

Application of the new electroanalytical technique AGNES to the determination of free Zn concentration in river water.

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Abstract

Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) is a recently developed electroanalytical technique specifically designed for the direct determination of free concentrations of metal ions. AGNES is here applied to the determination of free Zn concentration in a river water sample. The method has been validated with synthetic solutions of low ionic strengths containing Zn and 2,6-pyridinedicarboxylic acid (PDCA) and then applied to synthetic river waters and to a natural sample collected from Besòs River in Montcada i Reixac (Catalonia, North-Eastern Spain). In the river sample, an average free Zn concentration of 12.8(4) nM was obtained, while the total dissolved Zn concentration was 0.51(8) μ M. To control and maintain pH and pCO₂ constant during AGNES measurements, a novel device for N₂/CO₂ mixed purging has been developed.

Keywords: Speciation, AGNES, River water, Synthetic water, Zn, purging system

30 **Introduction**

31 Metal speciation in environmental waters is relevant to characterize the metal toxicity,
32 the mobility between different environmental compartments and the proposal of
33 remediation strategies in case of contamination [1]. Comprehensive speciation codes
34 [2;3] have been developed to describe metal species in environmental waters, but their
35 application requires the knowledge of the total concentration of all the components,
36 even of those present at very minor concentration (which might be ill-known despite
37 their crucial role) and of all the equilibrium reactions and their corresponding stability
38 constants, in order to accurately calculate the distribution of the metal among different
39 species. Thus, direct measurement of one metal species or a group of species is
40 necessary to validate the speciation models.

41

42 Several analytical techniques have been proposed and widely used to this aim [4-6], but
43 unfortunately, the interpretation of the results is not always straightforward, e.g. the
44 computation of the free metal from the measured “labile fraction” is not simple [7].

45

46 Absence of Gradients and Nernstian Equilibrium Stripping (AGNES) has been
47 suggested as a new electroanalytical technique [8] providing direct access to the free
48 activity of metal ions (in contrast to other operationally defined concentrations).
49 AGNES can become an alternative to other standard techniques such as ion selective
50 electrodes (ISE), especially for cases – such as Zn – where a commercial ISE is not
51 available. Zn was previously determined by AGNES in synthetic solutions [9], humic
52 acid titrations [10] and in real samples [11;12] with satisfactory results. Here, we extend
53 AGNES to analyse river waters, tackling two specific difficulties: i) the low ionic

54 strength (μ) of the medium and ii) the convenience of not disturbing the carbonate
55 speciation.

56 **1. Material and methods**

57 **1.1 Instrumentation**

58 Voltammetric measurements were carried out with the equipments specified in
59 previous works [8]. A Calcium Ion Selective Electrode 6.0504.100, Metrohm was used
60 for pCa monitoring. For on field measurements, a portable pH-meter 506 Crison and a
61 conductimeter micro CM 2200, Crison were used. Membranes 0.45 μm , Millipore, were
62 used for filtration.

63 Total Zn in acidified samples was determined by SW-ASV (square wave anodic
64 stripping voltammetry, $E_{\text{dep}} = -1.3 \text{ V}$; $t_{\text{dep}} = 100\text{s}$; scan from $E_1 = -1.1 \text{ V}$ to $E_2 = 0 \text{ V}$;
65 Amplitude= 0.02505 V; Scan rate= 0.2025 V/s) and by ICP-OES Activa Horiba Jobin-
66 Yvon ($\lambda = 213.8 \text{ nm}$).

67 **1.2 AGNES Technique**

68 The simplest implementation of AGNES [8;9;13-15] consists in applying a deposition
69 potential E_1 (which prescribes a preconcentration factor or gain Y between $[\text{Zn}^0]$ in the
70 amalgam and $[\text{Zn}^{2+}]$ in the solution) for a time t_1 , followed by a stripping potential at a
71 potential E_2 under diffusion limited conditions. The analytical response is the current at
72 a time t_2 (usually 0.2 s). To reduce t_1 , the potential program has been modified by
73 splitting the first stage into two sub-stages or pulses (i.e. the “AGNES 2P” or “2-pulse”
74 strategy [9]).

75

76 The free metal ion concentration is directly proportional to the AGNES faradaic current
77 with a factor of proportionality h . However, I vs. $[\text{Zn}^{2+}]$ was recently found [16] to

78 deviate from linearity for very high values of $[Zn^{2+}]$ at ionic strengths 0.05 M and
79 higher, due to a so-called “anomalous convex behaviour” *acb*.

80

81 For experiments run at different gains, the corresponding proportionality factors can be
82 related by using

$$83 \quad h = \eta Y \quad (1)$$

84 where η [8;16] only depends on the electrode characteristics and the measurement time
85 (t_2).

86 1.3 River water sample collection

87 Sampling from Besòs River took place on 15th July 2009 in Montcada i Reixac,
88 Catalonia (Spain). Water was collected at about 0.5 m from the riverside with a clean
89 polyethylene tube connected to a manual pump. River water samples were kept
90 refrigerated for the transfer to the laboratory where they were filtered within two hours.

91 The pH measured on field was 7.69, temperature 25.5°C and the conductivity (C) 1912
92 $\mu\text{S cm}^{-1}$. From this conductivity, an ionic strength $\mu=0.031$ M was estimated (see Table
93 2330 of ref. [17]) by using:

$$94 \quad \mu = 1.6 \times 10^{-5} C \quad (2)$$

95 The total Zn content was determined in portions of the sample acidified at pH 1.5.

96 Filtered samples for AGNES measurements were stored at 4°C without any treatment.

97

98 1.4 A novel device to control N_2/CO_2 purging

99 In natural samples, pH is mainly determined by volatile components such as CO_2
100 dissolved in the water. During electrochemical measurements the typical inert gas (N_2)
101 used for degassing O_2 , also removes other gases, such as CO_2 , resulting in changes of
102 pH and metal speciation, in particular for freshwater samples with low buffer capacity.

103 This can be solved by purging freshwater samples using a mixture of N₂ and CO₂.
104 Several N₂/CO₂ purging systems have been described since the seventies [18-20]. On
105 the basis of these studies, we decided to develop a new system where special valves to
106 control gas fluxes are not needed. This new purging device consists of two flasks
107 containing Milli-Q water and a peristaltic pump. In flask A, N₂ bubbles through water,
108 while in the other (B), CO₂ is the bubbling gas. The peristaltic pump moves: i) water
109 saturated with CO₂ from flask B to flask A and ii) water from the flask A to flask B (in
110 order to keep constant the volume in both flasks). From flask A, a flow of a mixture of
111 gases N₂/CO₂ is taken towards the voltammetric cell where we control pH and pCa
112 (related to carbonate speciation), by regulating with the pump the flow of exchanged
113 water. To avoid changes in the conditions of the electrochemical cell, flask A is
114 maintained at the same temperature as the voltammetric cell.

115

116 **2. Determination of free Zn(II) by AGNES in synthetic solutions**

117 2.1 AGNES calibration at low ionic strength

118 To compute the free Zn(II) concentration from the measured current, we need to know
119 the proportionality factor h (see section 1.2) evaluated at the same ionic strength as that
120 of the water sample. So, different calibrations were performed in KNO₃ solutions
121 ranging from 0.1 to 0.001 M. In all calibration experiments, the free Zn concentration
122 after each standard addition was computed by V-Minteq program [3] from the known
123 total metal content, KNO₃ concentration and pH of the solution. The η values obtained
124 with $\mu = 0.1$ - 0.004 M (see Table 1) yield an average η value of 2.1×10^{-3} and standard
125 deviation 0.1×10^{-3} AM⁻¹ (in good agreement with those previously reported for Zn: η
126 $= 2.2 \times 10^{-3}$ AM⁻¹ for $\mu = 0.1$ M [9], $\eta = 2.4 \times 10^{-3}$ AM⁻¹ for $\mu = 0.1$ M [10] and $\eta = 2.08 \times 10^{-3}$

127 3 AM^{-1} for $\mu=0.5 \text{ M}$ [11]). As expected, no systematic variation of η (or h) with μ is
128 seen. However, for increasing Zn concentrations with the lowest ionic strength ($\mu =$
129 0.001 M), we have found a deviation from the linear relationship between current and
130 concentration which resembled the *acb* previously reported in [16] at higher ionic
131 strengths. As the measured current depends on the quantity of metal reduced inside the
132 mercury drop, to better analyse the results, the current was normalized dividing it by the
133 Zn° concentration [16]

$$134 \frac{I(t_2)}{[\text{Zn}^{\circ}]} = \frac{I(t_2)}{Y [\text{Zn}^{2+}]} = \frac{h(t_2)}{Y} = \eta(t_2) \quad (3)$$

135 When working at ionic strength above 0.004 M , the registered normalized currents in
136 the second stage vs. t_2 in the calibration plots decays fast and continuously. However,
137 for $[\text{KNO}_3] = 0.001 \text{ M}$, $\eta(t_2)$ exhibits a slow decrease with a convex shape (see Fig. 1)
138 for high enough $[\text{Zn}^{\circ}] = Y \times [\text{Zn}^{2+}]$. Given the similarity between this stripping decay at
139 moderate Zn concentrations and that found [16] for higher Zn concentrations and higher
140 ionic strengths, we conclude that *acb* seems to be essentially due to a high proportion of
141 $[\text{Zn}^{\circ}]$ with respect to the background electrolyte concentration. This is consistent with
142 the explanation that there is a combination of several phenomena behind *acb* [16], but
143 with a conductivity limitation playing the leading role. The two different types of *acb*
144 behaviours can be also identified here (see Fig. 1): lower current intensities with a
145 levelling-off to a practically constant value (*sluggish stripping*) or an enhancement of
146 the current during the first moments (*exaltation* or enhanced current). We conclude that
147 for systems (either synthetic or natural) with an ionic strength above 0.004 M , we can
148 safely use the linear relationship between current and free metal concentration, specially
149 when the attained $[\text{Zn}^{\circ}]$ is below $1.2 \times 10^{-4} \text{ M}$, which is the higher $[\text{Zn}^{\circ}]$ in the calibration
150 plot at ionic strength 0.004 M not exhibiting *acb*.

151 2.2 Speciation in synthetic solutions

152 2.2.1 Speciation with PDCA in KNO₃ solutions

153 Zn was titrated with 2,6-pyridinedicarboxylic acid (PDCA) at constant pH (around 6).

154 Solutions with a known and constant total Zn concentration (around 10⁻⁶ M) and
155 different concentrations of PDCA (from 0 to about 2×10⁻⁵ M) were prepared.

156 AGNES parameters were chosen depending on the PDCA concentration. The deposition
157 times could be reduced taking advantage of the presence of labile PDCA complexes
158 which contribute to flux [13].

159 The [Zn²⁺] at different PDCA concentrations in KNO₃ 0.1 and 0.005 M is shown in Fig.

160 2. The experimental results (symbols) were compared with the theoretical ones
161 (continuous lines) obtained taking the protonation and complexation constants of PDCA
162 from the literature [21;22] and using MEDUSA [2] for its simplicity in the database
163 management. The error bars in the theoretical curves indicate the variability due to the
164 uncertainty on the values of the constants. All the measurements were reproducible and
165 in reasonable agreement with the theoretical curves.

166

167 2.2.2 Free Zn determination in synthetic river waters.

168 Because of the complexity of real samples, AGNES was firstly applied to synthetic
169 river waters with the main ionic composition of natural river waters, prepared following
170 the general instructions found in the literature [23;24] and 3×10⁻³ M added Zn. To
171 adjust and control the pH during the measurements, the mixed purging N₂/CO₂ system
172 was used.

173

174 A “soft” synthetic water at pH 8.3 (Table 2) was considered (no calcium carbonate
175 precipitation) and a “hard” synthetic river water (Table 3) at pH 7.6 and 8.1. The free

176 Zn concentrations determined by AGNES were $1.6(1)\times 10^{-7}$ M, $2.7(1)\times 10^{-7}$ M and
177 $1.7(3)\times 10^{-7}$ M, respectively ($n = 3$), in good agreement with the theoretical values
178 predicted by V-Minteq [3]: 1.57×10^{-7} M, 2.2×10^{-7} M and 1.65×10^{-7} M, respectively.

179 **3. Measurements of river water**

180 **3.1 Total Zn determination**

181 SW-ASV measurements of filtrated and acidified water yielded a dissolved total Zn
182 concentration of $2.8(4)\times 10^{-7}$ M ($n = 4$). Other portions of the same samples were
183 analysed by ICP-OES measurements obtaining an average value of $5.1(8)\times 10^{-7}$ M ($n =$
184 6), higher than that obtained by electrochemical measurements. The difference could be
185 due to acidification of the sample to pH 2 being not enough to ensure a complete release
186 of the complexed metal from the ligands. According to the most recent published data
187 from the Catalan Water Agency (Agència Catalana de l'Aigua – ACA, Generalitat de
188 Catalunya - Spain), the average concentrations reported for two samples of Besòs River
189 water collected in 2006 at Montcada i Reixac, were 7.9×10^{-7} M and 1.1×10^{-6} M. Our
190 smaller value could be due to the different year and/or season of sampling and a result
191 of the stricter current regulations, but, in any case, our data can be considered as
192 reasonably consistent.

193

194 **3.2 Free Zn determination by AGNES**

195 The free Zn concentration in the filtrated water was determined adjusting the pH to the
196 on field measured value 7.7 by means of the N_2/CO_2 purging device. In this way, the
197 pCa remained at 2.6. The temperature was fixed to 25.0°C.

198 A series of experiments were conducted using the 2-Pulse strategy. During the first sub-
199 stage a very negative potential $E_{1,a}$ is applied (corresponding to diffusion limited

200 conditions for reduction) for a time t_{1a} . In the second sub-stage a more positive
201 potential, E_{1b} (corresponding to the desired gain Y), is applied for a time t_{1b} [9].
202 “Overshoot” appears when t_{1b} is too short to compensate (via re-oxidation) the excess of
203 Zn^0 that entered the drop during t_{1a} . “Undershoot” appears when t_{1a} and t_{1b} are too short
204 for the required equilibrium amount of Zn^0 . Red triangles in Fig 3 correspond to various
205 t_{1b} (50s, 140s and 700s) for $Y=200$, with a common $t_{1a}=140$ s, following the rule of
206 thumb –for synthetic solution without complexant -

$$207 \quad t_{1a} = Y \times 0.7s \quad (4)$$

208 which has been observed in our laboratory [9]. The retrieved faradaic currents (of the
209 order of 8 nA) were very similar. Of these 3 experiments, the safer value ($[Zn^{2+}] = 13.3$
210 nM) arises from the longer t_{1b} which fulfils the condition [9]:

$$211 \quad t_{1b} = 3 \times t_{1a} \quad (5)$$

212

213 Another series of 3 experiments increasing the gain to $Y=500$ (see yellow circles in 3)
214 with $t_{1a} = 500 \times 0.7s = 350s$, indicated a slight overshoot for $t_{1b} = 50s$ and $t_{1b} = t_{1a}$. The
215 currents were proportionally larger (of the order of 18 nA), but the retrieved
216 concentrations (using eqn. (1) for the proportionality factor between current and $[Zn^{2+}]$)
217 agreed very well with those obtained with $Y=200$. The safer (i.e. longer $t_{1b}=1050s$ and,
218 thus, less likely to be affected by over- or undershoot) value yielded $[Zn^{2+}] = 12.7$ nM.
219 A replicate (with another filtrated portion of the sampled water) with $Y=500$, $t_{1a}=350$ s
220 and $t_{1b}=1050s$ (see black \times in Fig. 3) yielded $[Zn^{2+}] = 12.7$ nM. Finally, we performed
221 a 1-Pulse AGNES experiment (i.e. with a non-splitting deposition stage or “AGNES
222 1P”) with $Y = 200$ and $t_1 = 2000$ s. These 2000 s should yield a trustable value given
223 that, in our experience [9], the condition:

$$224 \quad t_1 > Y \times 7s \quad (6)$$

225 is suitable for estimating the 1-Pulse deposition time to reach the sought equilibrium in
226 synthetic solution without complexant. The 1-Pulse experiment (pink square in Fig. 3)
227 yielded $[Zn^{2+}] = 12.9$ nM.

228 From the data obtained at the longer times ($t_{1b} > 600$ s in Fig. 3), a free Zn concentration
229 equal to 12.8(4) nM was obtained. Since the total dissolved Zn content in the sample is
230 $5.1(8) \times 10^{-7}$ M, the free metal fraction is around 2.5% of total dissolved metal content.

231 **4. Conclusions**

232 In the present work, AGNES technique has been implemented for low ionic strengths
233 samples. The standard strategy of measuring the current at a fixed time (e.g. $t_2 = 200$ ms)
234 works well at ionic strengths above 0.004 M (as our sampled water) and $[Zn^0] = Y \times [Zn^{2+}]$
235 lower than 1.2×10^{-4} M.

236 When the ionic strength was up to 0.004 M, the anomalous convex behaviour (*acb*)
237 appears, affecting calibrations at higher metal concentrations. In case a natural water
238 had a lower ionic strength, the *acb* would affect calibrations at higher $[Zn^0]$, but the
239 measurement could still be possible by tuning a suitable gain, so that the target
240 $[Zn^0] = Y[Zn^{2+}]$ was low enough (to avoid *acb*) but high enough for the measured current
241 to be above the limit of detection.

242

243 To measure the speciation at the natural occurring conditions (pH and carbonate
244 content), a novel device for CO₂/N₂ purging has been proposed.

245

246 The free Zn concentration determined in synthetic river waters at low ionic strength was
247 in good agreement with the predicted one by a speciation program. A natural water from
248 river Besòs (Catalonia, Spain) has been analysed, obtaining a free Zn concentration of

249 12.8(4) nM. The critical evaluation of the free Zn concentration in freshwaters (where
250 AGNES can play a role together with other techniques) is timely.

251

252

253 **Acknowledgements**

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260 **References**

261

- 262 **1. Buffle, J. and Horvai, G.(Eds.) (2000) In Situ Monitoring of Aquatic Systems.**
263 **Chemical Analysis and Speciation. IUPAC Series on Analytical and Physical**
264 **Chemistry of Environmental Systems. John Wiley & Sons, Chichester.**
- 265 **2. I. Puigdomenech. Medusa: make equilibrium diagrams using sophisticated**
266 **algorithms. Windows program. 2001. Royal Institute of Technology KTH,**
267 **Stockholm, Sweden.**
- 268 **3. J. D. Allison, D. S. Brown, and K. J. Novo-Gradac. MINTEQA2/PRODEFA2,**
269 **A geochemical assessment model for environmental systems: version 3.0**
270 **user's manual. EPA 600/3-91/021; U.S. 1991. Washington, DC.7, U.S.**
271 **Environmental Protection Agency, Office of Research and Development.**
- 272 **4. Kalis EJJ, Weng LP, Dousma F, Temminghoff EJM, and van Riemsdijk WH**
273 **(2006) Environ. Sci. Technol. 40:955-961.**
- 274 **5. Batley GE, Apte SC, and Stauber JL (2004) Aust. J. Chem. 57:903-919.**
- 275 **6. Sigg L, Black F, Buffle J, Cao J, Cleven R, Davison W, Galceran J, Gunkel P,**
276 **Kalis E, Kistler D, Martin M, Noel S, Nur Y, Odzak N, Puy J, van Riemsdijk**
277 **WH, Temminghoff E, Tercier-Waeber ML, Toepferwien S, Town RM,**
278 **Unsworth E, Warnken KW, Weng LP, Xue HB, and Zhang H (2006)**
279 **Environ. Sci. Technol. 40:1934-1941.**
- 280 **7. Cheng T, De Schamphelaere K, Loftis S, Janssen C, and Allen HE (2005)**
281 **Anal. Chim. Acta 542:230-239.**

- 282 **8. Galceran J, Companys E, Puy J, Cecilia J, and Garcés JL (2004) J.**
283 **Electroanal. Chem. 566:95-109.**
- 284 **9. Companys E, Cecilia J, Codina G, Puy J, and Galceran J (2005) J.**
285 **Electroanal. Chem. 576:21-32.**
- 286 **10. Companys E, Puy J, and Galceran J (2007) Environ. Chem. 4:347-354.**
- 287 **11. Galceran J, Huidobro C, Companys E, and Alberti G (2007) Talanta 71:1795-**
288 **1803.**
- 289 **12. Companys E, Naval-Sanchez M, Martinez-Micaelo N, Puy J, and Galceran J**
290 **(2008) J. Agric. Food Chem. 56:8296-8302.**
- 291 **13. Alberti G, Biesuz R, Huidobro C, Companys E, Puy J, and Galceran J (2007)**
292 **Anal. Chim. Acta 599:41-50.**
- 293 **14. Domingos R.F., Huidobro C, Companys E, Galceran J, Puy J, and Pinheiro**
294 **JP (2008) J. Electroanal. Chem. 617:141-148.**
- 295 **15. Huidobro C, Companys E, Puy J, Galceran J, and Pinheiro JP (2007) J.**
296 **Electroanal. Chem. 606:134-140.**
- 297 **16. J. Galceran, D. Chito, N. Martinez-Micaelo, E. Companys, C. David, and J.**
298 **Puy. The impact of high Zn⁰ concentrations on the application of AGNES to**
299 **determine free Zn(II) concentration. Journal of Electroanalytical Chemistry,**
300 ***in press* 2010.**
- 301 **17. Clesceri, A.E.Greenberg, and A.D.Eaton (Eds.) (1998) in Standard methods**
302 **for the Examination of water and wastewater. APHA, AWWA, WEF,L.S..**
- 303 **18. Zirino A and Healy ML (1971) Limnol. Oceanogr. 16:773-778.**
- 304 **19. Lecomte J, Mericam P, Astruc A, and Astruc M (1981) Anal. Chem. 53:2372-**
305 **2374.**
- 306 **20. Pei JH, Tercier-Waeber ML, and Buffle J (2000) Anal. Chem. 72:161-171.**
- 307 **21. Anderegg G (1960) Helvetica Chimica Acta 43:414-424.**
- 308 **22. Tichane RM and Bennett WE (1957) J. Amer. Chem. Soc. 79:1293-1296.**
- 309 **23. Smith EJ, Davison W, and Hamilton-Taylor J (2002) Water. Res. 36:1286-**
310 **1296.**
- 311 **24. US-EPA. Methods for Measuring the Acute Toxicity of Effluents and**
312 **Receiving Waters to Freshwater and Marine Organisms (*Fifth Edition*). EPA-**
313 **821-R-02-012. 2002. Washington (US).**

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Tables

Table 1 h values obtained from calibrations at different ionic strength (μ) (mean values of 2 replicates). Number in between brackets indicates the standard deviation and refer to the last significant digit. AGNES parameters: $Y = 50$, $t_{1a} = 35$ s, $t_{1b} = 3$ $t_{1a} = 105$ s, $t_2 = 0.2$ s.

| μ /M | 0.1 | 0.02 | 0.01 | 0.004 |
|-----------------------|----------|----------|---------|---------|
| h /AM ⁻¹ | 0.104(4) | 0.101(9) | 0.11(2) | 0.11(2) |

321
 322

Table 2 Composition of soft synthetic water. pH adjusted to 8.3, $\mu = 0.004$ M

| | |
|-----------------------------------|-------------------------|
| MgCl ₂ | 6.00×10^{-5} M |
| CaCO ₃ | 1.70×10^{-4} M |
| CaCl ₂ | 8.00×10^{-5} M |
| Ca(NO ₃) ₂ | 1.50×10^{-5} M |
| KHCO ₃ | 2.50×10^{-5} M |
| NaHCO ₃ | 1.90×10^{-4} M |
| Na ₂ SO ₄ | 1.15×10^{-3} M |
| Zn(NO ₃) ₂ | 3.00×10^{-7} M |

323
 324
 325

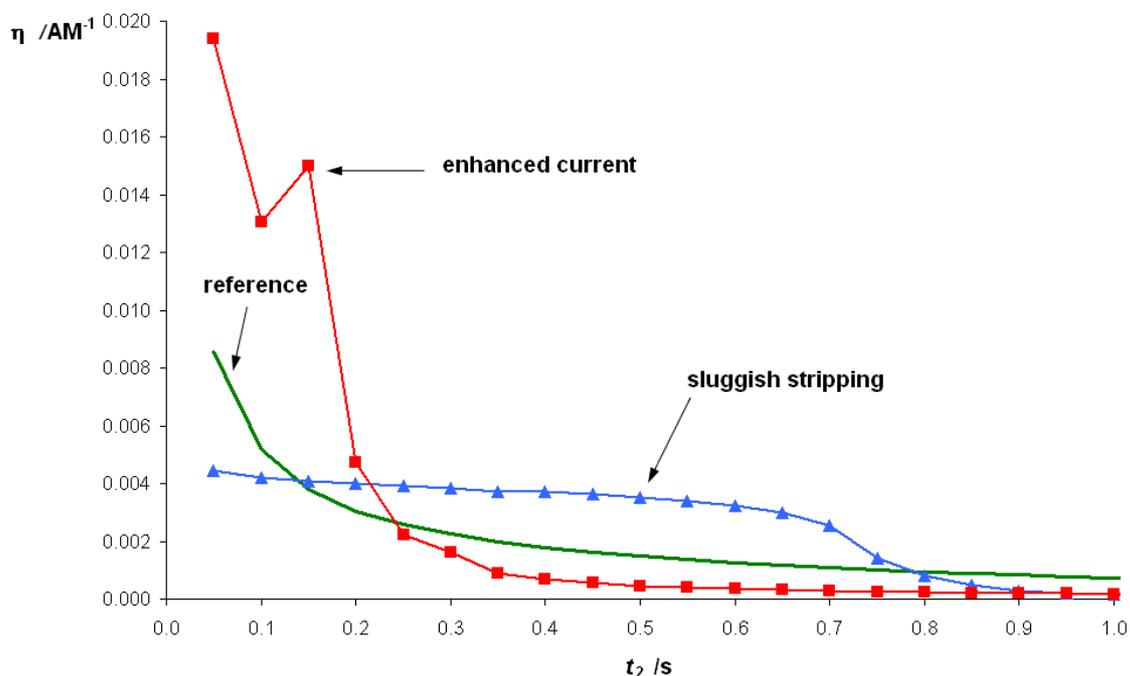
Table 3 Composition of hard synthetic water. Experiments at pH 7.6 and 8.1. $\mu = 0.008$ M.

| | |
|-----------------------------------|-------------------------|
| CaSO ₄ | 8.00×10^{-4} M |
| MgSO ₄ | 1.00×10^{-3} M |
| NaHCO ₃ | 2.28×10^{-3} M |
| KCl | 1.04×10^{-4} M |
| Zn(NO ₃) ₂ | 3.00×10^{-7} M |

326

327 **Figures**

328



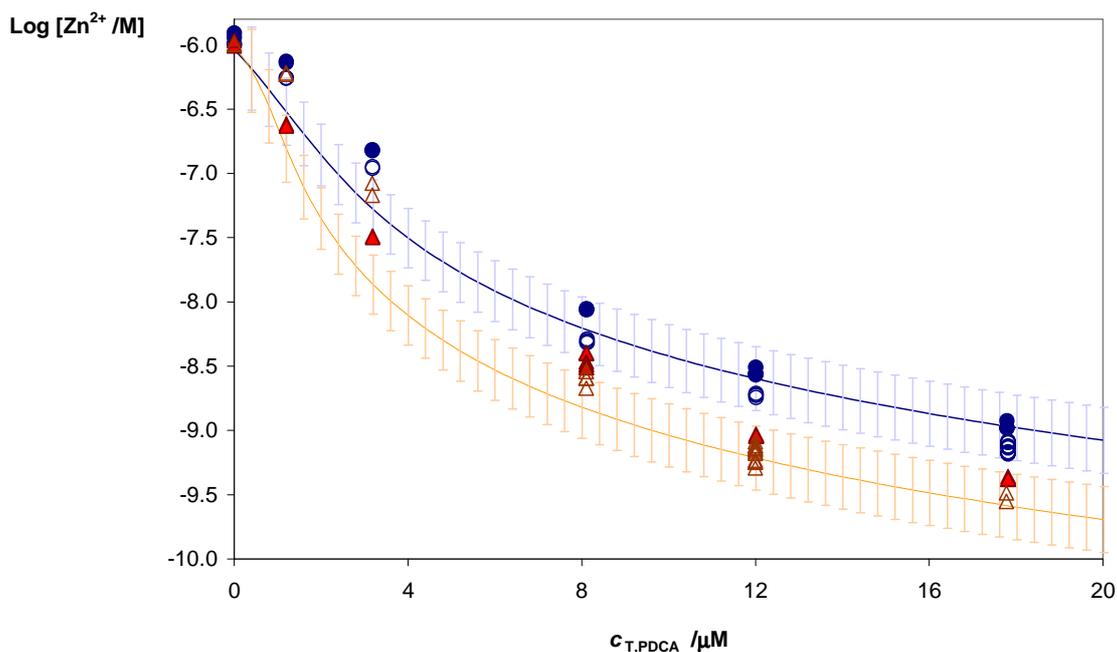
329

330 Fig 1: Normalized stripping currents for a fixed ionic strength 0.001 M and variable Y
 331 times $[Zn^{2+}]$. Stripping currents with low product Y times $[Zn^{2+}]$ (continuous green line
 332 taken as reference line; $Y=50$; $[Zn^{2+}] = 1.8\mu M$) show a behaviour as the standard one
 333 obtained with higher ionic strengths. Series with high product Y times $[Zn^{2+}]$ clearly
 334 exhibit *acb*. The exaltation variant of *acb* is seen in the series with $[Zn^{2+}] = 38\mu M$, $Y=10$
 335 (red squares), while the sluggish stripping variant of *acb* is apparent in the series with
 336 $Y=50$; $[Zn^{2+}] = 38\mu M$ (blue triangles).

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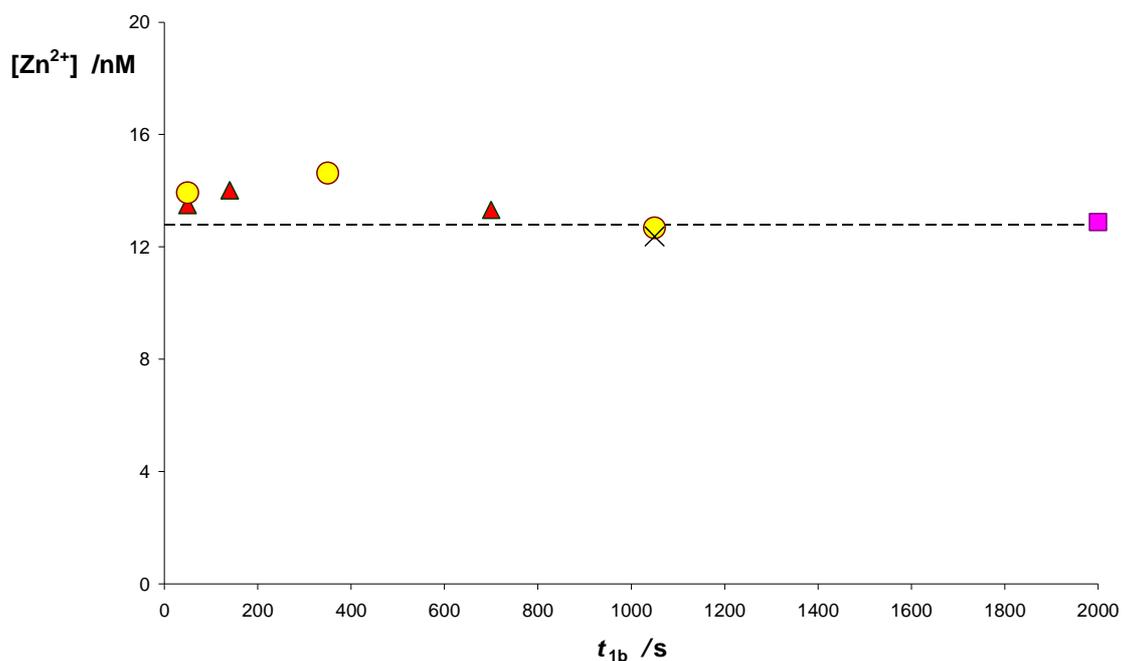
340

341 Fig 2: Free Zn concentration vs. added PDCA to a solution with a total Zn concentration
 342 of 1 μM for two different ionic strengths. The theoretical values are depicted in
 343 continuous lines (blue line for ionic strength 0.1M and red line for ionic strength
 344 0.005M), with the error bar indicating the uncertainty. AGNES experiments were
 345 replicated two different days (full and open markers) at each ionic strength KNO₃ 0.1 M
 346 (blue circles) and KNO₃ 0.005 M (red triangles). For each PDCA addition (and ionic
 347 strength), more than one AGNES measurement was performed by changing the
 348 combination of deposition times [*t*_{1a}, *t*_{1b}].

349

350

351



352

353 Fig 3: Free Zn concentration determined by AGNES in the Besòs River sample with
354 different settings. Red triangles: AGNES 2P, $Y=200$, $t_{1a}=140$ s; yellow bullets:
355 AGNES 2P, $Y=500$, $t_{1a}=150$ s; black x: AGNES 2P, $Y=500$, $t_{1a}=350$ s; pink square:
356 AGNES 1P, $Y=200$. The dashed horizontal line indicates the mean value of the longer
357 times.

358

359