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1 **Free Zn²⁺ determination in natural freshwaters of the Pyrenees:**
2 **towards on-site measurements with AGNES**

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12

13 **Environmental context**

14 Knowledge of the speciation of metals, especially of the free metal ion concentration, is
15 essential to understand the fate of these elements in rivers and their effects on living
16 organisms. On-site analyses are preferred for these measurements as they allow problems
17 associated with sample transportation and preservation to be avoided. In this context, an
18 on-site methodology, based on an electrochemical method and screen printed sensors has
19 been developed in the laboratory and validated on-site.

20 **Abstract**

21 An on-site methodology has been developed for the direct determination of free Zn^{2+} with
22 AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) in freshwaters. This
23 implementation includes: i) the use of screen printed electrodes, which provide good
24 limits of detection and easy transportation and deployment; ii) no need for sample
25 purging; iii) a calibration in a synthetic river solution that reproduces well the speciation
26 changes of the natural samples and allows the oxygen interferences to be minimised; iv)
27 the addition of a background electrolyte up to 0.01 mol L^{-1} in both the calibration and
28 freshwater samples; v) chemical stripping chronopotentiometry as the quantification
29 stage of AGNES. This procedure minimizes the effects of working at low ionic strength
30 and in the presence of dissolved oxygen.

31 In the laboratory, the methodology was checked with different natural samples taken from
32 rivers Garonne, Gave de Cauterets and Gave de Pau in the Pyrenees. Results appeared in
33 good agreement with theoretical estimations computed from Visual Minteq. On-site
34 measurements were performed for the first time with AGNES in the Gave de Cauterets
35 in Soulom (France) and the results were corroborated with purged measurements
36 performed in the laboratory.

37

38 **Keywords:** Free zinc (Zn^{2+}), Screen-Printed Electrodes, on-site measurements, AGNES,

39 geochemical model

40

41 1. Introduction

42 The free Zn^{2+} ion concentration in environmental aqueous systems is an important factor
43 in determining Zn deficiency or toxicity to organisms as the element in this form is
44 directly bioavailable. Many analytical techniques like ion exchange methods^[1], Donnan
45 Membrane Technique (DMT)^[2, 3] or Permeation Liquid Membrane (PLM)^[4] have been
46 developed to determine the free metal ion concentrations in natural samples. These
47 methods agree well with speciation models (WHAM or MINTEQ),^[5-8] but require
48 complementary equipment which cannot be moved into the field for on-site
49 measurements. Commercial ion selective electrodes (ISE) are of particular relevance for
50 trace metal studies,^[9, 10] but their commercial versions lack the required sensitivity and
51 cannot measure Zn.

52 During the last few years, an electroanalytical technique called Absence of Gradients and
53 Nernstian Equilibrium Stripping (AGNES)^[11] has been developed to determine free Zn^{2+}
54 concentration^[12-15]. Typically, it has been implemented with the hanging mercury drop
55 electrode (HMDE) and has been used, amongst other applications, to determine free Zn^{2+}
56 or Pb^{2+} concentrations in sea^[13, 16] and river^[14, 15] waters.

57 Recent developments of AGNES^[17-19] are making the possibility of on-site measurements
58 realistic which would avoid numerous problems that can potentially occur during
59 sampling and sample handling of natural solutions (contamination, changes in pH and
60 temperature, loss by adsorption, etc). Obviously, the HMDE is poorly adapted for on-site
61 studies. Consequently, the application of AGNES has been undertaken with thin film
62 mercury screen-printed electrodes (SPE) which represent an ideal alternative to the use
63 of the HMDE.^[19, 20] These sensors have a very small size (9.6 mm²) and use a thin mercury
64 film thickness (200 nm) which make them easy to deploy on-site. Unlike the HMDE,
65 SPEs do not need any N_2 pressure and, thus, the transport of N_2 bottles to the field, which
66 could be very problematic, is avoided. A recent work has demonstrated the feasibility of

67 measuring free Zn^{2+} and Cd^{2+} in non-deaerated synthetic solutions provided that the
68 changes in speciation, due to the reduction of the dissolved oxygen, is similar in the
69 calibration and sample solutions^[17]. Another challenge presented by on-site analysis are
70 measurements made in freshwaters of low ionic strength..The analytical signal obtained
71 using AGNES is affected by low ionic strength media^[18]. Finally, the last variant of
72 AGNES, called AGNES-SCP, where the reoxidation stage consists of stripping
73 chronopotentiometry (SCP) (also called potentiometric stripping analysis (PSA)), has
74 shown an important improvement as metal interferences can be avoided^[19, 20].

75 The objective of this work was to determine free Zn^{2+} concentration in natural freshwaters
76 from some rivers of the Pyrenees (Garonne, Gave de Cauterets and Gave de Pau) by
77 developing a new analytical strategy using AGNES-SCP.

78 In this work, two aspects limiting the on-site applicability of electrochemical techniques
79 to freshwater samples are tackled: the low ionic strength of the media, and the presence
80 of dissolved oxygen. For the first time using AGNES, the developed methodology has
81 been applied on-site in a highly contaminated natural freshwater sample of the Gave de
82 Cauterets.

83 This strategy has been validated by comparing results with measurements performed on
84 the same samples by applying the purged classical AGNES methodology in the
85 laboratory. The laboratory results have been corroborated with theoretical estimations
86 carried out with Visual Minteq modelling software^[21].

87

88 **2. Experimental**

89 **2.1 Reagents**

90 Zn 1000 mg L⁻¹ stock solution was obtained from Merck. KNO₃ (Trace Select), HNO₃
91 (69-70%, Baker Instra-Analysed for trace metal analysis), NaOH (Baker Analysed), HCl

92 (Baker Instra-Analysed for trace metal analysis) were purchased from Aldrich. Ultrapure
93 milli-Q water (resistivity 18.2 M Ω cm) was employed in all the experiments. Purified
94 water-saturated nitrogen N₂ (50) was used for deaeration and blanketing of solutions.
95 Synthetic river water was prepared from sodium hydrogen carbonate (Scharlau),
96 magnesium sulphate (Merck, Pro Analysis), calcium chloride (Merck, Pro analysis) and
97 potassium nitrate (Aldrich, Trace Select). A stock solution of synthetic river water was
98 prepared as follows: 10⁻² mol L⁻¹ NaHCO₃, 10⁻³ mol L⁻¹ MgSO₄·7H₂O, 2×10⁻³ mol L⁻¹
99 CaCl₂·2H₂O and 5×10⁻⁴ mol L⁻¹ KNO₃, which corresponds to an ionic strength of 0.0192
100 mol L⁻¹. For each experiment with synthetic river water, the stock solution was diluted to
101 obtain a solution having a composition close to the river sample (Table 1) leading to an
102 ionic strength of 0.002 mol L⁻¹ and a conductivity of 145 μ S cm⁻¹. To avoid voltammetric
103 problems derived from the low ionic strengths of the samples^[18], the solutions (both
104 synthetic and freshwater) were doped with KNO₃ up to 0.01 mol L⁻¹, to give a
105 conductivity close to 1500 μ S cm⁻¹. At this ionic strength, no problems derived from low
106 supporting electrolyte are expected. Using Visual Minteq, it has been observed that this
107 addition does not alter the speciation of the river samples. The pH was adjusted with 0.01
108 mol L⁻¹ NaOH or 0.01 mol L⁻¹ HNO₃ to reach the pH of the natural river sample.
109 Water samples were filtered on-site with 0.45 μ m acetate cellulose filters by using
110 Nalgene polysulfone, a reusable complete filter unit (from VWR) and a Mityvac hand
111 vacuum pump (model MV8010).

112

113

114

115 2.2 Equipment

116 Major cation concentrations were obtained with an Inductively Coupled Plasma Atomic
117 Emission Spectrometer (ICP-AES) (Horiba Jobin Yvon, Activa-M). Trace elements were
118 obtained with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent
119 7500ce). Major anions were measured with an ion chromatograph (Dionex DX-120).
120 Dissolved organic carbon (DOC) was obtained with a Total Organic Carbon Analyzer
121 (Shimadzu TOC-V CSN). Dissolved oxygen was measured with a multi-parameter
122 analyser Consort C535. Temperature, pH and conductivity were measured with a multi-
123 parameter analyser WTW 340i.

124 Voltammetric measurements were performed with an Eco Chemie μ -Autolab III
125 potentiostat attached to a Metrohm 663 VA Stand and to a computer by means of the
126 GPES 4.9 (Eco Chemie) software package. The auxiliary electrode was a glassy carbon
127 electrode. The reference electrode was a DRIFEF-5 (3 mol L⁻¹ KCl) purchased from
128 World Precision Instrument. All potentials were given versus this reference electrode.
129 Glass jacketed cells, provided by Metrohm, were used to maintain the temperature
130 constant (generally at 20°C). SPE were prepared using a commercial ink electrodag PF-
131 407A (Acheson Colloids). The electrodes were screen-printed on 1 mm-thick polystyrene
132 support for serigraphy (Sericol) (Figure 1). After a drying step (1 hour at room
133 temperature) and a curing step (1 hour at 60°C), an insulating layer was spread manually
134 over the conductive track, leaving a working disk area of 9.6 mm²[22]. A thin layer of
135 mercury was deposited onto the electrode surface for trace metal detection. The mercury
136 deposition on the SPE was carried out using an acetate buffer solution (0.2 mol L⁻¹, pH =
137 4.6) prepared from acetic acid (Trace select), sodium acetate trihydrate (Trace select) and
138 0.83 mmol L⁻¹ Hg(NO₃)₂ (all obtained from J.T. Baker). First, the working surface of the
139 electrode was conditioned by applying 4 cycles of cyclic voltammetry (CV) using the
140 following conditions: potential range from -0.1 V to +0.8 V, scan rate 100 mV/s, step

141 potential 2.4 mV. The Hg film was then deposited at -1.0 V, with stirring until the charge
142 associated with the deposited mercury (Q_{Hg}) reached 25 mC.

143

144 **2.3 Sampling and on-site analyses**

145 Two rivers in the Pyrenees have been studied in this work (Figure 2): the Garonne river,
146 which flows in Spain downstream from a Zn mining area and enters into France, and the
147 Gave de Pau which is supplied by a stream, the Gave de Cauterets, also located
148 downstream from a Zn mining area, and continues until Pau (France). The sampling
149 campaigns were carried out on two different dates: April 2012 with a high water level in
150 the Gave de Pau (due to the plentiful rainfalls during the month of April^[23]) and in May
151 2012 with a low water level.

152 At all sampling places, temperature, pH, conductivity and dissolved oxygen were
153 measured directly in the river. 250 mL of filtered water samples have been acidified with
154 HNO₃ at 2% and stored at 4°C in new polystyrene bottles to measure the concentrations
155 of major cations and trace metals. 250 mL of filtered water sample has been kept without
156 acidification for carbon analysis, anion analysis and AGNES experiments.

157

158 **2.4 Free Zn²⁺ determination**

159 The determination of the free Zn²⁺ using AGNES-SCP procedure^[19] consists of two
160 conceptual stages. Along the first (deposition) stage, the metal ion Zn²⁺ from the solution
161 is reduced to Zn⁰ until attainment of a special situation of Nernstian equilibrium and
162 absence of gradients in the concentration profiles ^[11]. This equilibrium is achieved by
163 applying a potential E_1 more negative than the standard formal potential of the couple
164 Zn²⁺/Zn⁰, E^0 , for a sufficiently long time t_1 . These conditions imply that identical
165 analytical signals (in the second stage) are obtained for deposition times longer than a

166 certain minimum t_1 . At the end of the deposition stage, Nernstian equilibrium is reached
167 and there is no gradient in the concentration profiles at each side of the electrode surface.
168 The Nernst equation allows the concentration ratio at each side of the mercury electrode,
169 also called gain Y , to be calculated as (Eq. 1):

$$170 \quad Y = \frac{[M^0]}{[M^{n+}]} = \exp\left[\frac{-nF}{RT}(E_1 - E^{0'})\right] \quad \text{Eq. 1}$$

171 where n is the number of exchanged electrons, F is the faraday constant, R the gas constant
172 and T the temperature.

173 The deposition potential E_1 corresponding to a given gain Y can be determined from the
174 peak potential of a differential pulse polarogram (DPP)^[11]. The higher the gain Y , the
175 higher the sensitivity of the AGNES measurement. However, higher gains will require
176 longer electrodeposition times to reach Nernstian equilibrium. Consequently, the chosen
177 deposition potential will correspond to the lowest gain that allows obtainment of a well-
178 shaped peak..

179 The goal of the second stage of AGNES-SCP is to measure the concentration of the
180 reduced metal M^0 inside the mercury amalgam, e.g. by applying a constant oxidizing
181 stripping current, generally between 1 and 10 μA ^[19]. The analytical signal is the time
182 taken for the analyte reoxidation (transition time, τ). SCP conditions of full depletion
183 allow measuring the total faradaic charge Q which is proportional to the free metal ion
184 concentration $[M^{2+}]$ according to Eq. 2.

$$185 \quad Q = nFV_{\text{Hg}}[M^0] = nFV_{\text{Hg}}Y[M^{2+}] = h_Q[M^{2+}] \quad \text{Eq. 2}$$

186 where V_{Hg} is the volume of deposited mercury and h_Q is the slope of the calibration plots.
187

188 2.5 Speciation models

189 The geochemical modelling program Visual MINTEQ, version 3.0^[21] (using the standard
190 databases) was used to predict metal speciation in the investigated rivers. The following
191 inputs were provided: pH, temperature, and total concentrations for Ca²⁺, Na⁺, K⁺, Mg²⁺,
192 Mn²⁺, NO₃⁻, SO₄²⁻, Cl⁻, CO₃²⁻, total Zn and DOC. The NICA-Donnan model was used to
193 describe the formation of metal-DOM (dissolved organic matter) complexes. It was
194 assumed that the ratio of active DOM to DOC (dissolved organic C) was 1.65^[24] and that
195 100% of the active DOM was fulvic acids (FA)^[24].

196

197 **3. Results and discussion**

198 **3.1 General physicochemical analyses of river waters**

199 As shown in Table 1, physicochemical properties show little difference between both
200 rivers. The pH of the samples were between 7.25 and 7.77 in the Garonne, with a slight
201 increase observed from upstream in the Gave de Pau (7.35 in Soulom) to downstream
202 (8.16 in Laroin). Dissolved oxygen does not show strong variations with an average
203 concentration of 13 mg L⁻¹, except in Pointis de Rivière in the Garonne (6.25 mg L⁻¹).
204 This low value can be explained by the presence of stagnant water. Conductivity recorded
205 at the different places appeared relatively low with values between 78 and 226 μS cm⁻¹.
206 An increase is observed from upstream to downstream related to the simultaneous
207 increase of the concentrations of cations (Ca²⁺, K⁺, Na⁺, Mg²⁺) and anions (Cl⁻, NO₃⁻,
208 SO₄²⁻). The DOC concentrations vary from 0.7 to 3.7 mg L⁻¹ except in Baudreix where
209 the value is higher (6.8 mg L⁻¹), probably due to human activity in the leisure area.

210 Table 2 presents the total dissolved trace metal concentrations measured in acidified
211 samples from both rivers. Total dissolved Pb and Cd concentrations are lower than 0.1
212 μg L⁻¹ except for Cd in Victoria which is the most contaminated site. Total dissolved Cu
213 concentrations are relatively low at all sampling sites, without obvious impact from

214 human activity, suggesting these values correspond to the natural geochemical
215 concentrations. Regarding Zn, the highest total dissolved concentrations are observed in
216 places near a mining area: Victoria ($549 \mu\text{g L}^{-1}$) and Liat ($73 \mu\text{g L}^{-1}$) in the Garonne, and
217 Soulom ($136 \mu\text{g L}^{-1}$) in the Gave de Pau. In both rivers, a dilution phenomenon is clearly
218 observed downstream from the mines due to many tributaries. Stable values around $5 \mu\text{g}$
219 L^{-1} are reached in the most downstream places, probably close to the geochemical
220 background concentration.

221

222 **3.2 Optimization of AGNES-SCP experimental conditions for on-site** 223 **analyses**

224 Since total Cd and Pb concentrations were found to be very low, only free Zn^{2+} was
225 determined. The optimization of the technique was performed in the laboratory with
226 synthetic river water samples before being applied to natural samples in the laboratory
227 and on-site.

228

229 **3.2.1 Low ionic strength effects on AGNES**

230 The low ionic strength reflected by the conductivity values found in the river (between
231 78 and $226 \mu\text{S cm}^{-1}$) can be problematic when working with electrochemical techniques.
232 As shown in Figure 3, for a common fixed deposition potential ($E_1 = -1.08\text{V}$) applied to
233 the purged solution, the analytical signal decreases when increasing the sample
234 conductivity. This can be rationalized from Nernst equation, eqn. 1 written^[18] as:

$$235 \quad [\text{Zn}^0] = \gamma_{\text{Zn}^{2+}} [\text{Zn}^{2+}] \exp\left[\frac{-nF}{RT} (E_1 - E^0)\right] \quad \text{Eq. 3}$$

236 where E^0 is the standard redox potential (which is constant at a given temperature). When
237 the ionic strength increases, the activity coefficient decreases, so the number of
238 accumulated moles of Zn^0 and the analytical signal decrease.

239

240 The analysis of low ionic strength by electrochemical techniques can be hindered by the
241 ohmic drop in the solution. At high ionic strength, the application of a potential difference
242 between the electrodes results in this potential drop being spatially localized between the
243 working electrode and the adjacent solution. At low ionic strength, the applied potential
244 accounts for the drop of potential at the electrode interface plus the ohmic drop across the
245 solution due to the non-negligible resistance of the solution. This impacts most
246 electroanalytical techniques, because the potential drop at the electrode interface does not
247 coincide with the nominal applied potential^[18]. Notice, however, that the ohmic drop at
248 the end of the deposition stage of AGNES in purged solutions is negligible due the low
249 current at equilibrium (arising from the traces of oxygen), but can be important in non-
250 deaerated solutions.

251 The impact of changing ionic strength (due to changes in the activity coefficients) is
252 pronounced for a KNO_3 concentration lower than $10^{-2} \text{ mol L}^{-1}$ which corresponds to a
253 conductivity lower than $1200 \mu\text{S cm}^{-1}$. This means that AGNES-SCP will be particularly
254 sensitive in the river samples where the conductivity measured in the rivers is around 100
255 $\mu\text{S cm}^{-1}$ (because the ionic strength is not accurately known). For this reason, the
256 conductivity of the natural freshwater sample has been fixed to avoid voltammetric
257 problems in AGNES-SCP derived from the low ionic strengths. Thus, both solutions,
258 synthetic and natural freshwaters, were doped with KNO_3 up to $10^{-2} \text{ mol L}^{-1}$ where no
259 problems derived from low supporting electrolyte are expected. Simulations made with
260 Visual Minteq and the estimated water composition have shown that the free Zn^{2+}
261 concentration was not affected when adding this amount of KNO_3 (data not shown).

262

263 3.2.2 Oxygen influence during AGNES deposition step

264 In non-purged solutions, the pH at the surface of the electrode is higher than that of the
265 bulk solution, due to the important reduction of O_2 ^[17]. The presence of oxygen hinders
266 the standard AGNES application by preventing the achievement of absence of gradients
267 in the solution concentration profiles by the end of the preconcentration step. Instead, a
268 steady-state situation is reached where the metal concentration at the surface of the
269 electrode (due to the speciation at a higher pH) is depleted with respect to the bulk
270 concentration. Thus, the aimed preconcentration gain Y (referred to bulk concentrations)
271 might not be achieved, but rather be far smaller^[17].

272 Additionally, the steady-state consumption of O_2 implies an increase of the residual
273 current and a concomitant decrease of the actual applied potential due to ohmic drop. pH
274 effects derived from the oxygen interference can be avoided with an effective buffer that
275 compensates for the OH^- production at the electrode surface without any change in the
276 metal speciation. Alternatively, calibration solutions in which the steady-state depletion
277 of the metal is similar to the depletion of the samples, may be used. The latter is the
278 strategy followed in this work. A calibration has been performed in a synthetic river
279 solution in which the chemical composition is close to the one of the river sample in terms
280 of pH and geochemical composition. In this way, we ensure that changes in calibration
281 and measuring samples due to the presence of oxygen are similar.

282 The determination of the required potential for a given gain has been obtained empirically
283 searching for a sufficient analytical signal. Thus, using E_1 -values between -1.165 and -
284 1.190 V, the gain was enough for a reliable measurement of Zn in Pyrenees river samples.

285

286 3.2.3 Oxygen influence during stripping step

287 In SCP, the analytical signal is the time taken for the analyte reoxidation (transition time,
288 τ) while a constant oxidizing stripping current is applied^[25]. However, this current
289 corresponds to the sum of the imposed stripping current (I_s) and the oxidants current (I_{ox})
290 due to oxidizing agents (e.g. oxygen) present in the solution^[17]. In classical analyses with
291 purging, I_{ox} is negligible in front of the I_s (10 μ A) usually imposed with AGNES-SCP^[19].
292 In non-purged solutions, it has been shown that interferences due to oxygen during the
293 stripping stage could be minimized by using specific stripping techniques such as square
294 wave anodic stripping voltammetry (SWASV) with high frequency^[26] or stripping
295 chronopotentiometry (SCP) with sufficiently high stripping currents^[19]. However, in
296 AGNES-SCP, a large oxidizing current can induce a fast stripping step which can lead to
297 a truncated signal. To avoid this, a chemical stripping (SCP_{chem}) was applied where the
298 reoxidation is only performed through oxidants current I_{ox} (mainly due to oxygen) present
299 in the solution without imposing any external current (i.e. $I_s=0$)^[27, 28]. The accumulated
300 charge Q , in this case, can be computed as (Eq. 3):

$$301 \quad Q = -I_{ox}\tau \quad \text{Eq.}$$

302 **4**

303

304

305 I_{ox} , obtained at the end of the deposition stage with the solution in quiescent conditions,
306 appeared to be stable with time, indicating that a steady state for the entire system,
307 including the transport of O₂ towards the electrode, was reached. It has been shown that
308 either Q or τ were proportional to the free metal concentrations at the electrode surface^[20].

309

310 3.2.4 AGNES-SCP implementation in the present work

311 When working with non-deaerated solutions, the deposition potential needs to be very
312 negative, because of the decrease in metal concentration at the electrode surface. This is
313 due to the reaction of the free metal with the OH^- species formed from the O_2 reduction
314 at the electrode surface^[17]. Using E_1 -values between -1.165 and -1.190 V, the gain was
315 enough for a reliable measurement of the metal as explained below.

316 Chemical stripping has been used during the second stage of AGNES-SCP to obtain a
317 well-shaped peak. In order to avoid confusion with classical SCP using a constant
318 stripping current, this new method will be called AGNES-SCP_{chem}.

319 As discussed below, calibration of AGNES was performed using synthetic river waters
320 whose characteristics were close to the ones of the Gave de Pau river samples in terms of
321 pH and geochemical composition. In this way, we ensure that changes in calibration and
322 measuring samples due to the presence of oxygen are similar. A typical calibration curve
323 is presented in Figure 4.

324

325 3.2.5 Temperature effect on AGNES-SCP_{chem} method

326 The influence of temperature on AGNES-SCP_{chem} was evaluated in a non-purged solution
327 (Figure 5). The analytical signal (τ) increased around 3.7 ms with each increase of 1 °C.
328 This evolution results from: i) the decrease of the dissolved oxygen concentration when
329 temperature increases (Table 1). Lower I_{Ox} values correspond to slower stripping
330 processes, leading to longer τ ; ii) the dependence of the E^0 potential with temperature.
331 For a fixed deposition potential, the increase in temperature in this system leads to higher
332 accumulations and analytical signals as expected from the endothermic nature of Zn^{2+}
333 reduction^[29]. So, the temperature has to be carefully controlled when performing AGNES
334 with Zn. All the experiments in the laboratory were performed with a thermostated bath

335 at 20 °C, except the on-site measurements and on-site calibrations which were performed
336 at the natural river temperature.

337

338 3.2.6 Interferences of Cu with Zn

339 In multicontaminated systems, a high concentration of metals can be accumulated in the
340 mercury amalgam, so that intermetallic compounds may form^[30, 31]. This phenomenon
341 arises when Cu and Zn concentrations are sufficiently high so that the solubility of the
342 intermetallic compounds in mercury is exceeded. Figure 6 shows how the analytical
343 signal was not affected by the presence of Cu in the solution up to a concentration of 2
344 $\mu\text{g L}^{-1}$ (well above Cu concentration in the river samples).

345

346 3.2.7 Limit of detection and limit of quantification

347 The limit of detection (LOD) has been statistically determined from the calibration curve
348 obtained from 12 calibration points in a synthetic river solution at pH 7.9 with AGNES-
349 SCP_{chem} without purging according to Eq. 4^[32]:

$$350 \text{ LOD} = (b + k S_b) / m \quad \text{Eq. 5}$$

351 where $k = 3$, b is the intercept of the regression line, S_b is the intercept standard deviation
352 of the regression line and m is the slope of the calibration graph. The quantification limit
353 (LOQ) was calculated with the same equation as for the detection limit, but with $k = 10$.
354 For each Zn concentration, three replicates were performed at three different deposition
355 times to be sure that AGNES conditions are fulfilled. Thus, by using a deposition potential
356 of -1.165V, a LOD of $0.6 \mu\text{g L}^{-1}$ and a LOQ of $0.9 \mu\text{g L}^{-1}$ have been obtained. If necessary,
357 more negative deposition potentials (which require longer deposition times) could be used
358 to detect lower free Zn^{2+} concentrations.

359

360 **3.3 In lab determination of free Zn²⁺ concentration in freshwaters**

361 The free Zn²⁺ concentrations were determined in the laboratory in different samples taken
362 from the Gave de Pau and Garonne rivers in May 2012 following the non-purged
363 methodology previously described. Calibration was performed in a synthetic river water
364 whose characteristics were close to the ones of the considered river sample^[17].

365 Table 2 shows the retrieved free Zn²⁺ concentrations applying $E_1 = -1.165$ V, $t_1 = 300-400$
366 s at 20°C. The proportion of free Zn²⁺ determined in the river is very high for all the
367 locations, ranging from 72 to 100 %, in comparison to previous studies carried out with
368 river waters^[15, 33, 34]. These results are consistent with the low levels of dissolved organic
369 matter found (around 3 mg L⁻¹) and low pH (pH<8). Calculations of metal speciation
370 show that as pH and carbonates increase, the concentrations of free ions decrease because
371 of the increased complexation with carbonate species and fulvic acid^[35].

372 Using the geochemical data measured for each sample, an estimation of the free
373 concentration was performed with Visual Minteq. Figure 7 shows that a good correlation
374 is observed between the experimental results obtained with AGNES-SCP_{chem} and the ones
375 computed from Visual Minteq which validates the AGNES-SCP_{chem} method applied in
376 natural water sample without purging. These results confirm the absence of Cu
377 interferences (consistent with the low Cu concentration, Table 2) and agree well with the
378 low conductivity (<200 μS cm⁻¹) and low organic matter contents indicative of low Zn
379 complexation capacity (Table 1).

380

381 **3.4 On-site free Zn²⁺ measurements**

382 On-site measurements were performed in the Gave de Cauterets at Soulom (France). In
383 April 2012, the pH of the river was 7.8, $T = 6^\circ\text{C}$ and conductivity 154 μS cm⁻¹. All the

384 material was deployed in the field and plugged into a portable battery if necessary. The
385 collected sample was filtered on-site at 0.45 μm . An aliquot of the sample was acidified
386 at pH 1.5 for ICP-AES analysis in laboratory. Another fraction of the sample was doped
387 with KNO_3 up to 0.01 mol L^{-1} for electrochemical analyses. The resulting free Zn^{2+}
388 concentration found on site was $374 \pm 54 \mu\text{g L}^{-1}$. In order to corroborate these results,
389 further classical AGNES-SCP were performed in the laboratory, purging with a mixture
390 of N_2/CO_2 in order to fix the pH in the most natural way possible without altering the
391 speciation of the sample^[14]. Since there is no interference from oxygen (no pH shift close
392 to the electrode), a more positive potential could be used ($E_1 = -1.065 \text{ V}$, $t_1 = 300\text{-}500 \text{ s}$)
393 and a 10 μA stripping current was applied. The calibration was performed in a KNO_3 0.01
394 mol L^{-1} solution at $T = 6^\circ\text{C}$. Given that, in purged samples, there is no need for the
395 calibration to be at the same pH as the sample, pH 5 was selected to minimize Zn
396 hydrolysis. The free Zn^{2+} concentration retrieved was $345 \pm 37 \mu\text{g L}^{-1}$ and appeared in
397 good agreement with the previous results obtained on-site.

398 The results measured in Soulom show huge differences in total Zn concentrations
399 between April 2012 ($647 \mu\text{g L}^{-1}$) and May 2012 ($136 \mu\text{g L}^{-1}$), but also the free Zn^{2+}
400 proportion: in May, all Zn was free, whereas only 58 % of the total Zn was free in April
401 2012. These differences could be explained by the plentiful rainfalls during the month of
402 April^[23] which induced a higher water level in the Gave de Pau. These events led to a
403 flooding of the old mines and, thus, to a high release of other components able to complex
404 Zn, such as carbonates and organic matter^[35]. This is supported by the highest conductivity
405 being recorded in April ($154 \mu\text{S cm}^{-1}$), relative to that in May ($78 \mu\text{S cm}^{-1}$).

406

407 **4. Conclusions**

408 A new methodology has been developed to measure on-site free Zn^{2+} in non-purged river
409 samples of the Pyrenees with AGNES-SCP_{chem}. The use of screen-printed electrodes
410 appeared very suitable for this purpose as they could be easily deployed on site.
411 Difficulties related to these measurements were removed by taking some precautions: i)
412 a calibration in a synthetic solution where the composition is similar to the one of the
413 sample; ii) calibration and sample analyses performed in the same conditions of pH and
414 temperature; iii) an ionic strength fixed by an addition of KNO_3 0.01 mol L^{-1} to avoid
415 anomalous voltammetric responses and ionic strength uncertainties.

416 Free Zn^{2+} measurements of samples taken from different locations in the Pyrenees rivers
417 have been performed in the laboratory to check the suitability of the AGNES-SCP_{chem}
418 methodology. Observed free Zn^{2+} concentrations appeared well correlated with the
419 estimated ones using Visual Minteq. Finally, AGNES experiments were carried out on-
420 site in the Gave de Cauterets in Soulom (France). The on-site measured free Zn^{2+} appear
421 in concordance with further measurements performed in the laboratory using the classical
422 N_2/CO_2 purge, validating the proposed methodology.

423 This study showed that the total and free Zn concentrations depend on the geographical
424 characteristics of the site (i.e. proximity to mines) and that an increase of the total Zn
425 concentration does not systematically lead to a proportional increase of the free Zn
426 concentration. This kind of approach is therefore of great interest in risk assessments,
427 given the different levels of toxicity of different metal species.

428

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435

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556

557 **Figure 4.** Calibration curve obtained with AGNES-SCP_{chem} in a synthetic river doped
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562 L⁻¹ with temperature. Inset: stripping signal at different temperatures: 5°C (—), 10°C
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571 **Figure 7.** Comparison of $[\text{Zn}^{2+}]$ determined from AGNES-SCP_{chem} with $[\text{Zn}^{2+}]$ computed
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574 stirring, $T = 20^\circ\text{C}$, chemical stripping without stirring.

TABLES

Table 1. Geochemical characteristics of rivers Garonne and Gave de Pau

		pH	T °C	Conductivity $\mu S\ cm^{-1}$	O ₂	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	CO ₃ ²⁻	DOC $mg\ L^{-1}$	Ca ²⁺	K ⁺	Na ⁺	Mg ²⁺
Garonne	Liat	7.25	8.6	111	12.05	0.42	0.86	9.05	45.1	2.0	21.44	0.14	0.63	0.21
	Vielha	7.77	10.8	142	13.15	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	23.93	0.44	1.18	2.48
	Victoria	7.68	11.6	226	11.1	1.20	1.08	40.82	74.1	2.7	39.61	1.15	1.96	1.83
	Les	7.44	10	116	12.85	2.24	0.91	6.86	46.2	2.4	19.94	0.30	1.73	1.58
	Fronsac	7.51	11.5	122	11.65	2.09	1.21	7.95	47.5	3.0	20.49	0.40	0.95	1.63
	Pointis de rivière	7.55	13.6	136	6.25	2.15	1.46	8.83	55.5	2.5	23.30	0.42	1.17	1.57
Gave de Pau	Soulom	7.35	8.8	78	14.15	0.67	1.78	4.95	29.2	3.7	14.05	0.19	0.26	0.72
	Villelongue	7.66	8.0	125	13.35	0.65	1.15	6.82	56.6	0.7	23.10	0.22	0.97	0.69
	Beaucens	7.66	9.1	125	13.40	0.72	1.38	6.78	57.2	2.0	23.07	0.25	0.90	0.74
	Lourdes amont	7.67	10.6	137	13.65	1.06	1.58	7.68	61.9	3.2	25.06	0.26	1.16	0.85
	Lourdes aval	7.69	10.9	142	12.50	1.10	1.45	7.51	66.6	2.9	27.13	0.27	1.18	0.94
	Baudreix	8.08	12.2	152	12.90	1.32	1.65	8.31	69.5	6.8	27.39	0.31	1.65	1.07
	Stade	8.05	13.7	166	13.25	1.67	2.35	8.57	77.2	2.8	29.68	0.38	1.83	1.24
	Laroin	8.16	14.4	185	12.50	2.55	2.84	8.80	87.1	1.0	34.11	0.53	1.95	1.76

Table 2. Total dissolved and free analysis results of rivers Garonne and Gave de Pau

		Total Cd	Total Pb	Total Cu	Total Zn	Free Zn
		$\mu\text{g L}^{-1}$				
Garonne	Liat	<i>LOD*</i>	<i>LOD*</i>	0.24 ± 0.01	73.0 ± 0.3	66
	Vielha	<i>LOD*</i>	<i>LOD*</i>	0.59 ± 0.02	13.4 ± 0.3	<i>nd**</i>
	Victoria	1.43 ± 0.02	<i>LOD*</i>	0.49 ± 0.01	549 ± 2	451
	Les	<i>LOD*</i>	<i>LOD*</i>	0.20 ± 0.02	8.7 ± 0.1	8.1
	Fronsac	<i>LOD*</i>	<i>LOD*</i>	0.18 ± 0.03	4.5 ± 0.1	3.5
	Pointis de rivière	<i>LOD*</i>	<i>LOD*</i>	0.19 ± 0.02	2.3 ± 0.1	2.0
Gave de Pau	Soulom	<i>LOD*</i>	<i>LOD*</i>	0.25 ± 0.03	136 ± 3	136
	Villelongue	<i>LOD*</i>	<i>LOD*</i>	0.23 ± 0.02	<i>LOD*</i>	<i>LOD*</i>
	Beaucens	<i>LOD*</i>	<i>LOD*</i>	0.07 ± 0.03	14.1 ± 0.4	11.7
	Lourdes amont	<i>LOD*</i>	<i>LOD*</i>	0.08 ± 0.02	10.1 ± 0.6	9.4
	Lourdes aval	<i>LOD*</i>	<i>LOD*</i>	0.21 ± 0.01	9.5 ± 0.5	7.2
	Baudreix	<i>LOD*</i>	<i>LOD*</i>	0.15 ± 0.02	6.8 ± 0.6	5.0
	Stade Eaux Vives	<i>LOD*</i>	<i>LOD*</i>	0.29 ± 0.01	5.7 ± 0.6	4.1
	Laroin	<i>LOD*</i>	<i>LOD*</i>	0.27 ± 0.01	4.1 ± 0.7	3.6

* *Limit of detection*; ** *not determined*

FIGURES

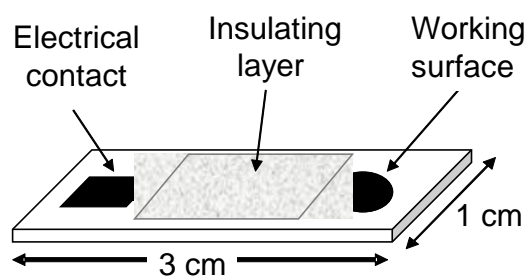


Figure 1. Scheme of a screen-printed electrode

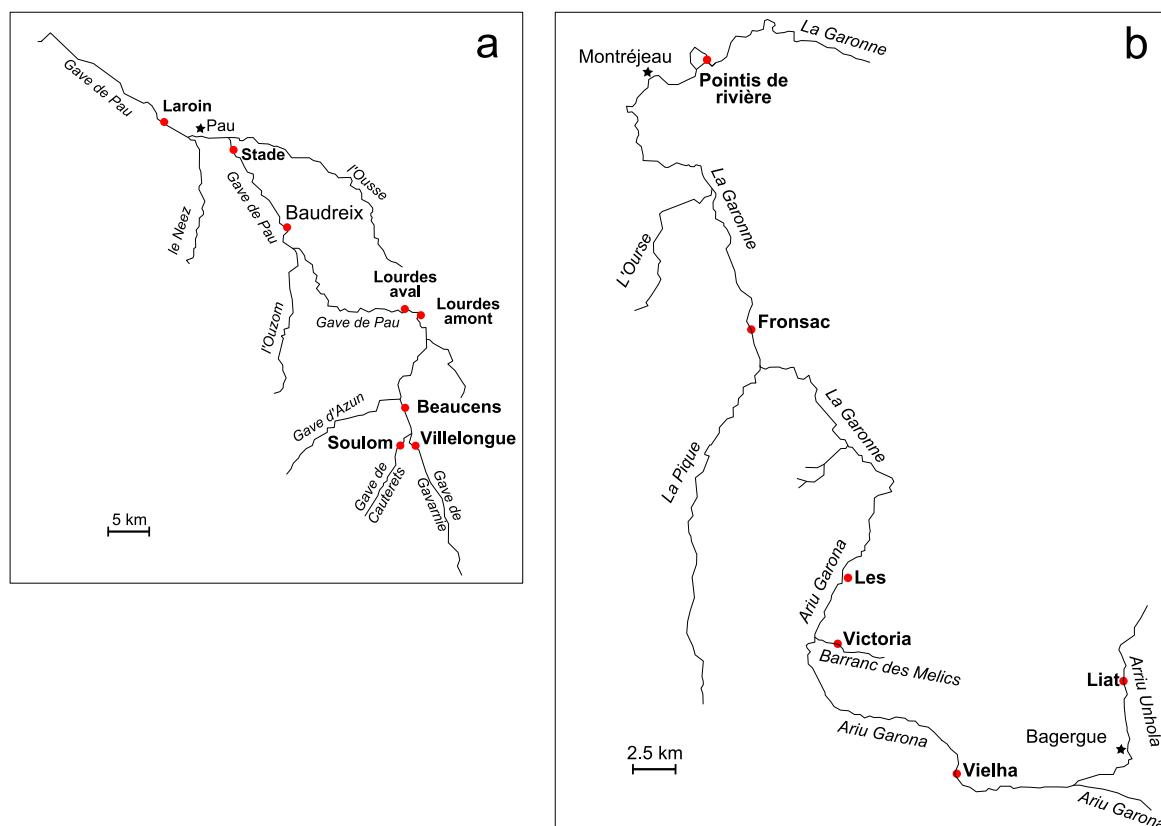


Figure 2. Map of the studied area: a. Gave de Cauterets and Gave de Pau and b. Garonne river. Sample sites are indicated with a red circle (●).

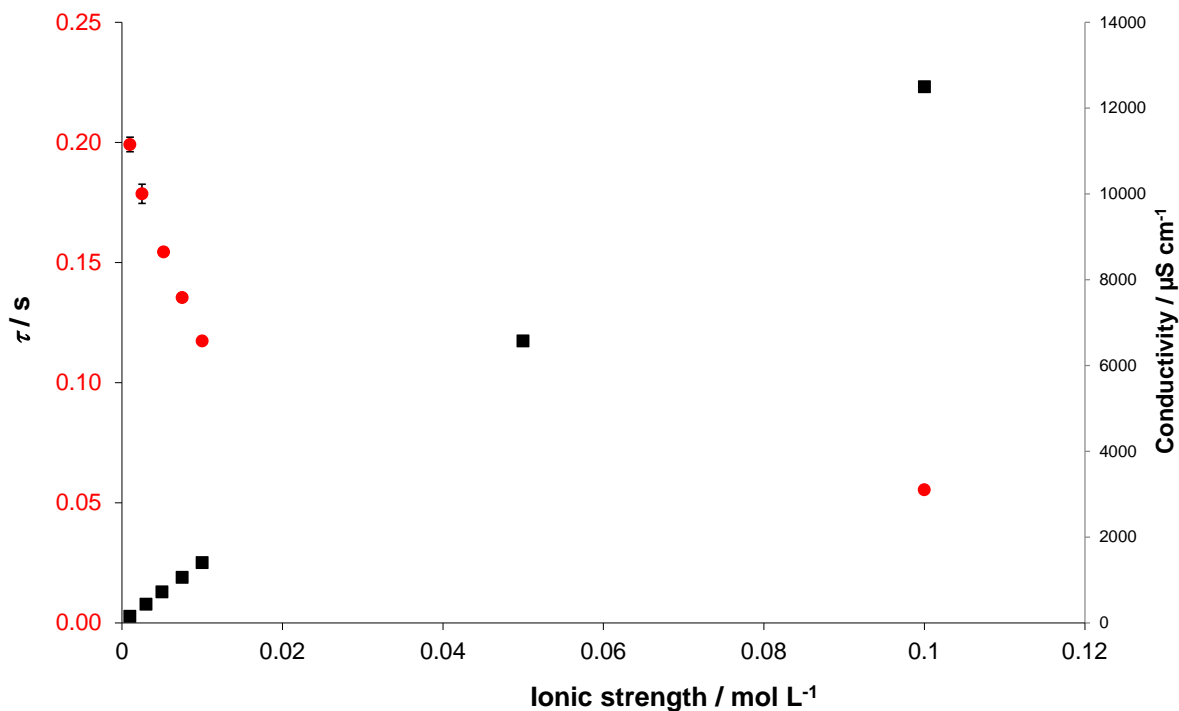


Figure 3. Zn analytical signals obtained in AGNES-SCP at different ionic strengths with purging (red bullets referred to left axis) for a total Zn concentration of 5×10^{-7} mol L⁻¹. Black squares stand for conductivity (referred to right axis). Deposition time between 300 and 800s at -1.08V, Stripping current $I_s = 10 \mu\text{A}$. Error bars of the 2 replicates indicated when larger than the marker symbol.

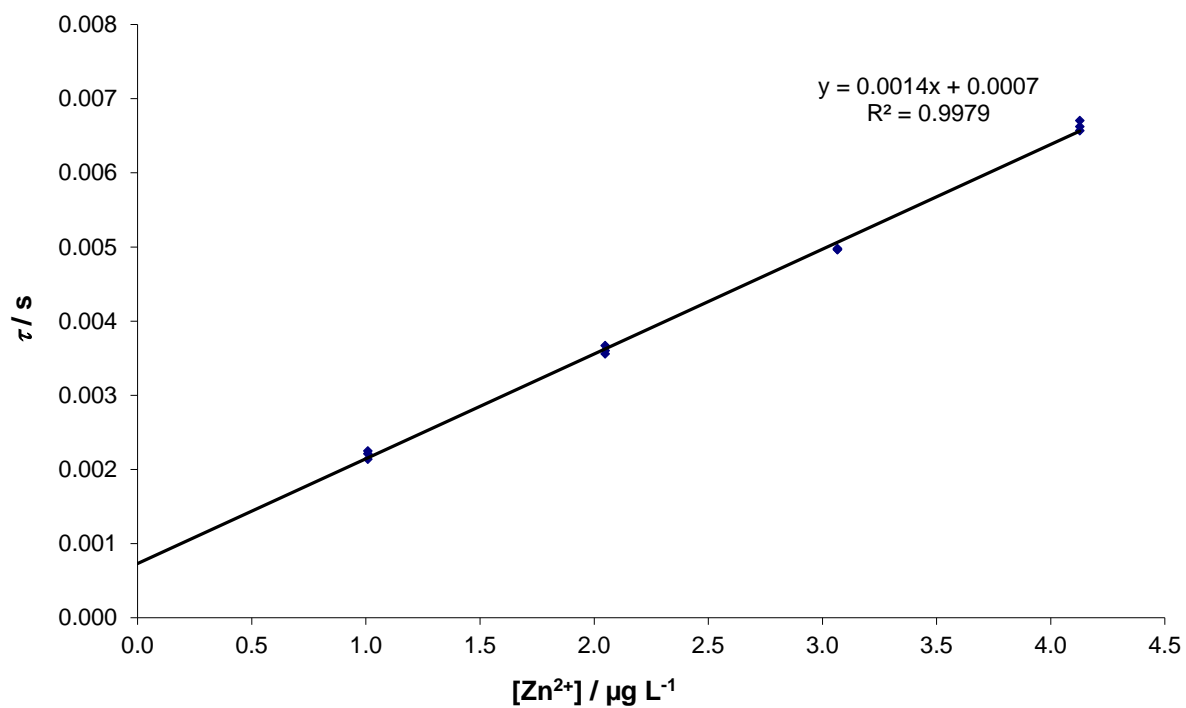


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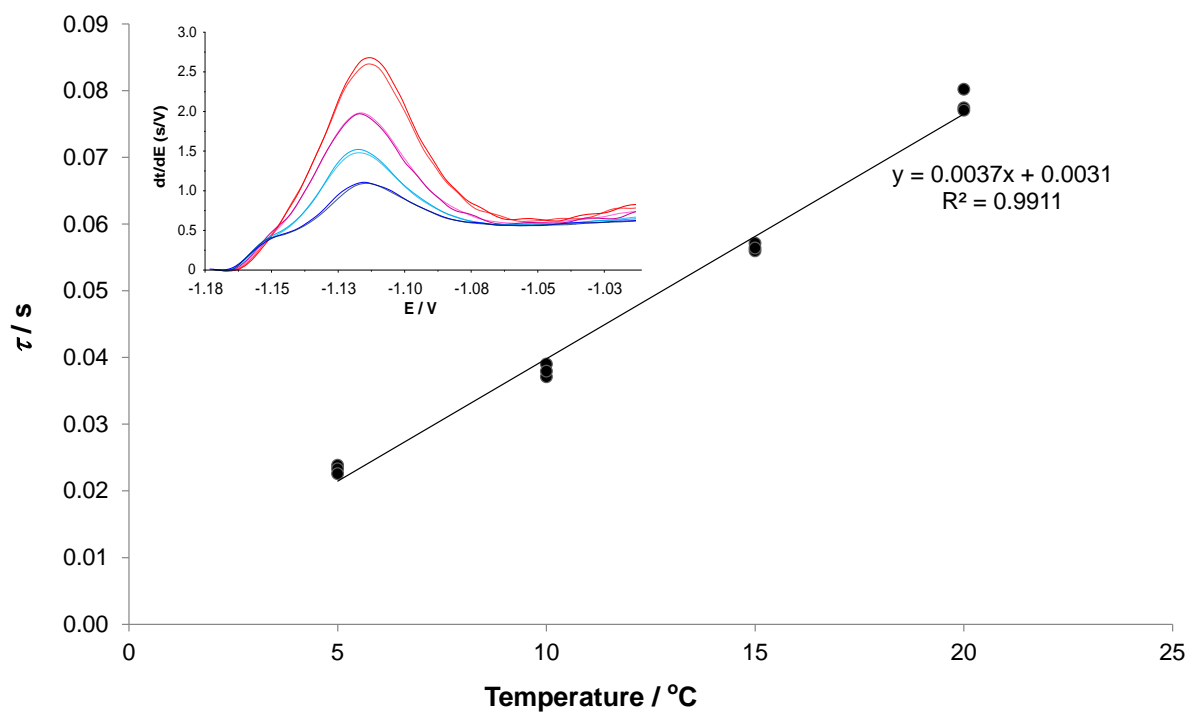


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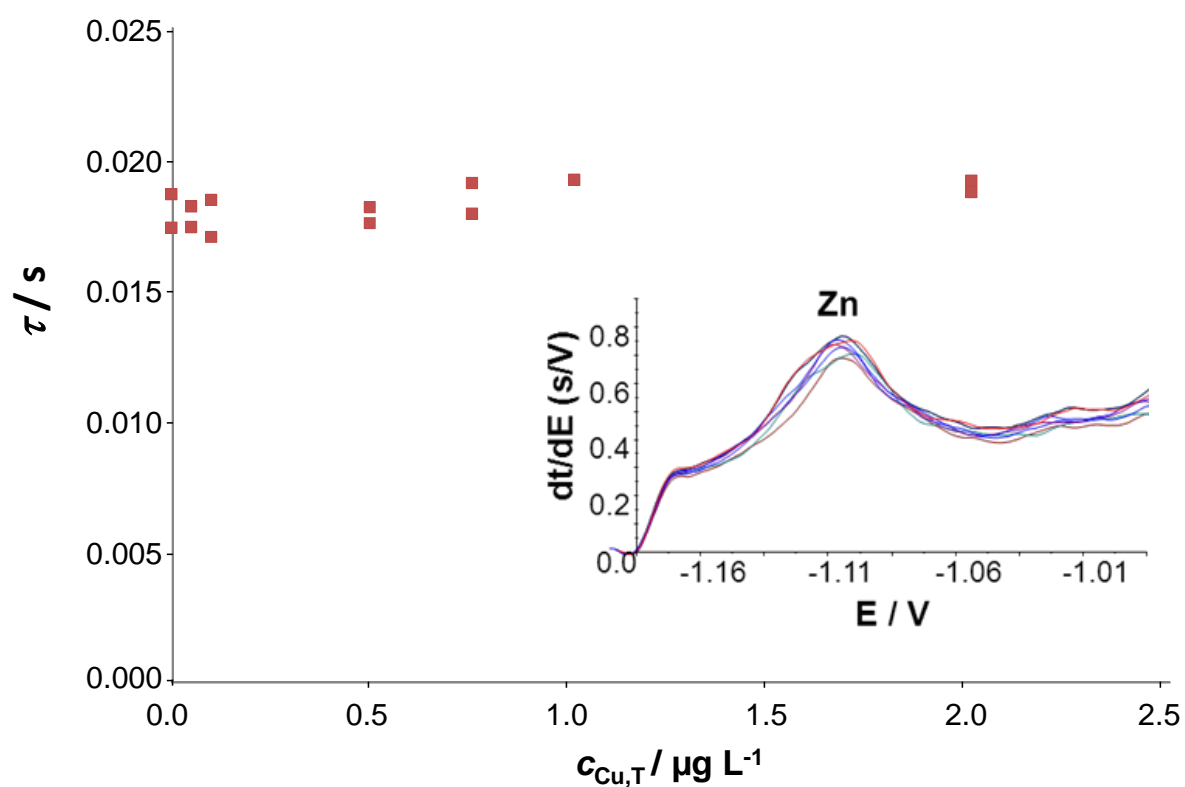


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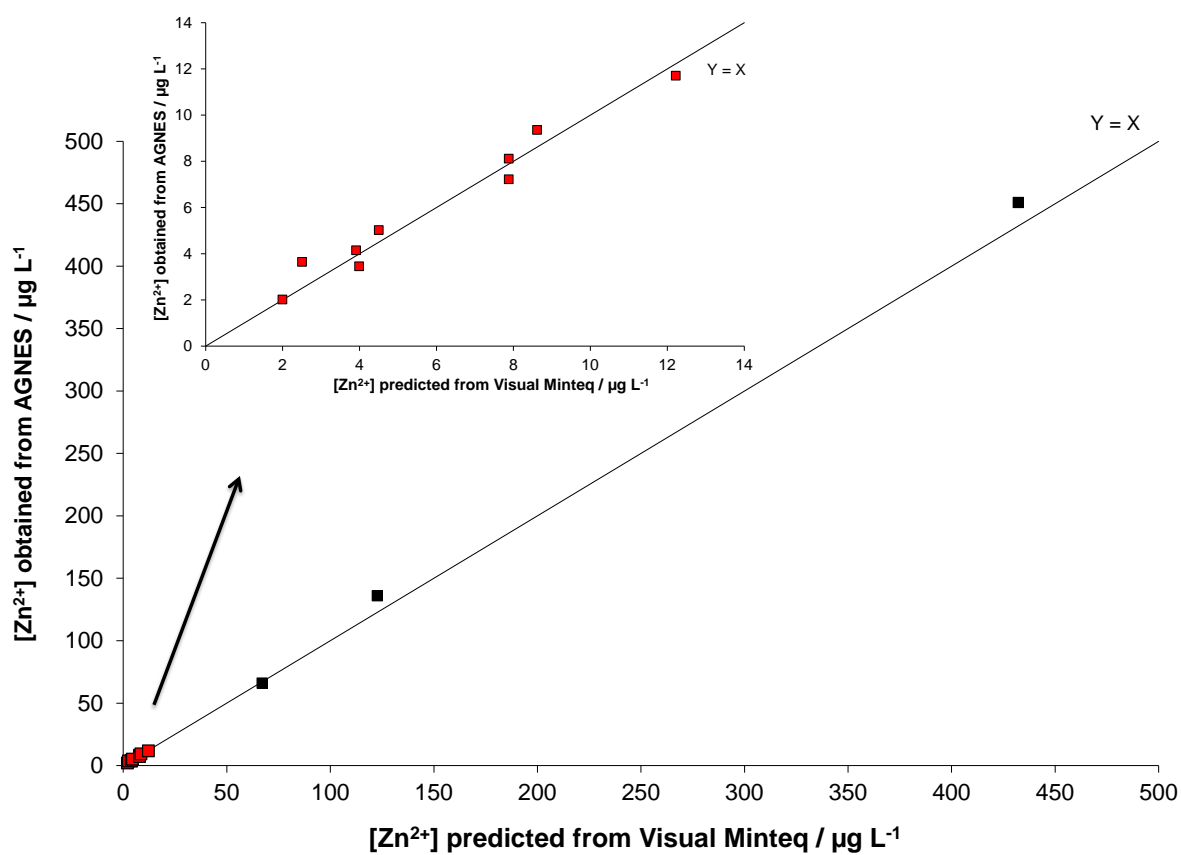


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