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]*IPREM, UMR 5254, L.C.A.B.I.E., Avenue Pierre 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

Supporting data

Determination of the faradaic charge: implementation of I_{ox} and τ'

We are specifically interested in an accurate computation of the faradaic charge because its physicochemical nature will allow a better understanding of the processes. Furthermore, when using the faradaic charge in

$$Q = nFV_{\mathrm{Hg}}\left[\mathrm{M^o}\right] = \eta_{\mathrm{Q}} Y[\mathrm{M}^{n+}] = h_{\mathrm{Q}}[\mathrm{M}^{n+}] \qquad \text{(S1)}$$

we will retrieve h_{Q} and η_{Q} values which can be compared and tested against literature values. Due to the interest in the charge associated to the accumulated M$^{\mathrm{o}}$, we apply SCP under conditions of total depletion.

The imposed stripping current can be splitted into several components: the faradaic current (I_{faradaic}, the one relevant for AGNES purposes), the capacitive current (I_{cap}) and the current due to other oxidants (I_{Ox}) [1]:

$$I_{\mathrm{s}} = I_{\mathrm{faradaic}} + I_{\mathrm{Ox}} + I_{\mathrm{cap}} = I_{\mathrm{faradaic}} + I_{\mathrm{Ox}} + C\frac{dE}{dt} \qquad \text{(S2)}$$

Indeed, the electrons provided to the galvanostat can come from the reoxidation of M$^{\mathrm{o}}$ (which is also helped by the reduction of other species such as traces of oxygen or other interfering cations, also called electroless effect [2]) or from the charging process of the electrode acting as a capacitor. The capacitance C can be computed by considering a (virtual) blank experiment where no analyte is present. From Eq. (S2) , with I_{faradaic}=0:

$$C = \left(I_{\mathrm{s}} - I_{Ox}\right)\left(\frac{dt}{dE}\right)_{blank} \qquad \text{(S3)}$$

As we are interested in the faradaic charge,

$$Q = \int I_{\mathrm{faradaic}} dt = \int\left(I_{\mathrm{s}} - I_{\mathrm{Ox}} - C\frac{dE}{dt}\right)dt = \int\left(I_{\mathrm{s}} - I_{\mathrm{Ox}}\right)\frac{dt}{dE}dE - \int\left(I_{\mathrm{s}} - I_{Ox}\right)\left(\frac{dt}{dE}\right)_{blank} dE \quad \text{(S4)}$$

In AGNES-SCP practice, the initial potential E_0 will correspond to the deposition potential associated to the desired gain Y. If we assume that the oxidant current is practically constant in the range between E_0 and E_f (the initial and final potential estimated for the reoxidation process):

$$Q = \left(I_\mathrm{s} - I_\mathrm{Ox}\right)\int_{E_0}^{E_\mathrm{f}}\left[\left(\frac{dt}{dE}\right) - \left(\frac{dt}{dE}\right)_{blank}\right]dE \tag{S5}$$

Traditionally, a similar integral has been measured from the *area above the baseline* and, thus, automatically discounting the electrode capacitive current:

$$\tau = \int_{E_0}^{E_\mathrm{f}}\left(\frac{dE}{dt} - \left[\frac{dE}{dt}\right]_\mathrm{baseline}\right)dt \tag{S6}$$

which results from just identifying the baseline with the blank.

However, we have found some special situations in which computing τ can represent a challenge to this direct method. One of these situations is shown in Figure 4, where a distorted stripping dt/dE peak appears while performing a speciation study with Cd^{2+} and oxalate in presence of Pb^{2+} as interference. Due to the initial dt/dE value (around 380 s/V) quite above with respect the usual baseline, it is not possible to apply previous Eq. (i.e. to read the area above the baseline directly).

We can split Eq. (S5) into two components:

$$Q = \left(I_\mathrm{s} - I_\mathrm{Ox}\right)\int_{E_0}^{E_\mathrm{f}}\left(\frac{dt}{dE}\right)dE - \left(I_\mathrm{s} - I_\mathrm{Ox}\right)\int_{E_0}^{E_\mathrm{f}}\left(\frac{dt}{dE}\right)_{blank}dE = \left(I_\mathrm{s} - I_\mathrm{Ox}\right)\left[\tau' - \int_{E_0}^{E_\mathrm{f}}\left(\frac{dt}{dE}\right)_{blank}dE\right] \tag{S7}$$

where we call τ' to the integral:

$$\tau' = \int_{E_0}^{E_\mathrm{f}}\left(\frac{dt}{dE}\right)dE \tag{S8}$$

which corresponds to the *total* area under the peak in the dt/dE versus E plots (see shaded region in Figure 4), i.e. from the abscissa axis up to the curve.

We need further assumptions to compute $\int_{E_0}^{E_\mathrm{f}}\left(\frac{dt}{dE}\right)_{blank} dE$. In the experiments found in this work, the baseline after the peak was practically horizontal. Thus, if we identify the baseline dt/dE with the blank dt/dE and assume its constancy also for the region E_0 to E_f:

$$Q=\left(I_\mathrm{s}-I_\mathrm{Ox}\right)\left[\tau'-\left(\frac{dt}{dE}\right)_\mathrm{baseline}\left(E_\mathrm{f}-E_0\right)\right]=\left(I_\mathrm{s}-I_\mathrm{Ox}\right)\tau \tag{S9}$$

So, when necessary in this work, the following determination of τ has been applied:

$$\tau=\tau'-\left[\frac{dt}{dE}\right]_{baseline}\left(E_\mathrm{f}-E_0\right) \tag{S10}$$

For example, in Figure 4, we read $\left[\frac{dt}{dE}\right]_{baseline}$ =30 s/V at E_f=-0.56 V. Notice that the shaded area below the dashed line corresponds to capacitive component given by the product $\left[\frac{dt}{dE}\right]_{baseline}\left(E_\mathrm{f}-E_0\right)$, while the area above the dashed line corresponds to τ.

Of course, more elaborate models for the variation of the baseline for the region E_0 to E_f can be derived to deal with other curves dt/dE.

In summary, taking into account all the current contributions, the stripped faradaic charge during an AGNES experiment with SCP as the second stage can be calculated with:

$$Q=\left(I_\mathrm{s}-I_\mathrm{Ox}\right)\tau \tag{S11}$$

τ can be either measured directly above the baseline, eqn. (S6), or, in some special situations like the one shown in Figure 4, from Eq. (S10).

Similar oxidants corrections have been suggested previously [1, 3]

References

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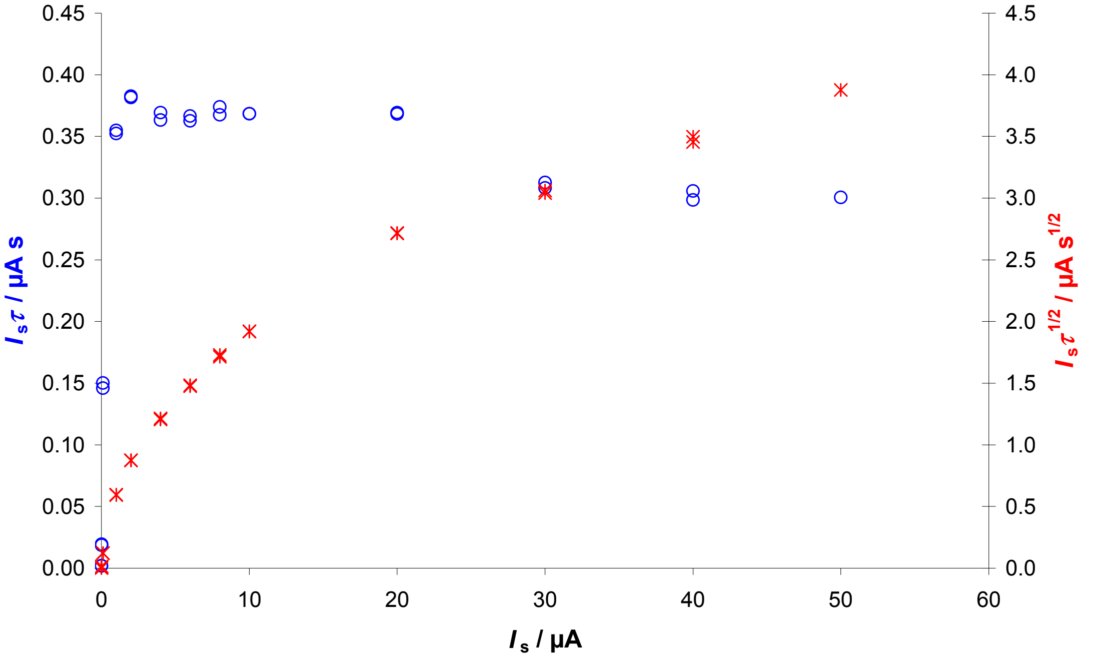

Figure S1. Behaviour of $I\tau$ (○) and $I\tau^{1/2}$ (✳) obtained with a SPE. $c_{T,Zn}$ = 100 nmol L^{-1}, [KNO$_3$]=0.1 mol L^{-1}, Y = 5000 and t_1 = 400 s. I_s from 10^{-10} to 5×10^{-5} A .

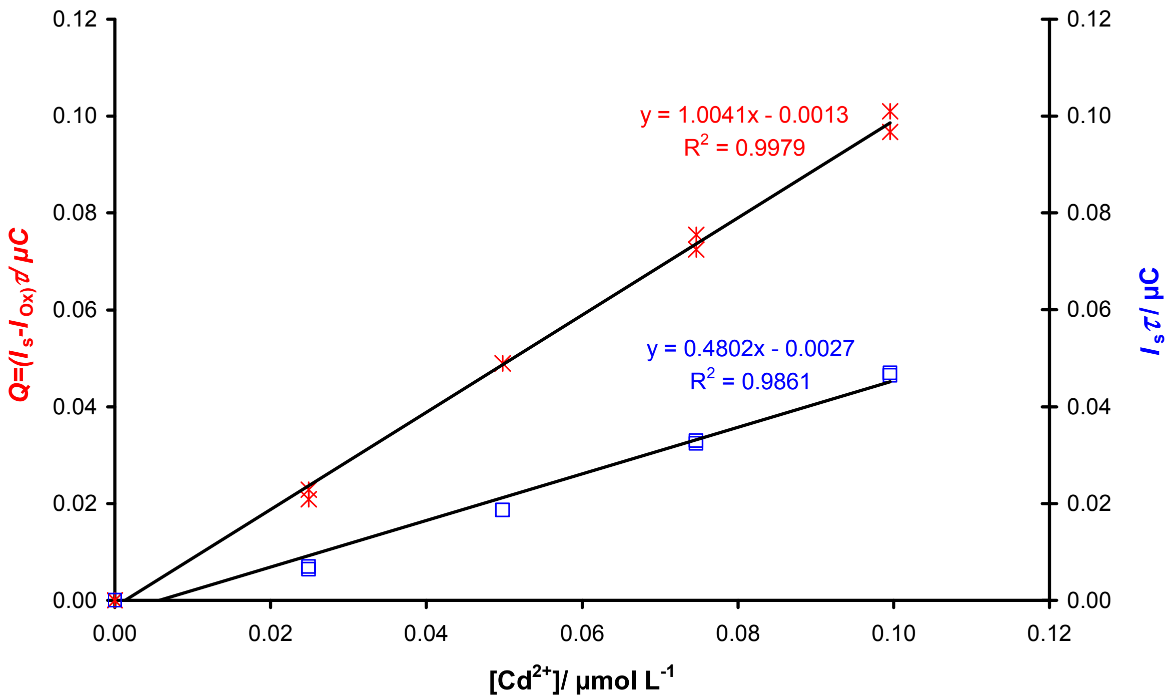

Figure S2. Cd^{2+} calibration in AGNES-SCP with a HMDE including the oxidants correction (✳, referred to the left hand side ordinate axis, computed with Eq. (S11) or without the oxidants correction (□, referred to the right hand side ordinate axis, computed as $I_s\tau$). $Y = 500$, $t_{1,a} = 350$ s, $t_{1,b} = 1050$ s, $I_s = 1$ nA, $[KNO_3]$=0.1 mol L^{-1}.

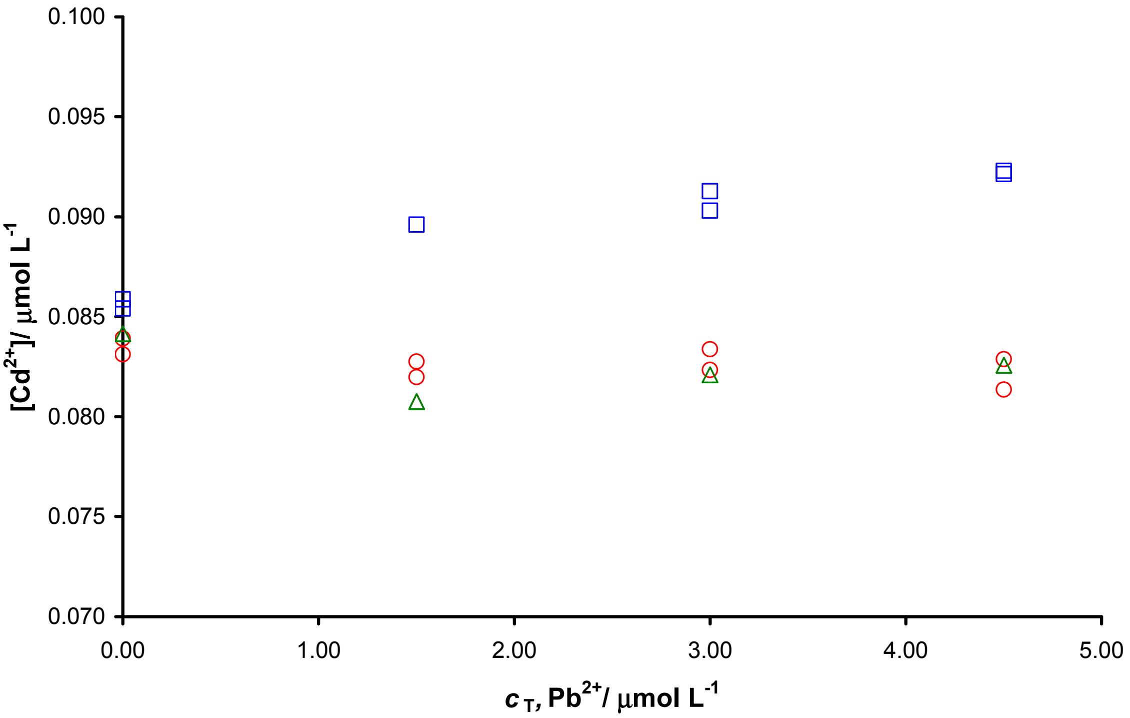

Figure S3. Free Cd concentration at different Pb additions (1 – 4.5×10 µmol L^{-1}) when a total Cd concentration of 3 µmol L^{-1} is complexed with oxalate 0.02 mol L^{-1} as determined by AGNES (□ stands for AGNES performed with $Y = 500$, $t_1 = 300$ s and a fixed potential in the stripping stage, ○ stands for AGNES-SCP with $Y = 500$, $t_1 = 300$ s, $I_s = 1$ nA) and ISE (Δ).