Direct determination of free metal concentration by implementing stripping chronopotentiometry as the second stage of AGNES

Corinne Parat, Laurent Authier, D. Aguilar, E. Companys, J. Puy, J. Galceran, Martine Potin-Gautier

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Direct determination of free metal concentration by implementing stripping chronopotentiometry as second stage of AGNES

C. Parat [a*], L. Authier [a], D. Aguilar [b], E. Companys [b], J. Puy [b], J. Galceran [b] and M. Potin-Gautier [a]

[a]*Université de Pau et des Pays de l'Adour, L.C.A.B.I.E., UMR 5254, IPREM, Av. P. Angot, 64053 Pau Cedex 9, France*

[b]*Departament de Química. Universitat de Lleida, Rovira Roure 191, 25198 Lleida, Spain*

*Corresponding author. E-mail: corinne.parat@univ-pau.fr; fax: +33 559 40 76 74

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Abstract

The electroanalytical technique Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) has been extended by applying stripping chronopotentiometry (SCP) as the reoxidation stage in the determination of the free concentration of Zn^{2+}, Cd^{2+} and Pb^{2+}. This new approach, called AGNES-SCP, has been implemented with screen-printed electrodes (SPE) and the standard Hanging Mercury Drop Electrode (HMDE). Clear advantages of this variant have been shown: i) the easy resolution of the peaks of different metals present in mixtures and ii) the sparing of blanks. A rigorous computation of the faradaic charge along the SCP stage takes into account the contribution of other oxidants, which can be efficiently measured at the end of the deposition stage of AGNES. The free Cd concentration determined in an oxalate solution at pH 6 with an HMDE as working electrode agreed well with values obtained with a Cd Ion Selective Electrode. The free metal concentration measured using an SPE for the system Cd and nitrilotriacetic acid (NTA) at pH=4.8 conformed also well with Visual Minteq results.

Keywords: Screen-Printed Electrodes, AGNES, stripping chronopotentiometry, trace metals, HMDE

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1. Introduction

Over the past decades, two equilibrium models, the free ion activity model (FIAM)[1] and the biotic ligand model (BLM)[2] have been developed to predict metal bioavailability and toxicity in environmental systems. In both models, the role of free metal ion concentration can be far more important that the one of the total concentration. Thus, its determination becomes a relevant analytical goal.

However, to date, there is a limited number of techniques[3] able to determine the free ion concentration with the required selectivity and detection limit such as Donnan Membrane Technique (DMT),[4] Complexing gel Integrated microelectrode (CGIME),[5] Permeation liquid membrane (PLM)[6]or Potentiometry with ion selective electrode (ISE).[7] ISE is, in principle, an ideal method for free trace metal determination, because it does not disturb the equilibria and the sample composition during the analytical procedure. Unfortunately, commercial ISEs, which exist only for a limited number of metal ions, generally lack the required sensitivity and suffer from interferences with other metal ions. Other voltammetric techniques, such a cathodic stripping voltammetry, require involved interpretations and the knowledge of several physicochemical parameters in order to yield an estimate of the free metal ion concentrations.

To overcome these limitations in the measurement of free metal concentrations, the electrochemical method Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) has been specifically designed and developed.[8, 9] This method consists of two stages: i) a first deposition stage in which a reduction potential E_1 is applied to accumulate reduced metal into the mercury amalgam until Nernstian and diffusion equilibrium are reached, and ii) a second (stripping) stage where a more positive potential program E_2 is applied, in order to reoxidate and quantify the metal accumulated in the amalgam. Several strategies have been used for this second stage: a)

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a constant potential step (or "pulse") under diffusion limited conditions, to take advantage of the limiting current being independent of the properties of the solution;[8] b) a linear re-oxidating potential sweep;[10] c) or a potential step at any given re-oxidation potential.[11, 12] Although AGNES yields results in good agreement with speciation models[13-15] and has been shown to be adequate for determining the free Zn concentration in natural water samples,[9, 16] previous variants could be affected by the interference from other cations (e.g. Cd^{2+} determination in the presence of Pb^{2+}). Also, in variants a) and c), a measurement of a blank is required to subtract the non-faradaic contribution.

In seeking an alternative second stage which could allow a discrimination of interferences and avoid the blank measurement, classical stripping methods such as "Differential Pulse" (DP), "Square Wave" (SW) or "Stripping Chronopotentiometry" (SCP) programs can be considered. Despite the widespread use of DP or SW, they are unsuitable for the second stage of AGNES as adsorption of organic species on the electrode surface appears as one of the most serious problems to obtain reliable measurements of trace metal speciation.[17-19] Indeed, phenomena such as complexation or adsorption can modify the response in these techniques and, thus, the analytical signal would not be directly proportional to the accumulated metal. On the other hand, SCP seems a better candidate as it does not present these problems (i.e. in its version of "complete depletion"), measures the total accumulated reduced metal and has proved to be a successful stripping technique to acquire information on different "labile" fractions of metals.[20, 21] SCP distinguishes the signals corresponding to the reoxidation of different metals (e.g. Zn, Cd, Pb) and does not require any blank.

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The aim of this paper is to describe the advantages of SCP as stripping method of AGNES (AGNES-SCP) for the free ion concentration determination with both HMDE and Screen-Printed Electrode (SPE). After finding suitable parameters for each kind of working electrode, calibration curves have been performed separately in synthetic solutions containing Zn^{2+}, Cd^{2+} or Pb^{2+}, and then in a mixture of these metals. Performances of each working electrode have been determined. Finally, free metal ion concentrations have been determined in synthetic solutions containing a complexing ligand and compared with results obtained from an ion selective electrode (ISE) and/or expected results computed from Visual MINTEQ.

2. Material and Methods

2.1 Equipment and Reagents

Zn, Cd and Pb 1000 mg L^{-1} stock solutions were obtained from Merck. Potassium nitrate was used as the inert supporting electrolyte at 0.1 mol L^{-1} and prepared from KNO_3 solid purchased from Aldrich (Trace Select). Potassium oxalate and nitrilotriacetic acid (NTA) in the H_3L form were used as ligands (all Fluka, analytical grade). Nitric acid (69-70%, Baker Instra-Analysed for trace metal analysis), sodium hydroxide (Baker Analysed), hydrochloric acid (Baker Instra-Analysed for trace metal analysis) were purchased from Aldrich.

SPE were prepared using a polystyrene support for serigraphy (Sericol), carbon commercial ink electrodag PF-407A (Acheson Colloids) and mesitylen (Aldrich). The mercury deposition on the SPE was carried out using an acetate buffer solution (0.2 mol L^{-1}, pH = 4.6) prepared from acetic acid (Trace select), sodium acetate trihydrate (Trace select) and mercury(II) nitrate 1000 mg L^{-1} (atomic absorption standard) (all obtained from J.T. Baker).

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Ultrapure milli-Q water was employed in all the experiments (resistivity 18 MΩ cm). Purified water-saturated nitrogen N_2(50) was used for dearation and blanketing of solutions.

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 a SPE or a HMDE from Metrohm (to reduce the deposition time, the smallest drop has been chosen, which corresponds to a radius around $r_0 = 1.41\times10^{-4}$ m). The auxiliary electrode was a glassy carbon electrode and the reference electrode was Ag | AgCl | KCl(3 mol L^{-1}), encased in a 0.1 mol L^{-1} KNO_3 jacket.

A glass combined electrode (Orion 9103) and Cd Ion-Selective Electrode (Crison, 9658) were attached to an Orion Research 720A ionanalyzer and introduced in the cell to control the pH and the Cd^{2+} concentration, respectively. Glass jacketed cells, provided by Metrohm, were thermostated at 25.0 ºC and used in all the experiments.

2.2 Preparation of screen printed electrode (SPE)

SPE were manually screen-printed on 1 mm-thick polystyrene plates using a commercial ink to produce an array of 8 electrodes.[12, 22, 23] After drying 1 hour at room temperature and 1 h at 60 °C, an insulating layer (made of polystyrene dissolved in mesitylen) was spread manually over the conductive track, leaving a working disk area of 9.6 mm^2 and an electrical contact.

Then, a thin layer of mercury was electrochemically deposited onto the electrode's surface to allow trace metal detection. First, the electrode's working surface was conditioned in a 0.2 mol L^{-1} acetate buffer solution containing 0.83 mmol L^{-1} $Hg(NO_3)_2$, by applying 4 cycles of cyclic voltammetry (CV) using the following conditions:

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potential range from -0.1 V to +0.8 V, scan rate 100 mV/s, step potential 2.4 mV. The Hg film was then deposited at -1.0 V, with stirring until the charge associated to the deposited mercury (Q_{Hg}) reached 25 mC. Assuming a uniform deposition, the corresponding thickness of the Hg film would be 400 nm. However, a previous study has shown the mercury does not form a true film but rather an assembly of micro-drops.[24]

A potential of -0.1 V was fixed in between experiments in order to prevent mercury reoxidation. A new SPE has been used every day.

2.3 AGNES principles

AGNES consists of two conceptual stages: a first deposition stage along which the metal ion M^{n+} from the solution is reduced to Mº which accumulates in the amalgam up to the attainment of a special situation of equilibrium by the end of it, and a second stripping stage whose aim is the quantification of the reduced metal concentration.[8]

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 $E^{0'}$, for a sufficiently long time t_1. A more elaborate potential program ("2 pulses") has also been suggested to reach the equilibrium faster.[25] In this case, the potential of the first sub-stage ($t_{1,a}$) practically corresponds to diffusion limited conditions, while the potential of the second sub-stage ($t_{1,b}$) corresponds to the desired preconcentration. 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 the concentration ratio at each side of the mercury electrode, or gain Y, to be calculated as:

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$$Y = \frac{\left[\mathrm{M}^0\right]}{\left[\mathrm{M}^{n+}\right]} = \exp\left[-\frac{nF}{RT}\left(E_1 - E^{o\prime}\right)\right] \quad (1)$$

being n is the number of electrons, F the Faraday constant, R the gas constant, T the temperature and $E^{o\prime}$ the standard formal potential of the couple.

The potential corresponding to a given Y can be determined from the peak potential of a differential pulse polarogram (DPP).[8] The higher the gain Y, the higher the sensitivity. However, higher gains will require longer electrodeposition times to reach Nernstian equilibrium.

The goal of the second stage of AGNES is to measure the concentration of the reduced metal M^0 inside the mercury amalgam. The response function can be the faradaic current at a fixed time t_2 (e.g. 0.2 s for HMDE)[8] or the total faradaic charge Q accumulated in the deposition stage.[11, 12]

In order to subtract the non-faradaic contributions to the current or the charge in variants a) and c) (mentioned in the Introduction), the shifted blank[9] has been used in this work. The shifted blank (SB) 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 and keeping the same potential jump as in the metal measurement ($E_{1,\mathrm{sb}} - E_{2,\mathrm{sb}} = E_1 - E_2$).

3. Results and discussion

3.1 Implementation of AGNES-SCP for HMDE

Preliminary studies have been carried out in order to establish adequate experimental conditions to apply chronopotentiometry as the stripping stage of AGNES. In SCP, the analytical signal is the time taken for reoxidation (the transition time τ) while applying a constant oxidising current I_s.[26]

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Depending on the magnitude of I_s, the conditions prevailing during the stripping stage can range from semi-infinite linear diffusion ($I_s\tau^{1/2}$ constant) to the complete depletion regime ($I_s\tau$ constant).[26] These conditions have been probed for HMDE applying stripping currents from 0.01 to 100 nA. All measurements have been performed with deareated solutions of $c_{T,Zn}$ = 10 nmol L^{-1} and with mechanical stirring during most of the deposition stage, in order to enhance the effectiveness of the mass transport. The first AGNES stage has been performed with a two pulse program in order to reduce the deposition time: $E_{1,a}$=-1.2070 V during $t_{1,a}$ = 350 s and $E_{1,b}$=-1.0502 V, which corresponded to a gain Y = 500, during $t_{1,b}$= 1050 s.[25] Fig. 1A shows that whatever I_s, the product $I_s\tau^{1/2}$ never attains a constant value indicating that diffusion limited conditions have not been reached.[26] On the other hand, conditions of complete depletion regime are clearly reached in the I_s around 5-10 nA as a constant product $I_s\tau$ is obtained. When I_s >10 nA, the product $I_s\tau$ decreases due to the lack of full depletion conditions (Fig. 1A). Below I_s = 5 nA, despite corresponding to the complete depletion region, the product $I_s\tau$ decreases because of the influence of oxygen and the chemical oxidation of other non-analyte metals dissolved in the sample (Fig. 1A).[27] In fact, electrons from the oxidation of Mº and from the discharging process (of the electrode acting as capacitor) are either consumed by the oxidants such as traces of oxygen or other interfering cations (also called electroless effect[27]) or fed to the potentiostat (as I_s). Thus, the imposed stripping current (I_s > 0) can be seen as the result of several components: the faradaic current ($I_{faradaic}$ > 0, the one relevant for AGNES purposes), the current due to other oxidants (I_{Ox} < 0, that would also appear in the absence of analyte) and the capacitive current (I_{cap} > 0).[28]

$$I_s = I_{faradaic} + I_{Ox} + I_{cap} \quad (2)$$

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As shown in the Supplementary data: i) measuring the area above the baseline in a dt/dE vs E plot provides an analyical signal (τ) where the capacitive component has already been subtracted; ii) the rigorous expression for the faradaic current leads to the following expression for the charge:

$$Q = (I_s - I_{Ox})\tau \quad (3)$$

Since $I_s > 0$ and $I_{Ox} < 0$, previous equation can be physically understood as the oxidants flux contributing (as "chemical stripping") to the fixed I_s. So, in the reoxidation of the amalgamated metal the "effective" stripping current (I_s - I_{Ox}) is larger than the nominal I_s. Eq. 3 can be seen as equivalent (for this technique) to Eq. (9) in [29].

The traditional product $I_s\tau$ can be, therefore, corrected taking into account the contribution of these other oxidants present in the solution. One advantage of AGNES-SCP is that I_{Ox} can be easily measured in the waiting stage (i.e. quiescent solution), between the deposition with stirring and the stripping SCP stage. In this waiting stage, a t_w of 50 s was found long enough for the practical extinction of the stirring effects. The measured current at the end of this stage, around -0.5 nA, can be used as I_{Ox} for the quantification of the SCP stage. The new corrected plot, representing the faradaic charge (Fig. 1B), shows how $Q = (I_s - I_{ox})\tau$ stabilizes at 0.135 μC even for the lowest I_s values, which confirms that the oxidants contributions can be effectively assessed with the aforementioned procedure. For I_s > 10 nA, complete depletion conditions are not achieved (Fig. 1B). This result has been validated against the stripped charge obtained (Q = 0.131 μC, see horizontal line) in classical AGNES with two pulses (Y_1 = 500, $t_{1,a}$ = 350 s, $t_{1,b}$ = 1050 s, $Y_{1,sb}$ = 0.01, $Y_2 = 10^{-8}$.[11]

On this basis, a stripping current of 1 nA was chosen to perform SCP in AGNES with HMDE, because it corresponds to the horizontally stabilized charge in a region

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sufficiently away from the I_s-interval where the computed charge decreases due to the lack of full depletion.

3.2 Implementation of AGNES-SCP for SPE

Preliminary studies have also been performed with SPE and stripping currents from 0.1 nA to 50 μA have been evaluated in a dearated solution with $c_{T,Zn}$ = 100 nmol L^{-1}. The deposition stage was carried out with a gain Y = 5000 and t_1 = 400 s. These conditions have been previously determined in other published works.[12] The plot of $I_s\tau^{1/2}$ never allowed to obtain a plateau whatever the I_s value (see supplementary data, Fig. S1), indicating that conditions of semi-infinite linear diffusion are not achieved. However, when a I_s in the range of 1 - 20 μA is applied, the product $I_s\tau$ is constant and, thus, under a complete depletion regime. Using these conditions, the slope of the potential E versus time is the same before and after the oxidation which corresponds to a well-defined baseline.[26] All results indicate that a SPE behaves as a microelectrode for which practically achievable conditions always correspond to the complete depletion regime.[30] For I_s lower than 100 nA, the product $I_s\tau$ decreases as the contribution of the other oxidants dissolved in the solution starts being noticeable. A stripping current of 10 μA was retained, since the total accumulated charge is measured and there is no need to apply any oxidants correction as they can be considered negligible ($I_{Ox} << I_s$).

3.3 Calibrations of Zn^{2+}, Cd^{2+} and Pb^{2+} in a solution containing only one metal

Analytical performances of AGNES-SCP with HMDE and SPE have been estimated from calibration curves based on triplicate analyses of each concentration level. These experiments have been carried out by using the conditions previously determined for

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each working electrode (for HMDE, $Y = 500$, $t_{1,a} = 350$ s, $t_{1,b} = 1050$ s and $I_s = 1$ nA; for SPE, $Y = 5000$, $t_1 = 400$ s and $I_s = 10$ μA) regardless of the studied metal. The calibration plots have been performed using the accumulated charge Q which has been computed from the transition time τ obtained during the SCP stage. A good linearity between charge and free concentration has been obtained for Zn^{2+}, Cd^{2+} and Pb^{2+} with both HMDE and SPE. However, as expected when working with HMDE, since the applied I_s is very low, the current due to other oxidants ($I_{ox} \approx$ -0.5 nA) becomes of great relevance and its inclusion to compute to the faradaic charge (Eq. 3) yields a significant improvement of the results (see Table 1 and Fig. S2 in supplementary information). Thus, the retrieved experimental h_Q values for HMDE (with the oxidants correction) and SPE in all the performed calibrations agree favourably with theoretical ones, which can be estimated from the mercury volume V_{Hg}, the number of exchanged electrons (n = 2) and the Faraday constant:

$$h_Q = nFV_{Hg}Y \quad (4)$$

Using Eq. 4, we obtain $h_Q = 1.14$ C/(mol L^{-1}) for HMDE with $Y = 500$ and $h_Q = 1.85$ C/(mol L^{-1}) for SPE with $Y = 5000$. The higher sensitivity of SPE is linked to a higher value of the product of the mercury volume (1.9×10^{-6} m^3) times the applied gain. The normalized sensitivity $\eta_Q = h / Y$ (Tables 1 and 2) for an electrode type (and various metals) is approximately constant, indicating an approximate constancy in the volumes of Hg of each type of electrode. The specific values of η_Q found with AGNES-SCP (Tables 1 and 2) are in good agreement with those previously published.[11, 12]

The limits of detection (LOD) have been statistically calculated for Zn^{2+}, Cd^{2+} and Pb^{2+} and both working electrodes as

$$LOD = \frac{kS_b}{m} \quad (5)$$

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where k = 3, S_b is the intercept standard deviation of the regression line and m is the slope of the calibration graph. The limits of quantification (LOQ) were calculated through the same equation as for the LOD, with the constant k = 10. Values of LOD and LOQ are also gathered in Table 1. Limits of detection obtained for a preconcentration factor of 500 and 5000, for HMDE and SPE respectively, appeared in the nmol L^{-1} range, which is of the same order as those obtained with classical SCP in the study of labile trace metals.[23] LOD and LOQ obtained for SPE are lower than HMDE ones (Table 1). Together with the required shorter deposition times, it clearly highlights the extraordinary performance of the screen-printed electrodes.

3.4 Interference study in a mixture of metals

Since many systems, such as natural waters, are mixtures of different metals, we turn now our attention to possible interferences. In other published work[12], it has been shown that using the charge as response function of AGNES, with a fixed stripping potential (not in the diffusion limited conditions) as second stage, can overcome some difficulties in complex samples, for example, Cd in presence of Pb. The strategy of adapting the stripping potential is efficient, provided that the supply of Pb to the electrode (e.g. either from free Pb or from labile and mobile complexes) is limited. In some cases (e.g. $c_{T,oxalate}$ = 0.02 mol L^{-1}, $c_{T,Cd}$ = $c_{T,Pb}$ = 3 μmol L^{-1}, pH = 6) the measurement was not even possible. Moreover, the presence of interferent metal ions can hinder the finding of suitable blanks and consequently the determination of the capacitive current.

First, the suitability of SCP as the stripping step of AGNES was checked by using a SPE as working electrode. The free Cd analytical signal obtained for a total Cd concentration of 100 nmol L^{-1} has been followed by adding increasing concentrations of Pb (from 50 to 500 nmol L^{-1}). The same experimental conditions as those previously

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303 determined for the monometallic study have been used. As shown in Fig. 2, the peaks
304 corresponding to Cd and Pb were clearly discriminated, although a gradual positively
305 shift of the Cd peak potential was observed when increasing Pb concentration.
306 Nevertheless, there was no difficulty in computing the Cd^{2+} reoxidation time τ which
307 equals to 21.3 ± 0.6 ms.
308 The ability of SCP as second stage of AGNES to handle interferences has been then
309 evaluated by carrying out calibrations of Zn^{2+}, Cd^{2+} and Pb^{2+} with HMDE and SPE in a
310 mixture of the three aforementioned metals. AGNES-SCP has been sequentially applied
311 to each metal (e.g. first with AGNES deposition potential for Zn, then for Cd and finally
312 for Pb) at each calibration point in a solution where the 3 metals reached the same total
313 concentration. The same experimental conditions as those used for monometallic study
314 have been applied and the oxidants correction has also been taken into account when
315 using HMDE as working electrode. As shown in Fig. 3, in all the performed
316 experiments, well shaped peaks were obtained whatever the analysed metal. As in the
317 monometallic study, a good linearity has been obtained between accumulated charge
318 and $[M^{2+}]$ (data not shown). The obtained sensitivities h_Q (Table 2) appeared very
319 similar to those obtained in a solution containing only one metal (Table 1), which
320 indicated that the interferences are negligible on the three metal measurements,
321 regardless the working electrode.
322

323 3.5 Speciation results

324 With HMDE and AGNES-SCP, we have tackled a system that could not be analyzed
325 with a fixed potential in the stripping stage: total cadmium of 3 μmol L^{-1} and oxalate
326 0.02 mol L^{-1} at a fixed pH of 6, in presence of increasing Pb concentrations. Two
327 replicates for three different Pb additions, from 1 to 4.5 μmol L^{-1}, were performed in

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order to check its influence on the determination of [Cd^{2+}]. When applying AGNES variant with two pulses ($E_1 \approx$ -0.63 V, $E_2 \approx$ -0.51V and a shifted blank with $E_{1,sb} \approx$ -0.28 V and $E_{2,sb} \approx$ -0.17 V to avoid Pb^o deposition and reoxidation), the apparent free Cd concentration incresased linearly with each Pb addition (see Fig. S3 in supplementary data). The reason of this undesirable increase is that, when applying E_1, not only Cd^o is preconcentrated, but also Pb^o and both metals are, thus, reoxidated and quantified together during the stripping stage. On the other hand, AGNES-SCP allowed measuring the free cadmium concentration in the same aforementioned samples with no influence of the Pb interference, since SCP separates the signals of Cd and Pb reoxidation. The experimental settings have been $Y = 500$, $t_1 = 300$ s and $I_s = 1$ nA. The deposition time t_1 could be reduced taking advantage of the presence of labile oxalate complexes that contribute to the flux.[31] However, in these experiments, a special situation has been found where determining the typical reoxidation time τ was a challenge as a "distorted" stripping dt/dE peak was obtained (Fig. 4). The baseline of these peaks at the more negative potential could not be recognized. In these cases, we suggest to first compute the total area under the metal peak (thus, including the capacitive current). This total area is called τ' in order to distinguish from τ, which is typically determined by integrating the peak area above the baseline (Fig. 4). Then, the capacitive contribution can be subtracted from τ' (see mathematical details and the underlying assumptions in supporting data) to calculate τ. With this methodology, a free metal concentration of 83 ± 1 nmol L^{-1} (n = 8) has been obtained, indicating that the successive Pb additions have not hindered the proper measurement of [Cd^{2+}]. The oxidants correction was also crucial. These results have been validated using a Cd-ISE, obtaining a free cadmium concentration of 82 ± 1 nmol L^{-1}, which is very similar to the one measured with AGNES (Fig. S3). These experiments are a relevant achievement of AGNES-SCP,

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since this interference could not be avoided when the second stage of AGNES was performed with a fixed stripping potential.

Finally, the performances of AGNES-SCP have been checked with a SPE, by carrying out a speciation experiment of Cd in a KNO_3 solution containing different NTA concentrations at pH 4.8. Prior to the speciation experiment, a calibration was carried out in solutions with total Cd concentration from 50 to 200 nmol L^{-1} (and no NTA) by plotting the faradaic charges against the free Cd concentrations computed with Visual Minteq.[32] Fig. 5 shows that experimental values obtained with SPE agreed well with the theoretical ones.

4. Conclusions

SCP has been used as the second stage of AGNES, allowing the determination of free Zn, Cd and Pb concentrations in aqueous samples. AGNES-SCP has been implemented not only for the hanging mercury drop electrode, but also for the screen printed one, which paves the way to further *in situ* analysis. It has been found that stripping currents of I_s=1 nA, for HMDE, and I_s=10 μA, for SPE, are suitable to work in the required full depletion regime. LOD close to the nmol L^{-1} were obtained for Zn, Cd and Pb with both kinds of electrodes, with good reproducibility. However, SPE appeared particularly promising because of the shorter electrodeposition time needed to reach these low concentrations.

The rigorous computation of the stripped faradaic charge from the recorded evolution of the potential is crucial in retrieving physicochemically sound calibration constants h_Q. This computation requires: i) A suitable reading of τ, which has been customarily taken as the area above the baseline in a dt/dE representation. However, when a large cadmium concentration (1 μmol L^{-1}) and oxalate (0.02 mol L^{-1}) are present in a sample

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at pH 6 and a low stripping current is applied (1 nA), metal peaks appear distorted and τ is not easy to compute. Then, the reading of τ procedure can be generalized by measuring the total area under the dt/dE vs E peak (called τ'), and then subtracting the capacitive component. ii) The taking into account of the oxidants correction; which consists in measuring I_{Ox} at the end of the deposition stage under quiescent conditions and to subtract it from I_s. The oxidants correction can allow to work with lower I_s, which yield larger transition times and improved accuracies. SPE uses so high stripping currents that, in most cases, this correction is negligible.

AGNES-SCP represents an important improvement over other AGNES variants, as it allows working easily in a large range of analyte concentrations, blanks can be spared and metal interferences are easily avoided. Different calibrations and studies with various mixtures of metals or ligands (NTA and oxalate) have been carried out and shown that the combination of SCP with AGNES is a technique suitable to handle interferences and to measure free metal ion concentrations properly.

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TABLE

Table 1. AGNES-SCP performances obtained from a calibration with HMDE (Y=500, $t_{1,a}$ = 350 s, $t_{1,b}$ = 1050 s, I_s = 1 nA) and SPE (Y = 5000, t_1 = 400s, I_s = 10 μA) with five metal concentrations (between 25 and 100 nmol L^{-1}) replicated three times.

		HMDE		SPE	
		from $I_s\tau$	from $Q=(I_s-I_{ox})\tau$	from $I_s\tau$	from $Q=(I_s-I_{ox})\tau$
Zn	Sensitivity h_Q (C/(mol L^{-1}))	0.48±0.02	1.09±0.03	1.86±0.02	1.90±0.02
	η_Q (C/(mol L^{-1}))	0.96×10^{-3}	2.18×10^{-3}	0.37×10^{-3}	0.38×10^{-3}
	LOD / (nmol L^{-1})	8.1	4.0	2.6	2.6
	LOQ / (nmol L^{-1})	27	13.4	8.6	8.5
Cd	Sensitivity h_Q (C/(mol L^{-1}))	0.48±0.02	1.00±0.02	1.40±0.01	1.41±0.01
	η_Q (C/(mol L^{-1}))	0.96×10^{-3}	2.00×10^{-3}	0.28×10^{-3}	0.28×10^{-3}
	LOD / (nmol L^{-1})	11.3	2.9	2.1	2.1
	LOQ / (nmol L^{-1})	37.5	9.8	7.0	6.9
Pb	Sensitivity h_Q (C/(mol L^{-1}))	0.51±0.03	0.99±0.02	1.93±0.01	1.93±0.01
	η_Q (C/(mol L^{-1}))	1.02×10^{-3}	1.98×10^{-3}	0.39×10^{-3}	0.39×10^{-3}
	LOD / (nmol L^{-1})	7.7	4.1	1.1	1.1
	LOQ / (nmol L^{-1})	25.6	13.6	3.7	3.6

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Table 2**.** Values of the proportionality factors, h_Q and $\eta_Q = h_Q/Y$ (in C/(mol L^{-1})), obtained in linear regressions of calibrations with HMDE and SPE in solutions containing a mixture of the 3 metals with equal concentrations. HMDE: $Y = 500$, $t_{1a} = 350$ s, $t_{1b} = 1050$ s, $I_s = 1$ nA; SPE: $Y = 5000$, $t_1 = 400$s, $I_s = 10$ μA. Means and standard deviations correspond to a calibration performed with 5 concentrations (between 0 and 100 nmol L^{-1}) replicated 3 times.

	HMDE			**SPE**		
	h_Q **C/(mol L^{-1})**	η_Q **C/(mol L^{-1})**	η_Q^{12} **C/(mol L^{-1})**	h_Q **C/(mol L^{-1})**	η_Q **C/(mol L^{-1})**	η_Q^{12} **C/(mol L^{-1})**
Zn	1.13 ± 0.02	2.22×10^{-3}	2.32×10^{-3}	1.95 ± 0.02	0.39×10^{-3}	0.33×10^{-3}
Cd	0.99 ± 0.03	1.98×10^{-3}	2.27×10^{-3}	1.45 ± 0.01	0.29×10^{-3}	0.32×10^{-3}
Pb	0.98 ± 0.02	1.96×10^{-3}	2.42×10^{-3}	2.47 ± 0.03	0.49×10^{-3}	0.32×10^{-3}

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FIGURE Caption

Figure 1. A) Behaviour of $I\tau$ (○) and $I\tau^{1/2}$ (×) obtained with a HMDE and B) Stripped charge, applying the oxidants correction shown in Eq. (3). The red horizontal line indicates the charge computed when the stripping stage is a fixed potential pulse under diffusion limited conditions (classical AGNES). $c_{T,Zn}$ = 10 nmol L^{-1}, [KNO_3] = 0.1 mol L^{-1}, Y = 500, $t_{1,a}$ = 350 s and $t_{1,b}$ = 1050s. I_s from 0.01 to 100 nA.

Figure 2. Cd peaks obtained during the oxidation step in AGNES-SCP with a SPE in a solution containing $c_{T,Cd}$ =100 nmol L^{-1} and increasing $c_{T,Pb}$ concentrations from 50 to 500 nmol L^{-1}. [KNO_3] = 0.1 mol L^{-1}, Y = 5000, t_1 = 400 s, I_s = 10μA.

Figure 3. Sequential analysis of [Zn^{2+}], [Cd^{2+}] and [Pb^{2+}] by using AGNES-SCP method with a HMDE for Zn, Cd and Pb total concentrations of 0, 25; 50, 75 and 100 nmol L^{-1}. [KNO_3]=0.1 mol L^{-1}, Y= 500, t_{1a} = 350s, t_{1b} = 1050s, I_s = 1 nA.

Figure 4. Stripping dt/dE vs E plot, in HMDE with Y = 500, t_1 = 300s and I_s = 1 nA, of a solution with total Cd and Pb concentrations of 3 μmol L^{-1} and total oxalate of 0.02 mol L^{-1} at pH = 6. The total shaded area is called τ'; being τ the area above the dashed line and the capacitive component the area below the dashed line.

Figure 5. Free Cd concentration variations in a 0.1 mol L^{-1} KNO_3 solution containing a total Cd concentration of 200 nmol L^{-1} and NTA from 0 to 31 μmol L^{-1} at pH 4.8, determined by AGNES-SCP with a SPE (circle marker, ○) and predicted by Visual MINTEQ (square marker, ■). Y = 5000, t_1 = 400 s and I_s = 10 μA.

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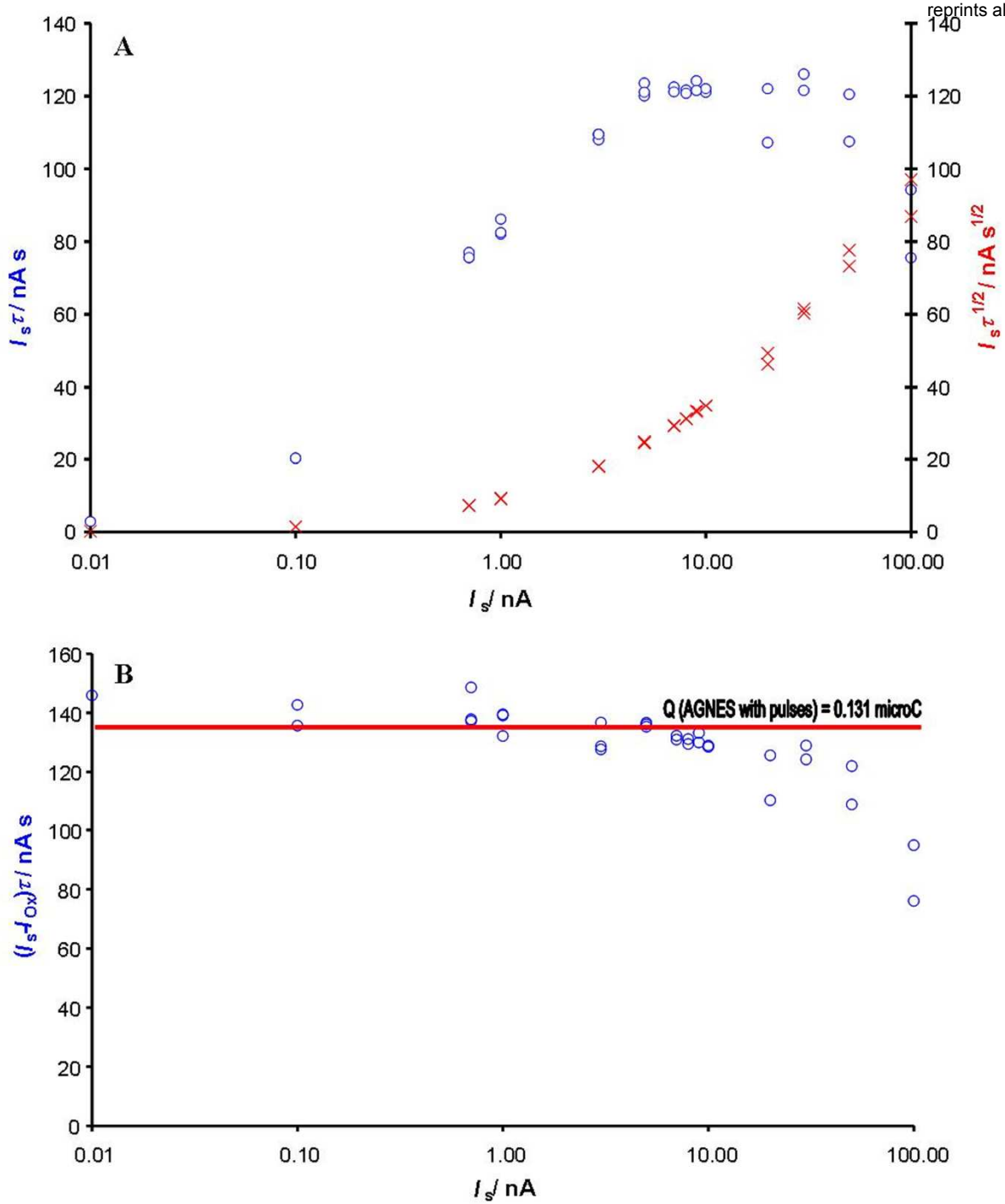

Fig 1

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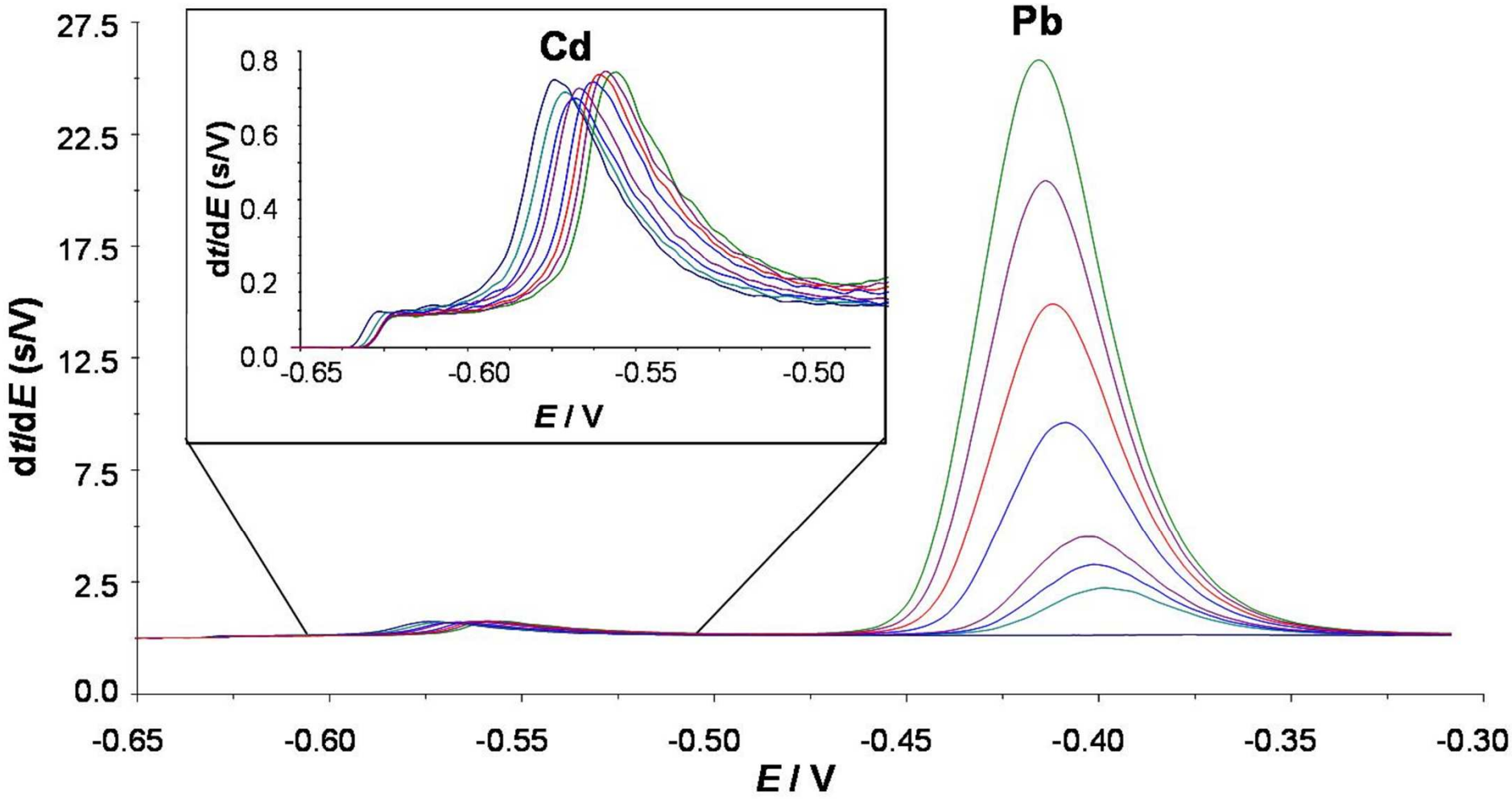

Fig 2

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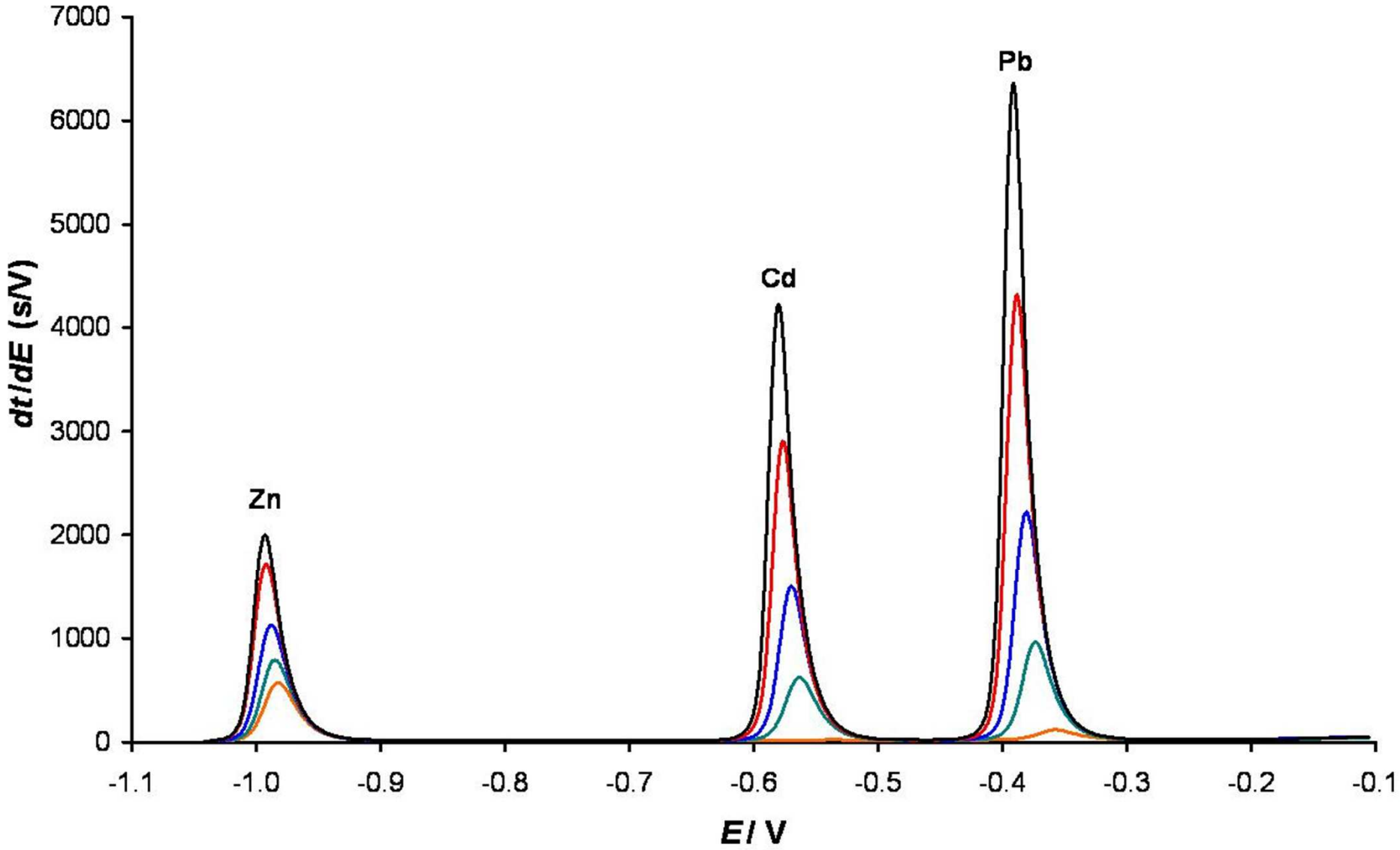

Fig 3

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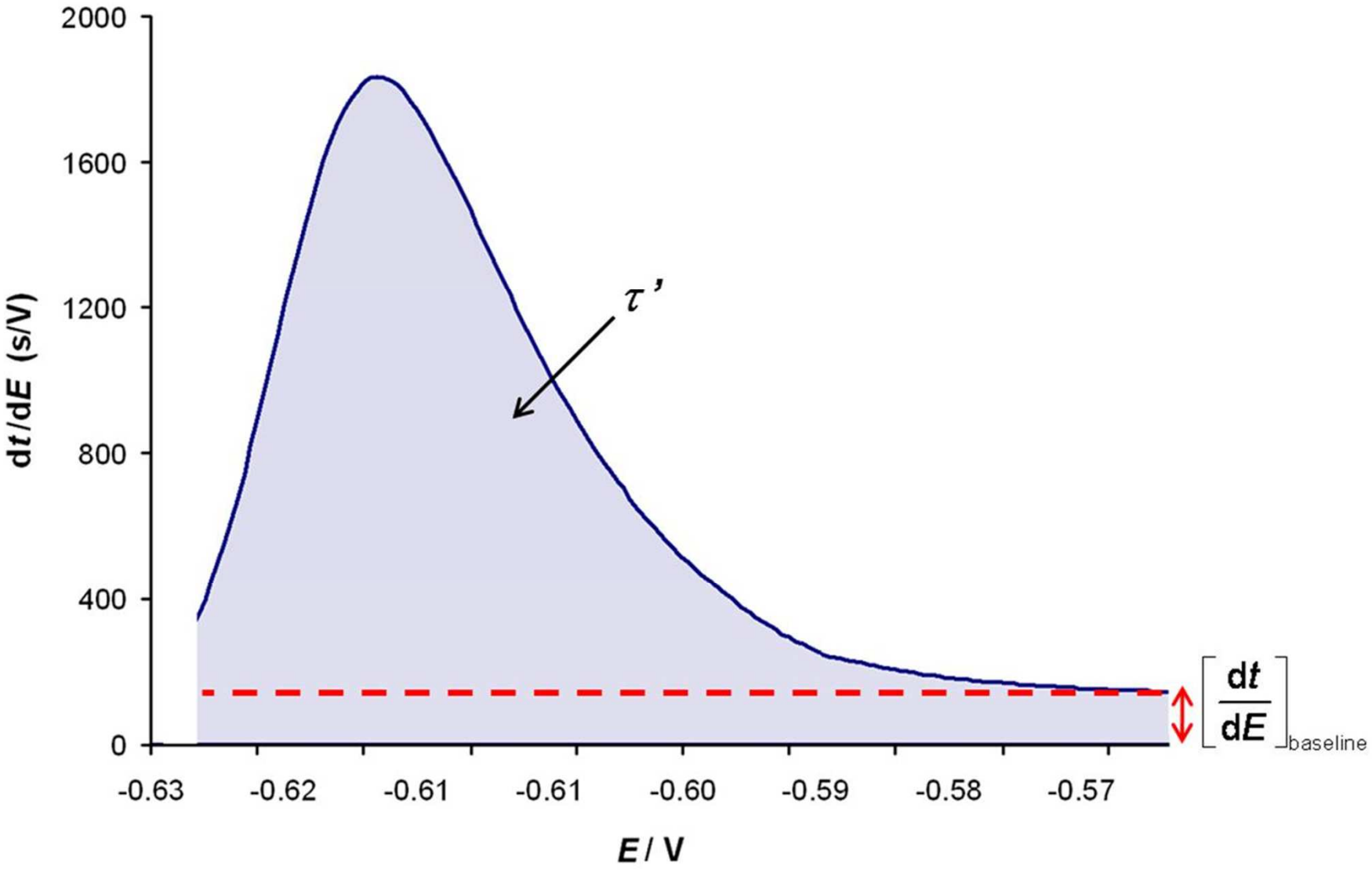

Fig 4

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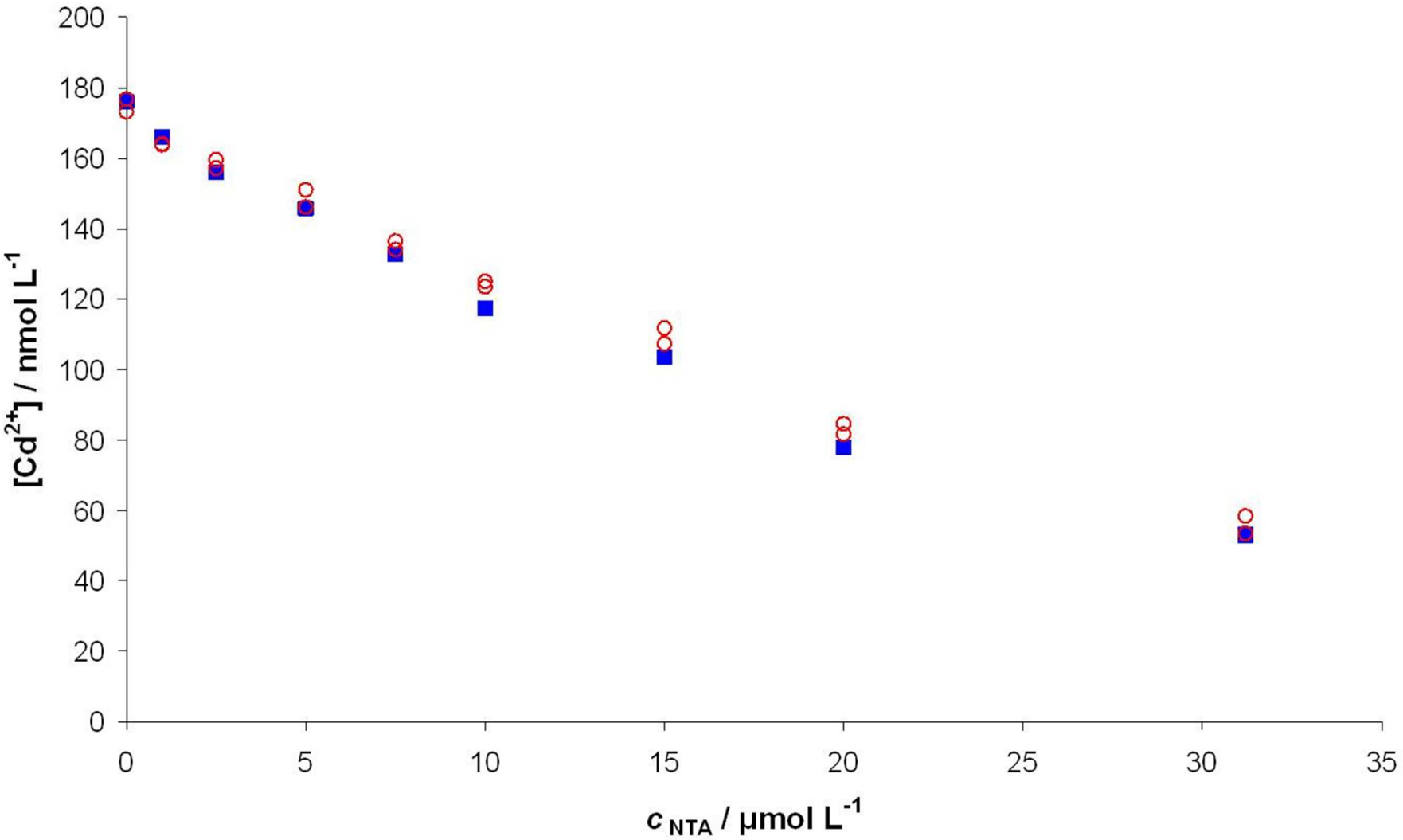

Fig 5