

Towards improving the electroanalytical speciation analysis of indium

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SI. Linearity range for In^{3+} in SCP with TMF/RDE.

The linearity range of SCP detection for indium is very large when using mercury electrodes. As can be observed in Figure S1, calibration plots can cover several orders of magnitude and reach total indium concentration of 10 μ M. This huge linearity range is due to the extraordinary amalgamation of indium in mercury (57% w/w), which is the highest of all metals [1].

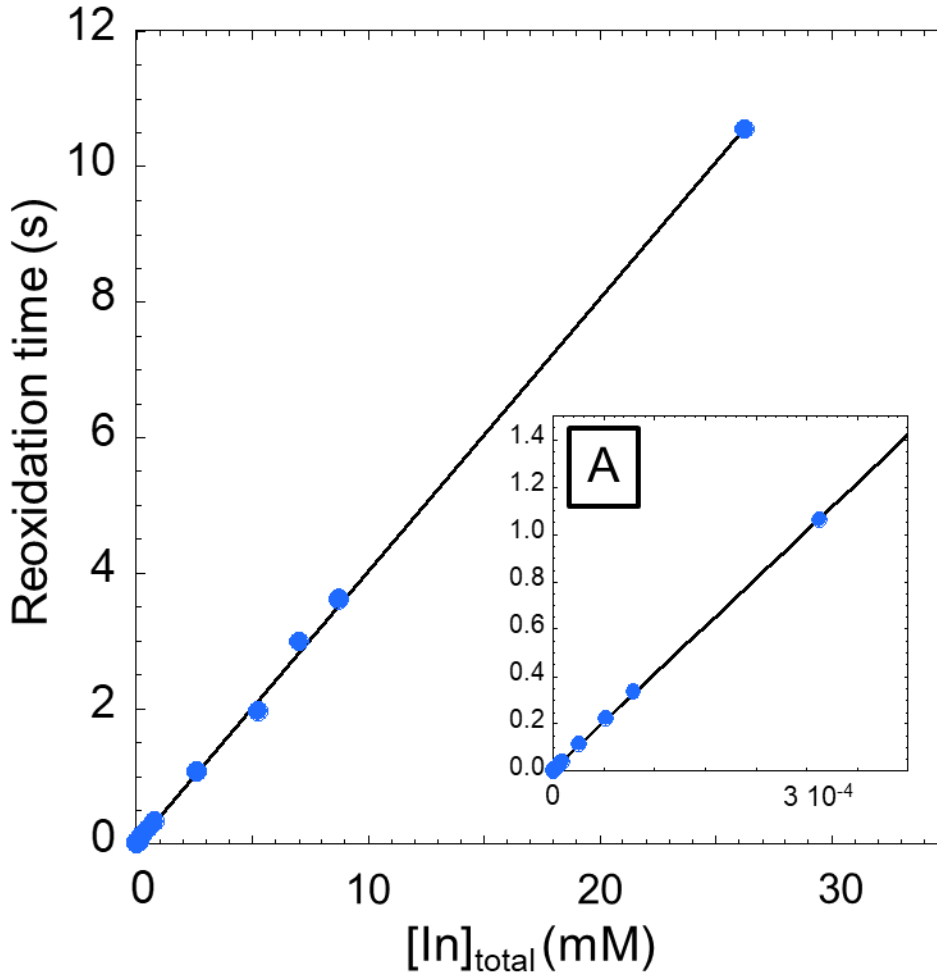


Figure S1: SCP calibrations for deposition time of 45 s obtained with the TMF/RDE of 2 mm, rotation speed 1000 rpm, in 100 mM NaClO₄ medium, pH 2.3. Inset A: SCP calibration in the low concentrations range.

S2. Stripping Chronopotentiometry (SCP) at the TMF/RDE

In SCP, the number of moles deposited equals:

$$N_{\text{deposited}} = I_{\text{d}}^* t_{\text{d}} / nF \quad (\text{S2.1})$$

where t_{d} is the deposition time, I_{d}^* is the limiting deposition current (of just the analyte), n is the number of exchange electrons and F is the Faraday constant.

The number of reoxidised moles (whenever the stripping current I_{S} is much larger than any background oxidants current) is given by:

$$N_{\text{reoxidised}} = I_{\text{S}} \tau^* / nF \quad (\text{S2.2})$$

where τ^* is the limiting transition time obtained for deposition potentials much more negative than the standard redox potential, $E_d \ll E_0$.

In the depletion mode, the number of deposited moles equals the number of reoxidised moles and the limiting transition time is given by:

$$\tau^* = I_d^* t_d / I_S \quad (\text{S2.3})$$

In the dt/dE vs. E representation of the SCP signal, the area under the peak is the transition time, τ^* , while the area under the baseline corresponds to the time associated to capacitive charge. If the baseline is determined by a well-defined charging process, no baseline distortions will occur and background corrections will not be necessary[2].

The limiting deposition current, I_d^* , at a TMF/RDE is given by:

$$I_d^* = nFAD_M c_{M,T} / \delta_M \quad (\text{S2.4})$$

where $c_{M,T}$ is the (total) metal concentration in the bulk solution, δ_M is the diffusion layer thickness and D_M the diffusion coefficient of the metal, and A the surface area of the electrode.

For the rotating disk electrode (RDE), according to Levich [3], δ_M is expressed by:

$$\delta_M = 1.61 D_M^{1/3} \omega^{-1/2} \nu^{1/6} \quad (\text{S2.5})$$

being ω and the angular speed rotation for the RDE ($\omega = 2\pi\nu_{\text{rot}}$, where ν_{rot} is the speed of rotation) and ν the kinematic viscosity of the test solution.

S3. Fundamentals of AGNES

AGNES experiment consists of two conceptual stages: deposition or first stage, and stripping or second stage. An essential condition for AGNES is to attain Nernstian

equilibrium by the end of the first stage, *i.e.*, after a sufficiently long deposition time t_d (also known as t_1). For a deposition potential E_d , equilibrium means [4]:

$$\frac{[\text{In}^0]}{[\text{In}^{3+}]} = Y = \exp\left(\frac{3F}{RT}(E_d - E^{0'})\right) \quad (\text{S3.1})$$

where $E^{0'}$ is the standard formal potential of the redox couple, R the gas constant, T the temperature and square brackets indicate concentration of the enclosed species ($[\text{In}^{3+}]$ for the analyte; $[\text{In}^0]$ for its reduced species). The ratio of concentrations is called pre-concentration factor or gain (Y). Nernst law defines the relationship between the activities of the free metal ion in solution and of the reduced metal in the amalgam (eqn. (S3.1)). Thus, by changing the deposition potential, the ratio between activities is changed, which, for analytical purposes, is converted into the gain value.

Under equilibrium conditions, the gain Y can be calculated from Faraday's law:

$$Q = 3FV_{\text{Hg}}[\text{In}^0] = \eta_Q[\text{In}^0] = \eta_Q Y[\text{In}^{3+}] \quad (\text{S3.2})$$

with V_{Hg} being the volume of the mercury electrode and Q the faradaic charge or the analytical signal. In this work typically used η_Q values ranged from 3.4 to 8.1×10^{-5} C L mol⁻¹.

In the second stage of AGNES, the amount of amalgamated metal is quantified. In this work, we have followed the variant called AGNES-SCP [5,6]. Here, stripping chronopotentiometry (SCP) is used in the second stage of AGNES, *i.e.* the time for complete depletion is determined from the evolution of the recorded potential in response to the imposed stripping current, I_s . The faradaic charge (Q) can be rigorously computed as:

$$Q = (I_s - I_{\text{ox}}) \tau^* \quad (\text{S3.3})$$

where I_{ox} is the oxidants current. In this work, $I_{ox} \ll I_s$. Then the slope of a calibration plot (Q vs $[In^{3+}]$) obtained for a given deposition potential (E_{calib}) will be $3FV_{Hg}Y_{calib}$. Since V_{Hg} can be determined from the reoxidation of the mercury film, a correspondence between E_{calib} and Y_{calib} can be obtained. Once this relationship is established, it is straightforward to obtain the gain (Y_j) for any given deposition potential (E_j) with equation S3.1 recasted as [7]:

$$\ln(Y_j/Y_{calib}) = -\left(\frac{3F}{RT}(E_j - E_{calib})\right) \quad (S3.4)$$

S4. Calibration plots obtained with AGNES.

Table S1 provides a few examples selected from a total of 51 calibration plots obtained with AGNES at two different ionic strengths, 30 mM and 100 mM, performed by three different operators using three different set-ups.

Table S1: Selected examples from the detection (LOD) and quantification (LOQ) limits for a series of AGNES calibrations at different ionic strengths, using approximatively the same pre-concentration value (Y). n is the number of calibration points, m is the slope, b is the intercept, S_y is the standard deviation of residuals.

I mM	Range of Indium concentrations nM	n	m (C*mol ⁻¹ *L)	b (C) 10 ⁻⁹	S_y 10 ⁻⁹	LOD nM	LQ nM	Y
100	10-80	12	5.51±0.03	-4±1	3.6	2.0	6.6	68000
100	10-50	12	3.52±0.09	0±3	5.8	5.0	16.5	43400
100	10-50	12	3.28±0.04	-1±1	2.3	2.1	6.9	40400
100	10-50	8	5.14±0.04	1±1	2.4	1.4	4.6	63400
100	10-40	12	6.28±0.07	4±2	3.5	1.7	5.6	77500
100	10-100	12	3.70±0.02	1±1	2.9	2.4	7.8	45600
100	20-100	12	4.25±0.04	-1±2	4.3	3.0	10.1	52400
100	5-25	12	3.82±0.07	3.6±0.9	2.1	1.7	5.5	26000
100	5-30	12	4.38±0.03	1±1	1.2	0.8	2.8	54000

100	10-30	9	4.34±0.07	-1±1	1.6	1.1	3.6	53600
100	5-20	9	4.47±0.06	-1.1±0.7	1.4	0.9	3.1	55100
100	5-30	10	3.21±0.04	1.7±0.7	1.6	1.5	5.0	45500
100	5-60	12	7.41±0.15	2±5	1.2	4.8	16.1	91400
100	5-60	15	3.22±0.02	0.9±0.4	1.2	1.2	3.9	39700
100	5-100	15	3.17±0.02	-1.3±0.8	2.5	2.3	7.7	39100
100	10-100	12	1.07±0.01	-0.4±0.6	1.3	3.7	12.4	31400
100	30-100	9	0.99±0.01	0.9±0.6	1.1	3.3	11.1	29100
100	100-300	9	1.412±0.007	3.4±1.5	1.7	3.5	11.8	41300
100	10-60	9	1.03±0.02	-0.5±0.7	1.0	2.8	9.5	30200
30	10-30	9	2.72±0.07	0.4±1.7	1.8	2.0	6.5	79600
30	10-30	9	2.37±0.03	-0.1±0.8	0.7	0.8	2.8	69200
30	10-30	9	1.81±0.03	0.0±0.7	0.7	1.1	3.6	52800
30	10-30	9	1.92±0.02	0.0±0.7	0.6	0.9	3.0	56150

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