HMDE reflect the difference in the mercury volume used in both electrodes, being around 10 times less with screen-printed electrodes, which represents an important advantage of them from an environmental point of view.

These experimental values can be also compared with the theoretical $\eta_O$ values calculated with Equation 6, where the volume of mercury has been computed from the theoretically deposited charge on the electrode (25 mC), molar mass ($M_{\text{Hg}}$) and density of mercury

$$\eta_O = nFV_{\text{Hg}} = Q_{\text{Hg}}M_{\text{Hg}}/\rho_{\text{Hg}}$$  

(8)

In all SPE cases, the experimental $\eta_O$ averages are lower than the theoretical ones (Table 1). Such a difference could be due to an overestimation of the Hg present
in AGNES experiments (which could be less than the nominally reduced mercury due to the falling down of drops or to the current of reduction of O$_2$ and H$^+$ contributing to the measured $Q_{Hg}$) or to inaccuracies in the computation of the gain $Y_1$ (from the peak potential of a Differential Pulse Polarogram, see Equation 10 in [7]). In HMDE case, the experimental $\eta_0$ values and the computed ones are similar.

### 3.5 Speciation Results

To confirm that the combination of AGNES and SPE correctly determines the free metal concentration, speciation experiments of Zn and Cd with oxalate at different pHs have been performed.

The cell initially contained a total Zn concentration of $2.0 \times 10^{-6}$ M, KNO$_3$ 0.1 M and oxalate 0.01 M. The [Zn$^{2+}$] of this mixture at pH between 2 and 7 is shown in Figure 6. The experiments were performed not only with SPE, but also with HMDE in order to compare both electrodes. The gains used during this study are low for expected high free concentrations ($Y_1 = 500–2000$ for SPE and $Y_1 = 20–50$ for HMDE) and high for low free concentrations ($Y_1 = 2 \times 10^{2}–1 \times 10^{3}$ for SPE and $Y_1 = 1 \times 10^{2}–2 \times 10^{3}$ for HMDE). The deposition times $t_1$ could be reduced, taking advantage of the presence of labile oxalate complexes [20] which contribute to the flux, lasting 400 s for SPE and 200 s for HMDE, irrespective of the aimed $Y$. Moreover, the experimental results were compared with the theoretical ones of MINTEQ [3]. The retrieved experimental free concentrations obtained with SPE follow the expected trend computed with MINTEQ and agree with HMDE measurements (Figure 6).

The same kind of study was carried out with Cd. A solution with a total Cd concentration of $3.0 \times 10^{-6}$ M and oxalate 0.02 M in KNO$_3$ was analyzed using AGNES and SPE at different pHs (2–7), using all the special settings explained in Section 3.3 (Figure 7). AGNES conditions were $Y_1 = 500–2000$ for high concentrations and $Y_1 = 5000–10000$ for low concentrations, being the $t_1$ in all cases around 500–600 s. A comparison with HMDE was also performed using $Y_1 = 50–500$ and $t_1 = 300$ s. SPE and HMDE measurements agreed between them and also with Cd-ISE (Figure 7). However, the theoretical free

![Fig. 5. Relationship between the normalised proportionality factor $\eta_0$ and the mercury volume deposited on the working surface area of the SPE obtained with [Zn$^{2+}$] = $7.5 \times 10^{-7}$ mol L$^{-1}$ for four different gains (100, 200, 500 and 1000). The standard deviation calculated from three calibrations obtained with three different SPE.

Table 1. Values of the proportionality factor $\eta_0$ obtained in linear regressions of calibrations and compared with the theoretical expectation according to Equation 6. Gains: $Y_1 = 500$ for SPE; $Y_1 = 20$ for HMDE. Except for Pb, the average and standard deviation of 3 calibrations for each electrode and metal are shown. Estimated HMDE radius: 141 nm.

<table>
<thead>
<tr>
<th>Element</th>
<th>SPE</th>
<th>HMDE</th>
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<tbody>
<tr>
<td>Zn</td>
<td>0.33±0.07</td>
<td>0.37</td>
</tr>
<tr>
<td>Cd</td>
<td>0.32±0.06</td>
<td>0.37</td>
</tr>
<tr>
<td>Pb</td>
<td>0.32</td>
<td>0.37</td>
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concentrations calculated with MINTEQ were higher than the experimental ones. These results suggest that MINTEQ is using not accurate enough Cd-oxalate complexation constants or omitting some Cd complexes formed in the solution.

4 Conclusions

AGNES has been successfully implemented for its use with SPE in Zn, Cd and Pb solutions, which represents a significant improvement in the technique as the screen-printed electrodes are cheaper, smaller and easier to
modify or move to the field than other classical instrumentation such as HMDE.

Due to the abnormal behaviour of the current during the stripping stage, it is not possible to use it as the response function. The stripped charge, which is directly proportional to the free metal ion concentration, can be taken as analytical response.

Suitable AGNES experimental conditions have been found for its use with SPE (25 mC of Hg deposited on a working disc area of 9.6 mm²) and the three aforementioned metals. On one hand, calibrations with Zn have been performed with a gain of \( Y_1 = 500 \) and \( t_1 = 400 \) s with stripping under diffusion limited conditions. On the other hand, Cd and Pb need the stripping potential to be moved to more negative values (\( Y_2 = 0.1 \)) in order to avoid Pb interference (when measuring Cd) or Hg reoxidation (when measuring Pb). Working away from diffusion limited conditions can be done as the charge is now the response function. Further work on the avoiding of the interferences in complex solutions is also timely. Experimental and theoretical data indicate that \( \eta_0 \) values obtained from the calibrations are proportional to the mercury volume. Further work is needed to improve the similarity between theoretical and experimental \( \eta_0 \) values which could allow avoiding the calibrations in some implementations of AGNES.

SPE can achieve a certain gain with much shorter deposition times than HMDE.

Speciation studies of the complexation of Zn and Cd with oxalate show that the combination of SPE and AGNES is a good and very promising technique to measure free metal ion concentrations.

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