Determination of free metal ion concentrations with AGNES in low ionic strength media

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

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

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

[b]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

*corresponding author. E-mail address: galceran@quimica.udl.cat. Tel.:+34-973-70-28-26; fax:+34-973-23-82-64

Abstract

The determination of free metal ion concentrations of heavy metals, like Zn^{2+} or Cd^{2+}, with AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) requires an adequate selection of parameters such as deposition potential (linked to the gain, $[M^0]/[M^{2+}]$) and deposition time. In systems with low ionic strength, the peak potential of the Differential Pulse Polarogram (DPP) measured with low supporting electrolyte is not always suitable for the computation of the gain with existing expressions. The application of AGNES with a constant potential (regardless of the ionic strength) provides a direct measurement of the metal ion activity. When working with low ionic strength solutions, the selection of appropriate instrumentation is important to avoid changes in liquid junction potentials or leakages from the employed electrodes. The deposition times (for a given gain) have not been found to be greatly affected by the probed ionic strengths when working with just metal. A new strategy for the practical

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implementation of AGNES to measure free metal ion concentrations in samples with low KNO_3 or $Ca(NO_3)_2$ concentrations consists in the computation of the deposition potential (to reach a certain gain) from the DPP peak potential at a sufficiently high ionic strength using a new expression. A speciation experiment with Zn^{2+} and Glycine at pHs between 4 and 7.5, where [KNO_3]=0.001 M, shows that this methodology works well and also proves that it is possible to perform AGNES in systems with very low ionic strength.

Keywords: low ionic strength, electrolyte, free metal concentration, AGNES.

1. Introduction

The knowledge of the free ion concentration of heavy metals such as Zn, Cd, Pb or Cu is very important for understanding the role and fate of nutrient and pollutant elements in natural waters [1]. Indeed, the Free Ion Activity Model [2] or the Biotic Ligand Model [3] highlight the free metal concentration as more relevant than the total concentration which can be determined with well established techniques.

Few methods exist for the free metal ion determination, for instance, ion selective electrodes (ISEs) [4], Donnan Membrane Technique (DMT) [5], Complexing gel Integrated microelectrode (CGIME) [6], Permeation liquid membrane (PLM) [7], etc. In recent years, AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) has proved to be a successful electroanalytical technique to measure free metal concentrations [8, 9]. Some of its advantages are the relatively short time for a measurement and the easy interpretation of the results [8, 9]. AGNES has been implemented with a wide range of electrodes like Hanging Mercury Drop Electrode (HMDE), Ir-Hg microelectrode [10], Mercury Thin Film in Rotating Disk Electrode

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[11] or Screen Printed Electrode (SPE) [12] and has been applied to the determination of Zn^{2+} in samples from seawater [13], relatively polluted river waters [14, 15], wine [16] and the dissolution of ZnO nanoparticles [17] and of Cd quantum dots [18].

The study of solutions, like pristine natural waters or synthetic preparations, with very low supporting electrolyte concentrations can become a challenge since voltammetric and potentiometric measurements can depart significantly from the traditional experiments with higher ionic strengths [19, 20]. In solutions with large amounts of supporting electrolyte, the electric field associated with the potential drop is confined to a narrow interfacial region, and the transport of ions from or to the electrode occurs only by diffusion (electroactive species migration is suppressed, see page 441 in [21]). Furthermore, a high ionic strength also provides a constant activity coefficient. On the other hand, insufficient excess of supporting electrolyte leads to solutions of very high resistance, i.e. the potential drop is not located just at the interphase, but extends into the solution phase leading to migrational effects [20, 22-24]. Additional potential drops at the liquid junction also arise. In solutions with low electrolyte concentration, one option to avoid these problems is the addition of an ionic electrolyte to increase the solution ionic strength, but it might impact on the investigated system by introducing additional chemical equilibria, changes in the activity coefficients and/or contamination.

In a previous work [15], we have determined the free Zn concentration of a natural water with relatively low ionic strength where a standard AGNES procedure proved sufficient. However, the lowest examined ionic strength in that work (0.004 mol L^{-1}) is higher than the ones needed for pristine natural waters or some synthetic solutions. An improvement of the accuracy would also be convenient. In the present work, we aim at a comprehensive physicochemical study on the impact of ionic strength on AGNES analytical signal, in order to develop a general methodology for determining the free

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concentration of heavy metals, like Zn^{2+} or Cd^{2+}, in solutions with ionic strengths between 0.001 and 0.1 mol L^{-1} without the addition of any extra supporting electrolyte. This study includes the impact of different supporting electrolytes, such as KNO_3 and $Ca(NO_3)_2$, to the free metal measurements and the finding of suitable experimental settings for these kinds of samples.

2. Materials and Methods

2.1 Procedures

AGNES consists of two conceptual stages [8, 9]. In the first one, a deposition potential E_1 is applied, for a time t_1, to reduce the analyte metal until a special situation of Nernstian equilibrium, with no concentration gradient at each side of the electrode, is reached. We call gain, Y, to the ratio between the reduced metal concentration inside the amalgam [M^0] and the free metal ion concentration [M^{2+}]. The gain can be computed with Nernst law as:

$$Y = \frac{\left[\mathrm{M^o}\right]}{\left[\mathrm{M^{2+}}\right]} = \frac{\gamma_{\mathrm{M^{2+}}}}{\gamma_{\mathrm{M^o}}} \exp\left[-\frac{nF}{RT}\left(E_1 - E^{\mathrm{o}}\right)\right] = \exp\left[-\frac{nF}{RT}\left(E_1 - E^{\mathrm{o}\prime}\right)\right] \quad (1)$$

where n is the number of electrons involved in the faradaic process, γ_i is the activity coefficient of species i (computed, when necessary, with Davies equation), F is the Faraday constant, R is the gas constant, T is the temperature, E^0 is the standard redox potential and $E^{0\prime}$ is the standard formal potential.

To avoid the explicit finding of E^0 or $E^{0\prime}$, the potential corresponding to a given Y has, up to date, been determined from the peak potential of a differential pulse polarogram (DPP)[8]:

$$Y = \sqrt{\frac{D_{\mathrm{M}}}{D_{\mathrm{M^0}}}} \exp\left[-\frac{nF}{RT}\left(E_1 - E_{\mathrm{peak}} - \frac{\Delta E}{2}\right)\right] \quad (2)$$

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where E_{peak} refers to the potential of the maximum obtained in a typical *I* vs *E* DPP plot, D_M (7.03×10^{-10} m^2s^{-1} for Zn and 7.30×10^{-10} m^2s^{-1} for Cd) is the diffusion coefficient for the free metal ion in solution, D_{M^0} (1.81×10^{-9} m^2s^{-1} for Zn and 1.60×10^{-9} m^2s^{-1} for Cd) is the diffusion coefficients for the reduced metal inside the amalgam (the changes of the diffusion coefficients with the ionic strength have been considered negligible), and ΔE is the modulation amplitude of the DPP experiment.

During the second stage of AGNES, the accumulated metal is reoxidated and quantified.

In the present work, we have applied a constant potential pulse E_2 under diffusion limited conditions, taking the charge *Q* as analytical response to avoid the anomalous stripping behaviours described for low ionic strengths in [15, 25] which could affect the intensity current.

From the combination of Nernst and Faraday laws, the charge can be correlated to the free metal concentration

$$Q = Y\eta_Q\left[M^{2+}\right] \quad (3)$$

where η_Q is a proportionality factor that can be obtained from a calibration plot.

In all cases, it is important to note that there is no need to exactly know the gain *Y* prescribed in the first AGNES stage, because the off-set in the measurement is cancelled out by the off-set in the calibration in the same medium. However, a good estimation of the *Y* helps in searching for adequate deposition times and to check the proportionality factor (η_Q) found in a new calibration with previously reported values [12, 26].

2.2 Equipment and Reagents

Potassium nitrate and calcium nitrate solutions were used as the inert supporting electrolytes to obtain ionic strengths between 0.001 and 0.1 mol L^{-1} and were prepared

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from solid KNO_3 (Fluka, TraceSelect) and $Ca(NO_3)_2$ (Merck, Suprapur). Glycine was obtained from Fluka (ReagentPlus, ≥99%). 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 obtained from J.T. Baker. The stock solutions of Zn and Cd were obtained from Merck (analytical grade).

Ultrapure water (Milli-Q plus 185 System, Millipore) of 18 MΩ cm resistivity was employed in all the experiments. Purified water-saturated nitrogen N_2 was used for deaeration of solutions.

Voltammetric measurements were carried out using 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 Metrohm multimode mercury drop electrode with the largest drop in our stand (drop 3)-if we perform DPPs- or the smallest drop in our stand (drop 1) -if we perform AGNES-, which corresponds, according to the catalogue, to a radius around $r_0=4.23\times10^{-4}$ or 1.41×10^{-4} m, respectively. DPP parameters used in this work have been: modulation time 10 ms, interval time 1 s, step potential 0.00105 V and modulation amplitude 0.04995 V. The auxiliary electrode was a glassy carbon electrode and the reference electrodes were: i) Ag | AgCl | KCl (3 mol L^{-1}) encased in a 1 or 0.1 mol L^{-1} KNO_3 jacket (ref. 6.0726.100 from Metrohm) which, for simplicity, is labelled here as "glass electrode"; ii) Ag | AgCl | KCl saturated 3% LGL agarose gel described in [27]; iii) Calomel with a KNO_3 0.1 mol L^{-1} jacket (ref. 421 from Radiometer Analytical); iv) Ag | AgCl | KCl saturated, without salt bridge, from Origalys Electrochem (ref. E11.OGL.014). During the execution of all the experiments, conductivity measurements were carried out with an Orion 0103010MD probe, from Thermo Scientific, to check the attainment of the different studied ionic strengths. With the Ag | AgCl | KCl (3 mol

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L^{-1}), Calomel or Ag | AgCl | KCl (agarose gel) electrodes, we observed small increases of the conductivity with time (15-20 μS/ hour), during the study of a unique ionic strength, due to a leakage from the reference electrode. The impact of these leakages in the results was so small that they could be considered negligible. With the Ag | AgCl | KCl saturated from Origalys, the sample conductivity increased around 90-120 μS/hour, which can be especially problematic when working with very low ionic strengths (in one hour, the ionic strength of a μ=0.001 mol L^{-1} sample could double).

A glass combined electrode (Orion 9103) was attached to an Orion Research 720A ionanalyzer and introduced sporadically in the cell to control de pH. A glass jacketed cell provided by Metrohm, thermostated at 25.0ºC, was used in all the experiments.

3. Results and discussion

3.1 The use of *Y* computed from the E_{peak} of a DPP at the same ionic strength of the sample medium

Up to date, the standard application of AGNES in a given medium has consisted in the determination of the deposition (and stripping) potentials by using eqn. (2), where the DPP peak potential E_{peak} was determined in the same medium or as close as possible to it. So, according to this classical methodology, to apply AGNES at low ionic strength, one should start by running a DPP in these conditions.

The influence of the supporting electrolyte concentration (KNO_3 or $Ca(NO_3)_2$ in the range 0.001 to 0.1 mol L^{-1}) on the potential peak of a DPP has been evaluated in different solutions with $c_{T,M}=7.5\times10^{-6}$ mol L^{-1} of Zn^{2+} or Cd^{2+}. The jacket/bridge of the Ag/AgCl reference electrode used was filled with a KNO_3 0.1 mol L^{-1} solution. The experiments were carried out with a fixed pH at 5.5 adjusted with the addition of acid or base and the ionic strength, in all the performed experiments, has been computed with

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Visual Minteq [28]. Figure **1** shows how E_{peak} changes with the ionic strength for a Zn^{2+} sample in KNO_3: it increases (i.e. moves towards less negative values) sharply at very low ionic strengths (0.001-0.005 mol L^{-1}) and, after reaching a maximum, the potential smoothly decays for higher KNO_3 concentrations (0.005-0.1 mol L^{-1}). The same kind of results were also obtained with Zn^{2+} in $Ca(NO_3)_2$ as supporting electrolyte (with 0.1 or 1 mol L^{-1} KNO_3 in the salt bridge; data not shown).

On the other hand, measurements of Cd^{2+} in both KNO_3 or $Ca(NO_3)_2$ (Figure SI-1 in the Supporting Information) were also carried out and we observed a general similar trend: the E_{peak} slightly increases for low electrolyte concentrations between 0.001 and 0.007 mol L^{-1} and decreases (more negative values) from 0.007 mol L^{-1} to higher ionic strengths.

The slow decrease of E_{peak} with sufficiently high ionic strength can be explained from the changes in the activity coefficients, see eqns. (7.3.20) and (2.1.45) in [29] and eqn. (5), below. The fast rising behaviour of the DPP peak potential at very low ionic strengths, with Zn^{2+} and Cd^{2+} in both KNO_3 or $Ca(NO_3)_2$, could be partially due to migrational effects and, especially in the Zn^{2+} case, the steep variation could, perhaps, also be associated to the irreversibility of the couple Zn^{o}/Zn^{2+} [30, 31]. For Zn^{2+}, analogous results were obtained with other reference electrodes such as Calomel or Ag | AgCl | KCl saturated from Origalys (Figure SI-2). However, given that the anomalous behaviour with Cd^{2+} has not been observed with Origalys reference electrode (see Figure SI-3), its most likely reason could be a sluggish response in the salt bridge junction. Unfortunately, Origalys has a large leakage (see section 2.2.) and it is not suitable for long experiments with AGNES at low ionic strength.

Following the standard methodology of computing E_1 from the peak potentials of DPP in the same medium (i.e. eqn. (2)), AGNES has been run with HMDE at different ionic

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197 strengths (μ=0.001, 0.002, 0.005, 0.01 and 0.1 mol L^{-1}). The study has been performed
198 with a deareated $c_{T,Zn} = 2.5\times10^{-6}$ mol L^{-1} sample in KNO_3, since, in that medium, Zn^{2+} is
199 the metal that presents a greater E_{peak} change at low electrolyte concentrations (compare
200 Figure **1** with Figure SI-1). Figure **2** shows the accumulated charge, Q, with increasing
201 deposition times t_1, between 100 and 3000 s, aiming at a gain of Y=50. These Q vs t_1
202 trajectories exhibited the typical shape: a fast initial increase followed by an
203 asymptotical tendency towards the stabilized AGNES equilibrium value. Previous
204 published results [8, 9, 32], indicated that, with HMDE and vigorous stirring, a
205 deposition time around seven times the gain is enough for reaching AGNES equilibrium
206 in samples with supporting electrolyte 0.05 mol $L^{-}1$ and higher. However, we see now
207 in Figure **2**, that for very low ionic strengths, the t_1–values needed to reach equilibrium
208 are much longer than those suggested with the rule t_1=7Y: e.g. t_1=2500 s was needed for
209 Y=50 when μ=0.001 mol L^{-1}. This is a warning that the gain aimed in these samples
210 might be higher than the supposedly prescribed one (Y=50).
211 In order to estimate which has been the real gain applied in all the different analysed
212 samples, we can apply Faraday law [12, 26] to find the "real" or "experimental from
213 charge" gain Y_Q

214 $$Y_Q = \frac{Q}{nFV_{Hg}\left[Zn^{2+}\right]} \quad (4)$$

215 where Q is the experimental accumulated charge up to reach Nernstian equilibrium, V_{Hg}
216 is the electrode mercury volume and [Zn^{2+}] is the free analyte concentration (which in
217 this case can be computed with Visual Minteq).
218 Red markers × in Figure **3** show that the gain really applied (Y_Q) was not constant at the
219 different ionic strengths, when the deposition potential was computed with eqn. (2) and
220 the potential peaks obtained from the DPP experiment. The obtained gains follow an

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opposite trend to the DPP peak potentials (compare with Figure **1**): the more negative the measured DPP potential, the more negative the computed E_1 and the higher the resulting real gain. As the electrolyte concentration increases (near 0.1 mol L^{-1}), the real gain begins to stabilize around the value of 50, which is the gain initially intended for all the samples. Comparing Figures **2** and **3**, the deposition times t_1 needed to reach equilibrium follow the aforementioned AGNES rule $t_1=7Y$ for all the ionic strengths studied between 0.001 and 0.1 mol L^{-1} (i.e. using the real gain). This result contrasts with the possibly expected reduction in the deposition times to reach a certain gain for low supporting electrolyte concentrations due to a greater contribution of migration between the working and reference electrodes (section 4.3, p140 in [29]).

Thus, the application of a deposition potential E_1 computed from its corresponding E_{peak}, at low ionic strengths, does not produce the intended gain and could lead to an underestimation of the achieved charge and, therefore, of the free metal concentration if the usual deposition times (rule $t_1=7Y$) was followed blindly (i.e. without checking for the attainment of the sought equilibrium). In experiments in Figure **2**, apart from the inadequacy of the deposition times, the equilibrium charges reached –assuming Y=50– lead to η_Q values ($1.1 \times 10^{-3} - 1.7\times10^{-2}$ C/M) at odds with the standard values for HMDE (around 2.0×10^{-3} C/M [12]) while values in the range $2.0 - 2.3 \times 10^{-3}$ C/M are obtained with the measured gains Y_Q.

These anomalous attained gains seem related to an inadequacy of Zn^{2+} DPPs at low ionic strengths. This fact has been corroborated by plotting the E_{peaks}, obtained from the DPPs between μ=0.001 and 0.1 mol L^{-1}, versus the activity coefficient logarithm (ln $\gamma_{M^{n+}}$). Indeed, combining eqn. (1) and (2),

$$E_{peak} = E^0 + \frac{RT}{nF}\ln\sqrt{\frac{D_R}{D_O}} - \frac{\Delta E}{2} + \frac{RT}{nF}\ln\frac{\gamma_{M^{n+}}}{\gamma_{M^{n0}}} \qquad (5)$$

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which prescribes that the relationship between E_{peak} and $\ln \gamma_{M^{n+}}$ (considering $[M^0]=\{M^0\}$, where $\{M^0\}$ is the metal activity) has to be lineal with a slope close to $RT/(nF)\approx 0.013$ V). Figure **4**, shows the plot corresponding to a $c_{T,Zn} = 7.5\times10^{-6}$ mol L^{-1} in KNO_3 sample (blue squares) where the expected linear behaviour with a slope close to 0.013 V is clearly found at least for ionic strengths equal or higher than 0.01 mol L^{-1}. This indicates that DPP at low supporting electrolyte concentrations cannot be safely used for determining AGNES gains. Similar results have been found for Cd and KNO_3 or $Ca(NO_3)_2$ as the background electrolyte (see Figure **4** red circles). When working with the $Ca(NO_3)_2$ electrolyte, we suggest the use of a reference electrode with a jacket filled with KNO_3 1 M, since DPPs are more reproducible and liquid junction potentials are minimized as observed in the attainment of more accurate Nernstian slopes in the E_{peak} vs. $\ln \gamma_{M^{n+}}$ plots. Our current interpretation of these results is that eqn. (2) was derived taking into account diffusion as the sole transport phenomenon, neglecting migration and the possible sluggishness of the reference electrode. We can conclude that eqn. (2) might be inaccurate for ionic strengths below 0.01 mol L^{-1} when working with Zn^{2+} or Cd^{2+} in KNO_3 and $Ca(NO_3)_2$.

3.2 The application of a fixed E_1 at all ionic strengths

Since, at low ionic strengths, the deposition potentials cannot be computed with eqn. (2), we proceed to study how AGNES behaves when a unique fixed deposition potential (E_1) is applied at different ionic strengths in an aqueous sample. This study will allow us to establish under which conditions AGNES principles can be applied.

3.2.1 Theory for a fixed deposition potential

3.2.1.1 Determining the metal ion activity

Faraday law can be written as

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$$Q = nFV_{\mathrm{Hg}}\left[\mathrm{M}^{\mathrm{o}}\right] \tag{6}$$

Assuming $\gamma_{\mathrm{M}^0} = 1$, Nernst law (1) can be recast as

$$\frac{Q}{\left\{\mathrm{M}^{2+}\right\}} = nFV_{\mathrm{Hg}} \exp\left[-\frac{nF}{RT}\left(E_1 - E^{\mathrm{o}}\right)\right] \equiv f \tag{7}$$

where we have introduced a new proportionality factor *f*. So, when applying a fixed deposition potential, the accumulated charge in AGNES equilibrium is directly proportional to the analyte activity $\{\mathrm{M}^{2+}\}$ regardless of the ionic strength of the medium.

One possible way of implementing AGNES could be to measure the activity with a fixed potential and then, via the estimation of activity coefficients in the medium, compute the analyte concentration. However, in this work, we aim at a direct determination of the free concentration and we will use eqn. (7) only to confirm the range of validity of the obtained results within the current interpretative framework.

3.2.1.2 Relationship between formal potential and activity coefficient

When changing the ionic strength, the formal potential and the standard redox potential are related through (see eqn. 2.1.45 in [29])

$$E^{0\,\prime} = E^0 + \frac{RT}{nF}\ln\left(\frac{\gamma_{\mathrm{M}^{2+}}}{\gamma_{\mathrm{M}^0}}\right) \tag{8}$$

Assuming $\gamma_{\mathrm{M}^0} = 1$, one expects a linear relationship between $E^{0\prime}$ and the logarithm of the activity coefficient with a slope equivalent to $RT/(nF) \approx 0.013$ V at approximately 25ºC. This property will be used next to establish conditions for an adequate AGNES implementation.

In practice, we can compute $E^{0\prime}$ from an AGNES measurement: combining Nernst law (1) with Faraday law (6)

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$$\frac{Q/(nFV_{Hg})}{\left[M^{2+}\right]} = \exp\left[-\frac{nF}{RT}\left(E_1 - E^{o'}\right)\right] \quad (9)$$

so that

$$E^{o'} = E_1 + \frac{RT}{nF}\ln Y_Q \quad (10)$$

where Y_Q is the experimental gain computed with eqn. (4).

3.2.2 Results with KNO_3 as supporting electrolyte

Experiments at fixed deposition potential were carried out in solutions containing $c_{T,M}$=2.5×10^{-6} mol L^{-1} of Zn^{2+} or Cd^{2+}, μ between 0.001 and 0.1 mol L^{-1}, at pH=5.5 and 25.0ºC. A KNO_3 0.1 mol L^{-1} salt bridge was used in the reference electrode. AGNES stripping stage consisted in the application of a fixed potential under diffusion limited conditions (for reoxidation), while E_1 (regardless of the ionic strength of the solution) has been computed using eqn. (2) and the E_{peak} corresponding to the highest electrolyte concentration studied (μ=0.1 mol L^{-1}), aiming at a gain Y=50.

In the studied samples, we have observed that the deposition time needed to reach Nernstian equilibrium in HMDE measurements is around 1000 s for samples with ionic strengths between 0.001 and 0.01 mol L^{-1}, indicating, again, that the experimental gain applied in these solutions (which can be estimated with eqn. (4)) is not the intended one (Y=50) (see the Zn^{2+} case in Figure SI-4). On the other hand, for the KNO_3 0.1 mol L^{-1} sample, the computed experimental gain and the deposition time needed to reach equilibrium (around 400 s) are consistent with Y=50 (Figure SI-4).

With eqn. (10), we computed the corresponding $E^{0'}$ for the samples with the different ionic strengths tested. All the obtained $E^{0'}$, for solutions with Zn^{2+} or Cd^{2+} in KNO_3, follow Nernst law, since their representation versus the logarithm of the activity

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coefficient is linear with the expected slope $RT/nF \approx 0.013$ V (see blue squares in Figure 5) according to eqn. (8).

These results indicate that, under the aforementioned conditions, AGNES can be applied satisfactorily in solutions with very low supporting electrolyte concentrations. For the practical computations, though, one must take into account the change in the activity coefficients (e.g. via Davies equation) at each of the ionic strengths tested.

The same conclusion can be drawn from eqn. 7. It predicts the collapse of curves $Q/\{Zn^{2+}\}$ vs t_1, seen in Figure 6 for sufficiently long deposition times (i.e. once AGNES conditions are reached) in all the studied samples. Very similar results were also obtained with Cd^{2+} (Figure SI-5, blue squares).

This property paves the way for future work where the proportionality factor f in AGNES could be calibrated in activities at a fixed potential at a (comfortable) given ionic strength, and, then, the measured charge in the sample is converted into metal ion activity.

3.2.3 Results with $Ca(NO_3)_2$ as supporting electrolyte

On the other hand, when $Ca(NO_3)_2$ is the supporting electrolyte, we observe the same trends as with KNO_3: applying a fixed E_1 in samples with different ionic strengths between 0.001 and 0.1 mol L^{-1}, does not produce a fixed gain, especially at low ionic strengths.

However, when representing $E^{0'}$, computed at each ionic strength using eqn. (10), versus the activity coefficient logarithm, we observe that the linear behaviour, with the expected $RT/(nF)$ slope, is only fulfilled for ionic strengths lower than 0.01 M (see Figure 5, red circles). In the same way, the f factor, eqn. (7), for these $Ca(NO_3)_2$ solutions, is only constant for μ<0.01 M (Figure SI-5, red circles). We did not observe any improvement in the results when working with other salt bridges concentrations

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(KNO_3 0.1 or 3 mol L^{-1}) or other reference electrodes like Calomel or the gel salt bridge described in [27]. However, the Ag/AgCl reference electrode saturated with KCl from Origalys Electrochem showed a Nernstian linearity for all the ionic strength range studied μ=0.001 – 0.14 mol L^{-1} (Figure SI-6). Compared with the glass reference one, the applicability range of this electrode would be larger if it did not present a large leakage (see Section 2.2.).

The reason for the deviation of $E°'$ from the expected linearity when using $Ca(NO_3)_2$ as supporting electrolyte and μ>0.01 M (see Figure 5, red bullets) is unclear to us. We discard problems derived from a bad estimation of the activity coefficients, since good results were observed in the same range of ionic strengths when measuring DPP peak potentials with the same background electrolyte (Figure 4, red circles). A similar reasoning could discard liquid junction potential, unless the discrepancy in behaviour with $Ca(NO_3)_2$ at μ>0.01 M in Figures 4 and 5 was due to the different time scale (and/or the stirring) of DPP and AGNES measurements (e.g. via a different impact of the uncompensated resistance at low ionic strength in both techniques). We also discard effects of ion pairing association between Ca and nitrate ions, because of the observed linear increase of conductivity with increasing concentration of $Ca(NO_3)_2$.

We conclude that the existing methodologies of AGNES can be applied, when using $Ca(NO_3)_2$ below 0.01 M as supporting electrolyte. For instance, this should not be a problem when studying a freshwater where the total concentration of Ca is usually below 0.01 M.

3.3 The computation of the gain for any ionic strength from a DPP peak at high enough ionic strength

In previous sections, we have explained how, in some cases, E_{peaks} from DPPs at low ionic strengths (μ<0.01 M) are unsuitable for the gain computation and how AGNES

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368 can be applied properly in the low ionic strength range ($\mu \leq 0.01$ M) with Zn^{2+} or Cd^{2+}
369 and KNO_3 or $Ca(NO_3)_2$ as supporting electrolytes. Now, we consider whether it is
370 possible to use the peak potential of a DPP run at a sufficiently high ionic strength
371 (where the DPP follows the behaviour prescribed by eqn. (5), say $\mu \geq 0.01$ as seen in
372 Figure **4**), in order to compute the deposition potential for a certain gain in an AGNES
373 experiment at any other ionic strength.
374 We can equate eqn. (1) for the desired gain at a sufficiently high ionic strength with eqn.
375 (1) for the same gain at another supporting electrolyte concentration:

376 $$\frac{\gamma_{M^{2+}}}{\gamma_{M^0}} \exp\left[-\frac{nF}{RT}\left(E_1 - E^{\circ}\right)\right] = \frac{\gamma_{M^{2+}}^{\mu \geq 0.01}}{\gamma_{M^0}^{\mu \geq 0.01}} \exp\left[-\frac{nF}{RT}\left(E_1^{\mu \geq 0.01} - E^{\circ}\right)\right]$$

377 (11)
378 Combining eqn. (11) with eqn. (2), we obtain an expression that allows the computation
379 of E_1 at any ionic strength, to reach a certain Y, just using the DPP of a solution with
380 $\mu \geq 0.01$ and a correction involving the activity coefficients:

381 $$E_1 = E_{peak}^{\mu \geq 0.01} + \frac{\Delta E}{2} + \frac{RT}{nF} \ln\left(\frac{\gamma_M}{\gamma_M^{\mu \geq 0.01} Y} \sqrt{\frac{D_M}{D_{M^0}}}\right) \quad (12)$$

382 To illustrate this method, eqn. (12) has been used to compute the corresponding
383 deposition potential in AGNES measurements in order to reach a certain gain.
384 Trajectories Q vs t_1 have been studied by applying AGNES to a deareated
385 $c_{T,Zn}=2.5\times10^{-6}$ mol L^{-1} solution with μ=0.001, 0.005, 0.01 and 0.1 mol L^{-1} provided by
386 KNO_3. The corresponding deposition potentials E_1, aiming to Y=50, have been
387 computed using eqn. (12) with $E_{peak}^{\mu=0.1}$ (μ =0.1 has been selected to be on the safe side,
388 but –according to the study in section 3.2– any E_{peak} for μ between 0.01 and 0.1 mol L^{-1}
389 should be also valid). Figure 7 shows the representation of $Q/[Zn^{2+}]$ in front of t_1. The
390 curves for the different electrolyte concentrations tested practically collapse indicating
391 that the achieved accumulation is the same for all the samples at each deposition time.

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Moreover, the accumulated charge reaches AGNES conditions for a t_1 around 350 s (Figure 7), which is the suggested time for a gain Y=50.

On the other hand, with the deposition potentials E_1 values from section 3.1, (obtained from DPPs at different ionic strengths), we can calculate, with eqn. (12), the theoretical gain applied in the AGNES experiment (blue circles in Figure 3). These theoretical Y values compare very well with the experimental ones (Y_Q, × marker in Figure 3) obtained with eqn. (4).

3.4 Practical strategies

We discuss here a possible strategy to determine the free metal ion concentration in a sample, synthetic or natural, at known low ionic strength (i.e. we assume that we can estimate or compute the value of the activity coefficient of the metal ion in the sample; e.g. when the ionic strength of the sample could be estimated from its conductivity [33]).

At very low ionic strengths, we have observed that for Zn or Cd with KNO_3 or $Ca(NO_3)_2$ as the background electrolytes, the use of DPP is problematic and could lead to large errors in the deposition potentials or times and, thus, in the equilibrium charge.

Therefore, we suggest a general methodology to apply AGNES in low ionic strength samples. First of all, we obtain the DPP peak potential in our experimental setup with a high ionic strength ($\mu \geq 0.01$ mol L^{-1} fixed, for instance, with KNO_3). With this $E_{peak}^{\mu \geq 0.01}$, we apply eqn. (12) to estimate the corresponding deposition potential E_1 and deposition time t_1 (for both calibration and measurements), at the sample's low ionic strength, to reach any desired gain Y. This estimation is very convenient to have a good guideline of the required deposition time to reach equilibrium and helps avoiding the performance of a full trajectory experiment (similar to the one shown in Figure **2**) which is quite long

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when using HMDE (especially if the Y is rather high). Then, we calibrate our system using solutions of known free metal ion concentrations at the same ionic strength of the sample and assuming the Y previously aimed with eqn. (12). The obtained η_Q value should be similar to those found for high ionic strengths and should be comparable to other published results [12]. Finally, in the sample measurement (e.g. river water), AGNES can be applied using a desired gain (Y) whose corresponding deposition potential can be computed with eqn. (12) and $E_{peak}^{\mu \geq 0.01}$. With the measured accumulated charge Q_{sample} and the previously found η_Q constant from the calibration, the free concentration of metal [M^{2+}] can be obtained using eqn. (3). Errors in the estimation of the gain Y could appear, but they are not a problem at all, provided that one checks that the used deposition times are enough to reach Nernstian equilibrium. The effect of the uncompensated resistance, arising between the working and the reference electrode due to the low ionic strength of the electrolyte solution, could slightly affect on the determination of the E_{peak} in a DPP measurement and could lead to a small error in the estimation of the gain Y. However, the final error in the determination could be much less than the imprecision in the gain Y, since the error in the gains cancels out between calibration and measurement. This uncompensated resistance does not affect neither to the AGNES deposition stage, since the measured intensity tends to zero once equilibrium is reached, nor to the stripping stage, as we work under diffusion limited conditions (and a small variation of the stripping potential is negligible).

To check how reliable are AGNES experiments in low ionic strength samples, we have applied this new strategy to the measurement of the free Zn^{2+} concentration in a solution containing $c_{T,Zn}=3.0\times10^{-6}$ mol L^{-1}, glycine 0.01 mol L^{-1} and [KNO_3]$=9\times10^{-4}$ mol L^{-1} at different pHs (4-7.5).The ionic strength in all the performed experiments has been 0.001 mol L^{-1}. The experimental settings have been E_1=-1.0980 V (computed

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using eqn. (12) with $E_{peak}^{\mu=0.1}$=-0.9590 V and aiming at Y=50) during t_1=350 s and E_2=-0.7534 V, under diffusion limited conditions. The retrieved free Zn^{2+} concentrations at the different pHs studied are in good agreement with the theoretical ones computed with Visual Minteq (Figure 8). This experiment demonstrates how it is possible to perform AGNES measurements in systems with very low supporting electrolyte concentrations.

4. Conclusions

In the present work, AGNES technique has been implemented to measure free concentrations of heavy metals (such as Zn^{2+} or Cd^{2}) in very low ionic strength synthetic systems using both KNO_3 and $Ca(NO_3)_2$ as supporting electrolytes. We have observed that the peak potentials of the DPPs performed at μ below 0.01 mol L^{-1} could be not suitable for the computation of the deposition potential E_1 needed to prescribe an intended gain Y when working with Zn^{2+} or Cd^{2+} in both electrolytes. Although the exact knowledge of the applied Y is not strictly necessary (provided that AGNES calibration and measurement use the same E_{peak}, E^0 or $E^{0'}$), the estimation of a good value is very helpful in establishing adequate deposition times t_1 that ensure Nernstian equilibrium and in checking the obtained proportionality factors with those in the literature.

The accumulated charges in AGNES, when applying the same fixed deposition potential at different ionic strengths, strongly depend on the supporting electrolyte concentration, due to the changes in the metal ion activity. We have shown that the metal ion activity can be directly measured with AGNES using a constant deposition potential E_1 (see eqn. (7)). The quotient $Q/\{M^{2+}\}$ appears to be constant in the low ionic strength range ($\mu \leq 0.01$ mol L^{-1}), for a fixed E_1 and sufficiently long deposition time for both KNO_3 and $Ca(NO_3)_2$ as background electrolytes (see, for example, Figure 6). So,

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one possible strategy (not developed here) with AGNES consists in first measuring the activity and, then, computing the concentration.

For directly measuring the free concentration (see section 3.4) in the range $\mu \leq 0.01$ mol L^{-1} with HMDE, we suggest a new general methodology, for both metals and both supporting electrolytes, consisting in the use of equation (12), which allows estimating the deposition potential at any ionic strength to reach a certain Y, using a proper DPP peak at a high ionic strength ($\mu \geq 0.01$ mol L^{-1}). When working with so low ionic strengths, special care has to be taken to avoid changes in liquid junction potentials or leakages from the used electrodes. In this work, a reference Ag | AgCl encased in a 0.1 mol L^{-1} KNO_3 jacket was employed and the aforementioned problems were considered negligible, but a salt bridge solution of 1 mol L^{-1} KNO_3 was specifically appropriate for solutions with $Ca(NO_3)_2$ as background electrolyte. We have not found any relevant impact of ionic strength on the deposition time required for AGNES equilibrium, so the standard rule $t_1=7Y$ is applicable at all assayed concentrations of supporting electrolyte (provided that the real Y is used).

Eqn. (12), which can be seen as an extension of eqn. (2), represents a step further towards the application of AGNES to systems with low ionic strength. A speciation study in a system containing Zn^{2+} and glycine with μ=0.001 M, at pHs between 4 and 7.5, confirms the validity of the new methodology and the possibility of applying AGNES to solutions with very low supporting electrolyte concentrations.

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Figures

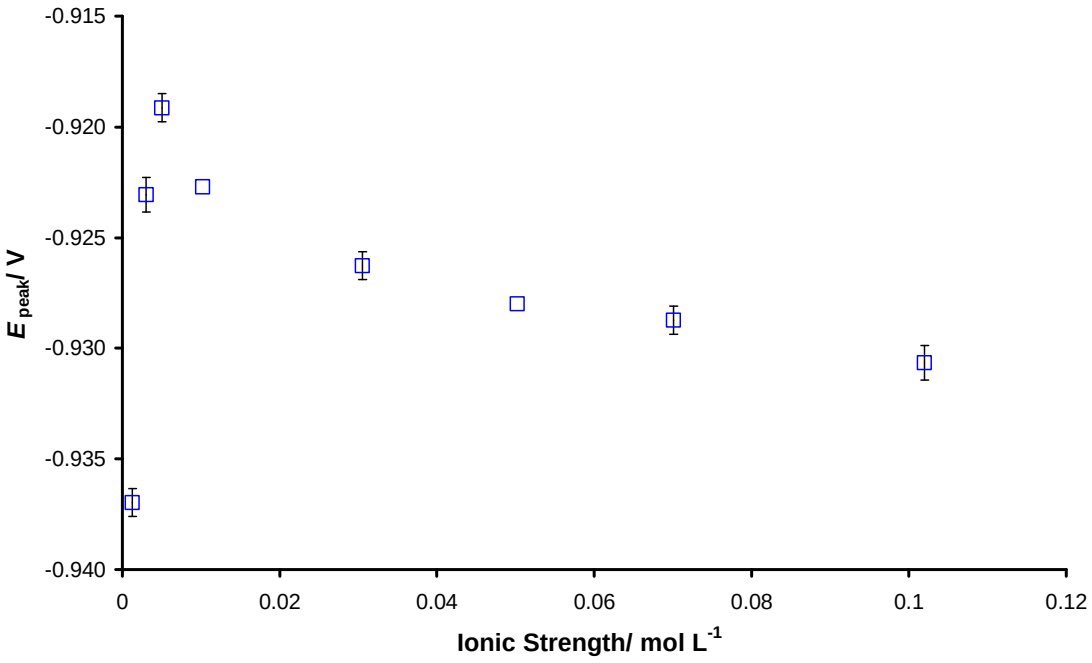

Figure 1. Peak potentials from different DPPs performed in a $c_{T,Zn} = 7.5\times10^{-6}$ mol L^{-1} solution with KNO_3 as supporting electrolyte and ionic strengths between 0.001 and 0.1 M at pH=5.5. Reference electrode with KNO_3 0.1 mol L^{-1} in the salt bridge. Three different replicates of each measurement have been performed and the standard deviation is shown whenever larger than the marker.

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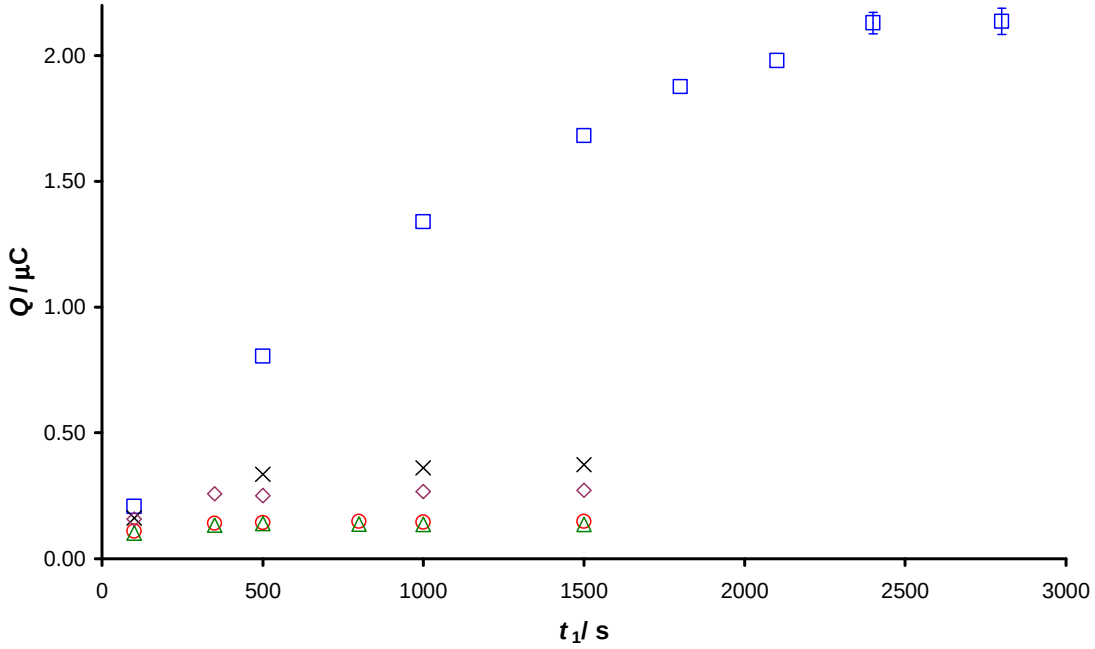

565

566 **Figure 2**. Trajectories Q vs t_1 for different solutions containing $c_{T,Zn}$ = 2.5×10^{-6} mol L^{-1}
567 and KNO_3 = 0.001(□), 0.002(×), 0.005(○), 0.01(Δ) and 0.1(◊) mol L^{-1} at pH = 5.5.
568 AGNES deposition potential has been computed using eqn. (2) with the corresponding
569 E_{peak} at each electrolyte concentration and aiming at Y=50 (though the real gain was
570 different, see text). KNO_3 0.1 mol L^{-1} was used as the salt bridge in the reference
571 electrode. Two replicates have been carried out and the standard deviation is shown
572 whenever is larger than the marker.

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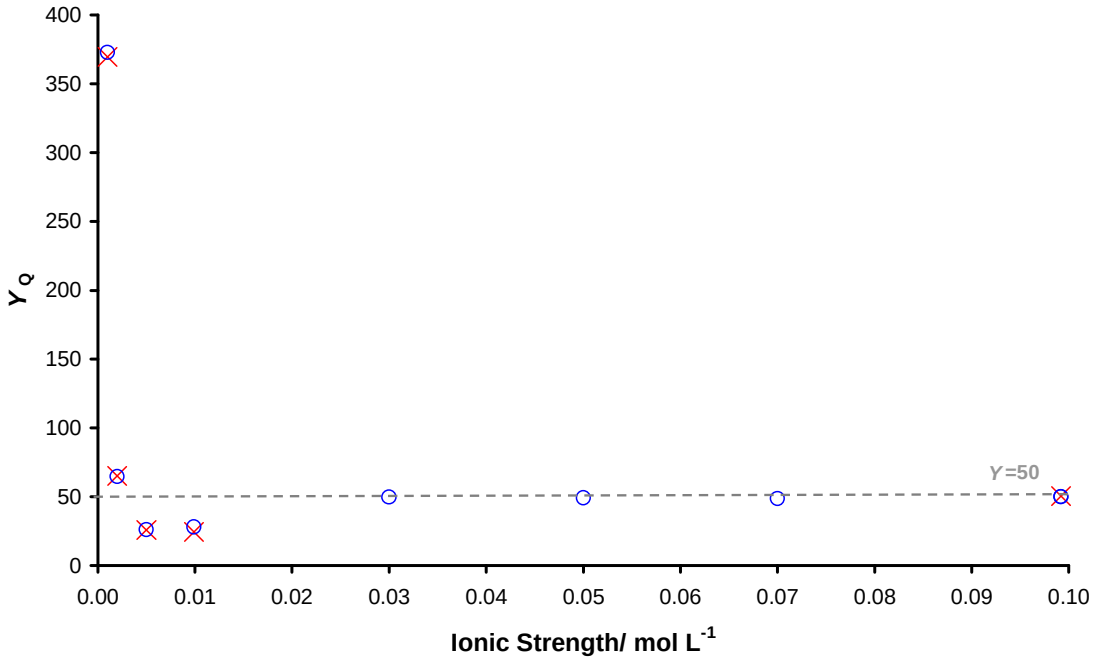

574

575 **Figure 3**. Comparison between the aimed (*Y*=50, horizontal dash line) and the attained
576 gains (×, using eqn. (4) and the DPP peaks at the same ionic strength from Figure 1).
577 $c_{T,Zn}$=2.5×10^{-6} mol L^{-1} in KNO_3 as supporting electrolyte. The blue circles (○) stand for
578 the theoretical gain computed with eqn. (12). Reference electrode with a KNO_3 0.1 mol
579 L^{-1} jacket.

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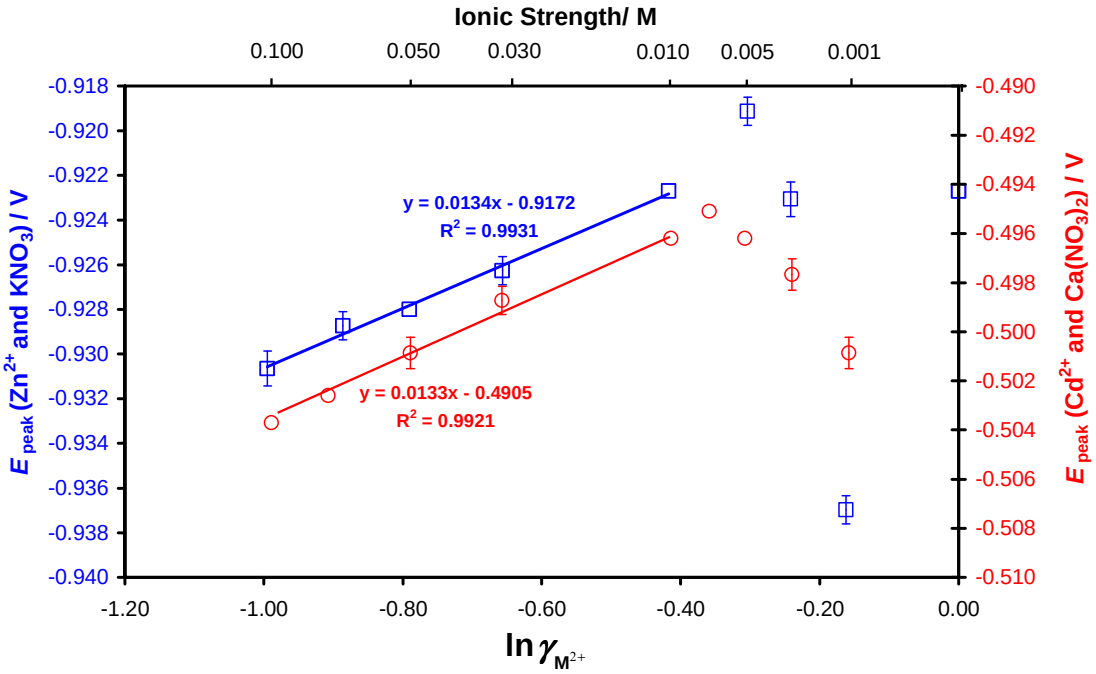

Figure 4. DPP E_{peak} in front of the activity coefficient logarithm in a solution containing $c_{T,Zn}$=7.5×10^{-6} mol L^{-1} and KNO_3 as supporting electrolyte (referred to the left hand side axis, □) or $c_{T,Cd}$=7.5×10^{-6} and $Ca(NO_3)_2$ as supporting electrolyte (referred to the right hand side axis, ○). The ionic strengths studied were between 0.001 and 0.1 mol L^{-1} (see upper horizontal axis) at pH = 5.5. Reference electrode with salt bridge KNO_3 0.1 mol L^{-1} (for KNO_3 background electrolyte) or 1 mol L^{-1} (for $Ca(NO_3)_2$ background electrolyte). Three replicates have been carried out and the standard deviation is shown whenever larger than the marker.

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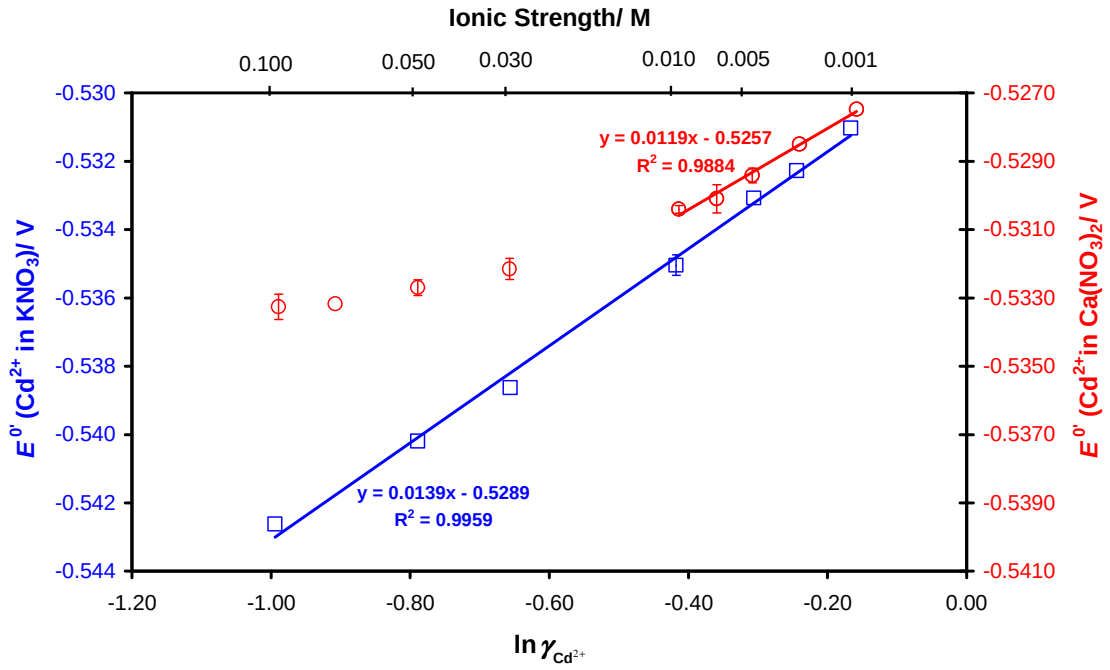

590
591 **Figure 5**. Representation of $E^{0'}$, obtained using eqn. (10) from AGNES experiments, in
592 front of the activity coefficient logarithm in a solution containing $c_{T,Cd} = 2.5\times10^{-6}$ mol
593 L^{-1} and KNO_3 (referred to the left hand side axis, □) or $Ca(NO_3)_2$ (referred to the right
594 hand side axis, ○) as supporting electrolytes. The ionic strengths were between 0.001
595 and 0.1 mol L^{-1} at pH = 5.5. The deposition potential was E_1=-0.5708 V with a KNO_3
596 0.1 mol L^{-1} salt bridge in the reference electrode when working with KNO_3 or
597 E_1=-0.5690 V with a KNO_3 1 mol L^{-1} salt bridge when working with $Ca(NO_3)_2$. Two
598 replicates have been performed and the standard deviation is shown whenever larger
599 than the marker.

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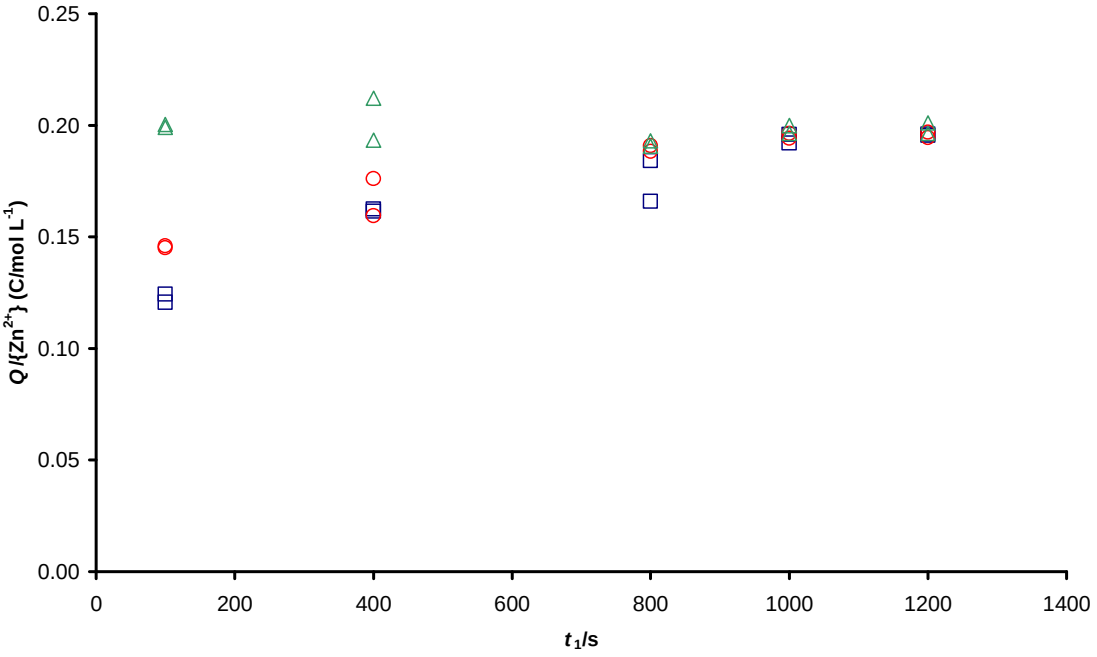

600

601 **Figure 6**. Trajectories of the quotient $Q/\{Zn^{2+}\}$ vs t_1 for different samples with
602 $c_{T,Zn}=2.5\times10^{-6}$ M and [KNO_3]= 0.001(□), 0.01 (○) and 0.1(Δ) mol L^{-1} showing the
603 collapse of the quotient between retrieved charges and metal activity for sufficiently
604 long times. AGNES has been carried out with a fixed deposition potential (E_1=-1.0248
605 V, computed from the DPP of a 0.1 M KNO_3 M sample), KNO_3 0.1 mol L^{-1} in the salt
606 bridge and with a fixed Y=50 at pH = 5.5. Two different replicates for each experiment
607 have been carried out.

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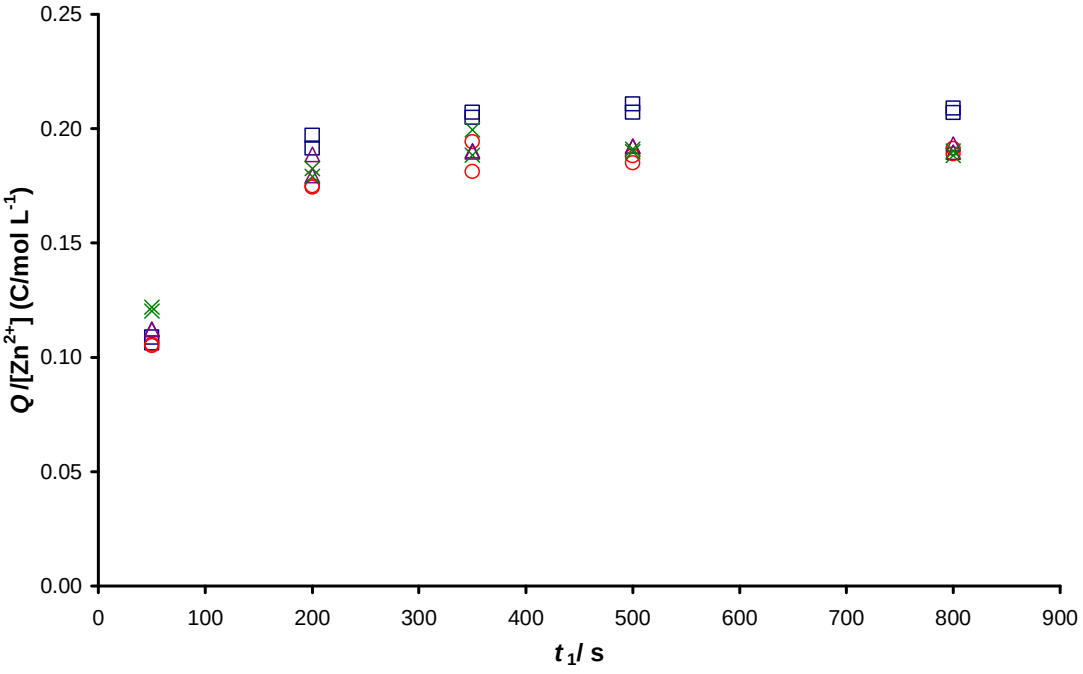

609

610 **Figure 7**. Representation of $Q/[Zn^{2+}]$ vs t_1 for solutions with $c_{T,Zn}=2.5\times10^{-6}$ mol L^{-1} and
611 μ=0.001 (□), 0.005 (○), 0.05 (Δ) and 0.1 (×) mol L^{-1} at pH = 5.5. AGNES has been
612 performed applying the corresponding deposition potential E_1, needed to reach Y=50,
613 computed with eqn. (12) and using the DPP peak potential of a solution with μ=0.1 mol
614 L^{-1}. A reference electrode with a KNO_3 0.1 mol L^{-1} jacket was used. Two different
615 replicates for each experiment have been performed.

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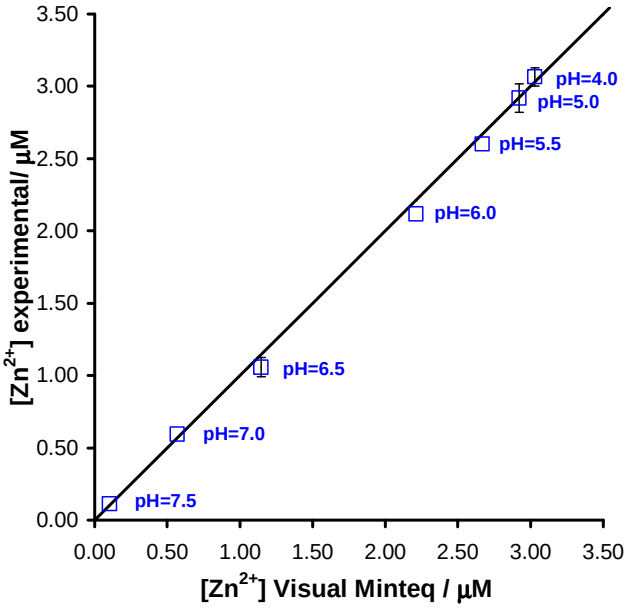

617

618 **Figure 8**. Free Zn^{2+} concentration, determined with AGNES, in front of the Visual
619 Minteq predicted concentrations at various pHs when a total Zn^{2+} concentration of
620 3.0×10^{-6} mol L^{-1} is complexed with glycine 0.01 M and the ionic strength is 0.001 mol
621 L^{-1}. AGNES was performed with Y_1=50, t_1=350 s, Y_2=10^{-8} and $Y_{1,sb}$=0.01. KNO_3 0.1 mol
622 L^{-1} was used as the salt bridge in the reference electrode. Two replicates have been
623 carried out and the standard deviation is shown whenever larger than the marker.

624