

by the end of the first stage. This deposition time has to be long enough so that all dynamic processes (diffusion, electron transfer kinetics, complexation kinetics, adsorption kinetics, etc.) have reached the equilibrium state. Previous work [33] showed that the application of two potential steps ($E_{1,a}$ during a time $t_{1,a}$ and $E_{1,b}$ during a time $t_{1,b}+t_w$ as shown in Fig 5) along the first stage could reduce the overall deposition time (t_1) needed with respect to that of the simplest implementation depicted in Fig 1. The first potential ($E_{1,a}$) corresponds to diffusion limited conditions and the second one ($E_{1,b}$) corresponds to the desired Y of the experiment.

Preliminary tests in seawater indicated that the AGNES Zn-reoxidation current obtained with $Y=500$ was sufficiently different from the shifted blank current; so this Y was taken as the target preconcentration factor.

The "recipe" developed in previous work [33] prescribed a ratio of times given by $t_{1,b}=3\times t_{1,a}$. Taking into account that the goal of this work is the measurement of one concentration (and not very different from one sampling site to the other) in each solution (i.e. there is no change of ligand concentrations), we decided to optimize the required times of the potential program for the particular conditions of our Mediterranean seawater. The key idea is to apply the first potential step $E_{1,a}$ (in diffusion limited conditions) for a convenient time $t_{1,a}$ so that the desired number of moles of Zn have practically entered the mercury drop. Thus, a time $t_{1,b}$ (say $t_{1,b} = t_{1,a}$) much lesser than $3\times t_{1,a}$ can be used for the fine-tuning and stabilization of $[Zn^0]$ to the desired value $Y\times[Zn^{2+}]$.

Fig 6 shows the last phase of the search for a convenient $t_{1,a}$. When we conducted the experiment with $t_{1,b} = t_{1,a} = 800$ s (see open square) we obtained (within the experimental accuracy) the same current as when applying the "recipe" $t_{1,a} = 800$ s; $t_{1,b} = 2400$ s (see

open diamond). In order to decide whether to increase or to reduce $t_{1,a}$, we analysed whether at $t_{1,a}=800$ s the actual concentration of Zn^0 built up inside the drop was higher or lower than the desired value $Y \times [Zn^{2+}]$. We call "overshoot" [33] to the existence (inside the drop) at $t=t_{1,a}$ of an amount of Zn^0 larger than desired, i.e. $[Zn^0]_{actual} > Y \times [Zn^{2+}]$; this leads to a decaying current for $t_{1,a} < t < t_1$ because the excess of accumulated Zn^0 has to be re-oxidized to reach the prescribed Nernstian equilibrium by $t=t_1$. For samples with high metal concentrations, this overshoot can be easily seen in the evolution of the current along the first stage [33]. We can call "undershoot" the opposite situation where, at $t=t_{1,a}$, we have $[Zn^0]_{actual} < Y \times [Zn^{2+}]$, so that Zn continues to enter the mercury drop for $t > t_{1,a}$. Due to the low Zn concentration in the samples here analysed, the currents in case of "overshoot" or "undershoot" are difficult to be distinguished in the evolution of the currents. So, we decided to probe the "overshoot" or "undershoot" situation by measuring the currents at the second stage (i.e. at $t_2=0.25$ s within the second stage) with a very short $t_{1,b}=50$ s (this usually leaves not enough time for the reaching of conditions i and ii of section 2.1.1 by the end of the first stage). As seen on the right of Fig 6 (open circle), the use of $t_{1,a}=800$ s with $t_{1,b}=50$ s produces a current higher than with a $t_{1,b}$ (say 800 s or 2400 s) allowing AGNES conditions to be attained: we conclude that with the combination $t_{1,a} = t_{1,b} = 800$ s there has been overshoot, so we can look for a $t_{1,a}$ shorter than 800 s. On the left of Fig 6, we see that using $t_{1,a}=650$ s with $t_{1,b}=50$ s produces a current less than the one obtained with $t_{1,b}=2400$ s, this indicating that there is undershoot when using $t_{1,a}=650$ s and that we could try a better $t_{1,a}$ in between 650 s and 800 s. We finally found that $t_{1,a}=t_{1,b}=700$ s was a safe combination exhibiting neither overshoot nor undershoot and fully agreeing with the results from the recipe $t_{1,b}=3 \times t_{1,a}$.

So, the potential program for the main measurements (i.e. not blanks) applied in this work is:

- $E_{1,a}$ under reduction diffusion limited conditions (with stirring) corresponding to $Y=10^{10}$ for $t_{1,a}=700$ s.
- $E_{1,b}$ corresponding to $Y=500$ for $t_{1,b}=700$ s (with stirring) and waiting time $t_w=50$ s (without stirring).
- E_2 corresponding to re-oxidation diffusion limited conditions corresponding to $Y=10^{-8}$ for 50 s, with the response current being read at $t_2=0.25$ s.

4.3. Validation of the determination of free Zn^{2+} in a synthetic solution

Prior to the application of AGNES to real samples, a validation procedure was designed based on the determination of a known low concentration of free Zn (due to known NTA and Zn total concentrations with known pH) in a medium of higher ionic strength than those used with AGNES up to now [33].

The value of h for the medium KNO_3 0.5 M was obtained from AGNES values using a concentration range of Zn between 0.1 to 1 μ M. One calibration plot is shown in Fig 7: in this particular instance an $h=1.04$ A M^{-1} was found from the linear regression of I vs. $[Zn^{2+}]$ data.

The total concentrations of the prepared mixture were 10^{-5} M in NTA and 1.2×10^{-7} M in Zn. The pH of the solution was varied around the interval 5.2-6.1. The difference between the pH values of the validation procedure and that of the seawater sample was considered immaterial, given experimental evidence of h being the same for a large set of pH values. According to the speciation codes VMINTEQ [35] and MEDUSA [36], in

this range of pH, with the combination of total concentrations of Zn and NTA here considered, the concentration of free Zn moves around 2-20 nM. The logarithm of the concentrations of free Zn obtained with AGNES (in two different days) at each pH is shown in Fig. 8 with markers. The slight disagreement (around 0.2 log units) between the replicates of different days can be mainly ascribed to small differences in the prepared sample and uncertainties in pH measurements. The continuous line represents the computed values obtained considering the complexation equilibria Zn/NTA and the hydrolysis of Zn at the ionic strength used with the code MEDUSA. The dashed line corresponds to the theoretical values predicted by MINTEQ for the same mixture at the same pH-range. Differences between MEDUSA and MINTEQ can be traced to be mainly due to differences in: i) the computation of the activity coefficients (MINTEQ uses Davies' equation while MEDUSA uses equations by Helgeson, Kirkham and Flowers [37] and ii) the value of the stability constant for the complex ZnNTA (MINTEQ takes $\log K_{\text{ZnNTA}} = 12.01$ while MEDUSA takes 11.84). Considering the difficulties in theoretically ascertaining the free metal concentration [38], the experimental results can be accepted as satisfactory.

4.4 Determination of free Zn^{2+} in seawater samples

From the experience gained in the previous results, the parameters used for AGNES aiming at probing the seawater samples were: i) for measurement $t_{1,a}=t_{1,b}=700$ s; $Y=500$; $t_2=0.25$ s; $Y_2=10^{-8}$ ii) for the shifted blank $t_{1, \text{sb}}=400$ s; $Y_{\text{sb}}=0.01$; $t_2=0.25$ s; $Y_{2, \text{sb}}=2 \times 10^{-13}$. For each speciation determination the required h -value was determined in a calibration, conducted within a few days proximity, in a medium with a similar ionic strength to that corresponding to the seawater. For this purpose, a concentration of background electrolyte KNO_3 0.7 M was used.

An estimation of the limit of detection (LOD) and the limit of quantification (LOQ) of this implementation of AGNES (basically defined by $Y=500$ and the shifted blank) was obtained carrying out 10 repetitions of shifted blanks in a solution of KNO_3 0.7 M without any added Zn (notice that, from the 0.005 ppm maximum impurities given by the manufacturer, one estimates up to 5 nM in Zn for this solution which could have been taken for the "classical blank"). The same kind of experiment was performed also in seawater, in order to compare the results. Table 1 gathers the average value of the current, the standard deviation (SD) and the values of LOD and LOQ (computed respectively from the ratios $3 \times \text{SD}/\text{slope}$ of the calibration curve and $10 \times \text{SD}/\text{slope}$ of the calibration curve) [39]. These results show the high sensitivity and the good precision of the AGNES measurement even in a natural complex matrix as seawater, provided a low blank, such as the shifted one developed here, can be accepted. It is also important to highlight that the capability to determine free Zn concentration at so low concentration, renders AGNES a very promising technique for speciation analysis, especially if one takes into account that better limits would be obtained with larger Y -values.

Results of the application of AGNES to the sample from Castelldefels are gathered in Table 2. Measurement currents around 5.6 nA and blank currents around 0.8 nA lead to difference currents around 4.8 nA. Applying eqn. (3), with $h=1.53 \text{ A M}^{-1}$ from its corresponding calibration at $I=0.7 \text{ M}$, one finally reaches the average of this determination of $[\text{Zn}^{2+}]$ as 3.1(4) nM.

In order to check whether an intermetallic [21,22,40,41] amalgam complex between Cu^0 and Zn^0 could affect the response from AGNES current at $t_2=0.25 \text{ s}$, we performed an

experiment with Castelldefels seawater as usual and obtained a current $I=4.89$ nA. After the additions of Cu up to a total concentration of 5 nM, the new currents in the two replicates were 4.94 nA and 5.30 nA. If there was an interference due to the formation of an intermetallic complex, there would be a substantial decrease of the current of Zn^0 -reoxidation, which did not appear in our experiment. So, we concluded that for the level of Cu and Zn concentrations present in our seawater, the used preconcentration factor and deposition time, there is not evidence of the formation of intermetallic Cu-Zn. Results for the sample from La Rabassada are gathered in Table 3. One can see a very similar structure to the results of Castelldefels. Measurement currents span from 2.0 nA to 2.8 nA yielding concentrations from 1.0 nM to 1.4 nM via the corresponding h -value of 1.40 A M^{-1} . The resulting average is 1.2 nM with a standard deviation 0.2 nM.

Total Zn concentrations were determined by Anodic Stripping Voltammetry and Square Wave Stripping Voltammetry in samples acidified to pH 1.5. The average value for Castelldefels sample was 10.6(6) nM. This means that the free fraction in Castelldefels is about 29% of the total. The average value for La Rabassada sample was 9(1) nM. So, the free fraction in La Rabassada seawater was around 21% of the total Zn.

The high values of total concentrations are consistent with the general trend of higher concentration in coastal waters than in open ocean ones [16,18,42,43]. Regarding the fraction of free Zn over total, our results differ from several authors who have found that Zn in seawater is more than 95% complexed by organic matter [18,24,25,27,44]. However, there exist some other reports finding -as we have done- a much lower organic fraction. For instance, Lewis *et al.* [27] found ca 28% of total Zn was free or weakly bound according to their pseudopolarographic method; [28] found 30% of total

Zn as organically bound in seawater; [26] reported 26% of organically bound in South Atlantic surface waters. Caution must, thus, be exercised because of the particularity of the speciation of any sample from a given location, depth, season, etc. [18,43,45], which hinders a proper comparison between different experimental techniques with just literature data. In any case, one should keep in mind that different experimental techniques are -in fact- measuring different fractions of any metal in a given complex matrix [15].

5. Summary and perspective

AGNES is a recent electroanalytical technique designed to quantify the free metal activity (or concentration) [32]. The first stage consists in the preconcentration of the reduced metal inside the amalgam up to a level prescribed by the preconcentration factor (Y) which is controlled by the applied potential via Nernst equation (1). The second stage consists in the measurement of the preconcentrated metal via stripping. In the current implementation there is a proportionality factor (h) between the faradaic intensity current (I) and the concentration of the free metal ion in the solution (3).

The development of the shifted blank strategy, introduced for the first time in this work, allows a crucial lowering of the limit of detection of AGNES with respect to the "synthetic" blanks, where it was hard to obtain a synthetic reproduction of a complex matrix (such as seawater) free from trace amounts of the analyte. In essence, the shifted blank consists in the application of an analogous potential program to that of the main measurement, but with the potential values shifted towards a region where the analyte is not appreciably preconcentrated along the first stage. Thus, the shift blank

fundamentally evaluates the capacitive current for the same potential jump between the two stages of AGNES in the same sample where the measurement is intended.

The two-pulse strategy (i.e. the application of two potential steps along the first stage, see Fig 5), described in a previous work [33], has been specifically optimised for our particular setup with Zn^{2+} and $Y=500$, so that an important reduction of the deposition time has been achieved ($t_{1,a}=t_{1,b}$).

The developed methodology has been applied to the system NTA+ Zn (with changing pH, see Fig 8) in a validation phase. The results obtained by AGNES are in good agreement with theoretical predicted concentrations by two independent speciation codes.

Two Mediterranean seawater samples have been analysed with the described strategies. The sample from Castelldefels yielded a free Zn(II) concentration of 3.1 nM (see Table 2) from a determined total of 10.6 nM, while the sample from La Rabassada (Tarragona) yielded $[Zn^{2+}]=1.2$ nM (see Table 3) from a total of 9.2 nM. The results of this first implementation of AGNES to measure seawater indicate that Zn in Mediterranean coastal waters is much more available than in reported estimations corresponding to open oceans [24,25], but similar to a few other measurements [26-28,46].

AGNES has been shown to determine free Zn in these seawater samples. We have begun by tackling Zn due to the lack of a standard procedure to measure its free concentration and its intrinsic interest, but AGNES can also be a useful tool in the

determination of free metal concentrations in seawater for a series of elements (such as Cu, Cd or Pb). Further work, with Zn and other metals, should address other aquatic systems of environmental interest where an even lower limit of detection is required.

Acknowledgements

The authors gratefully acknowledge support of this research by the Spanish Ministry of Education and Science (DGICYT: Projects BQU2003-9698 and BQU2003-07587) and from the "Comissionat d'Universitats i Recerca de la Generalitat de Catalunya".

Tables

Table 1: Limit of detection (LOD) and limit of quantification (LOQ) for AGNES procedure with $Y=500$ in KNO_3 0.7 mol L^{-1} and in a seawater sample (Castelldefels sample).

	I_{sb} average /nA	I_{sb} SD /nA	LOD nM	LOQ nM
KNO_3 0.7 M	2.0	0.1	0.20	0.65
Seawater	1.61	0.09	0.18	0.59

Table 2: Results obtained applying AGNES to the seawater sample collected in Castelldefels. Free Zn^{2+} concentrations, $[\text{Zn}^{2+}]$, calculated with eq (3) with an h value of 1.53 A M^{-1} obtained in a calibration experiment with $\text{KNO}_3 = 0.7 \text{ M}$. Number between brackets indicates the standard deviation and refers to the last significant digit. Parameters used: i) for measurement $t_{1,\text{a}}=t_{1,\text{b}}=700 \text{ s}$; $Y=500$; $t_2=0.25 \text{ s}$; $Y_2=10^{-8}$ ii) for the shifted blank $t_{1,\text{sb}}=400 \text{ s}$; $Y_{\text{sb}}=0.01$; $t_2=0.25 \text{ s}$; $Y_{2,\text{sb}}=2 \times 10^{-13}$.

experiment (n replicates)	I /nA	$I-I_{\text{sb}}$ /nA	$[\text{Zn}^{2+}]$ /nM	pH
1 ($n = 3$)	6.0(6)	5.2(5)	3.4(3)	8.7
2 ($n = 5$)	5.2(3)	4.4(4)	2.8(2)	8.9

Table 3: Results obtained applying AGNES to the sea water sample collected in Tarragona (La Rabassada). Free Zn^{2+} concentrations, $[Zn^{2+}]$, calculated with eq (3) with an h value of 1.40 A M^{-1} obtained in a calibration experiment with $KNO_3 = 0.7 \text{ M}$. Parameters used: i) for measurement $t_{1,a}=t_{1,b}=700 \text{ s}$; $Y=500$; $t_2=0.25 \text{ s}$; $Y_2=10^{-8}$ ii) for the shifted blank $t_1=400 \text{ s}$; $Y_{sb}=0.01$; $t_2=0.25 \text{ s}$; $Y_{2, sb}=2 \times 10^{-13}$.

experiment (n replicates)	I /nA	$I-I_{sb}$ /nA	$[Zn^{2+}]$ /nM	pH
1 ($n = 6$)	2.3(2)	2.0(2)	1.4(2)	8.9
2 ($n = 5$)	2.0(2)	1.64(8)	1.17(5)	8.9
3 ($n = 6$)	2.8(3)	1.44(9)	1.0(7)	8.9

Figures

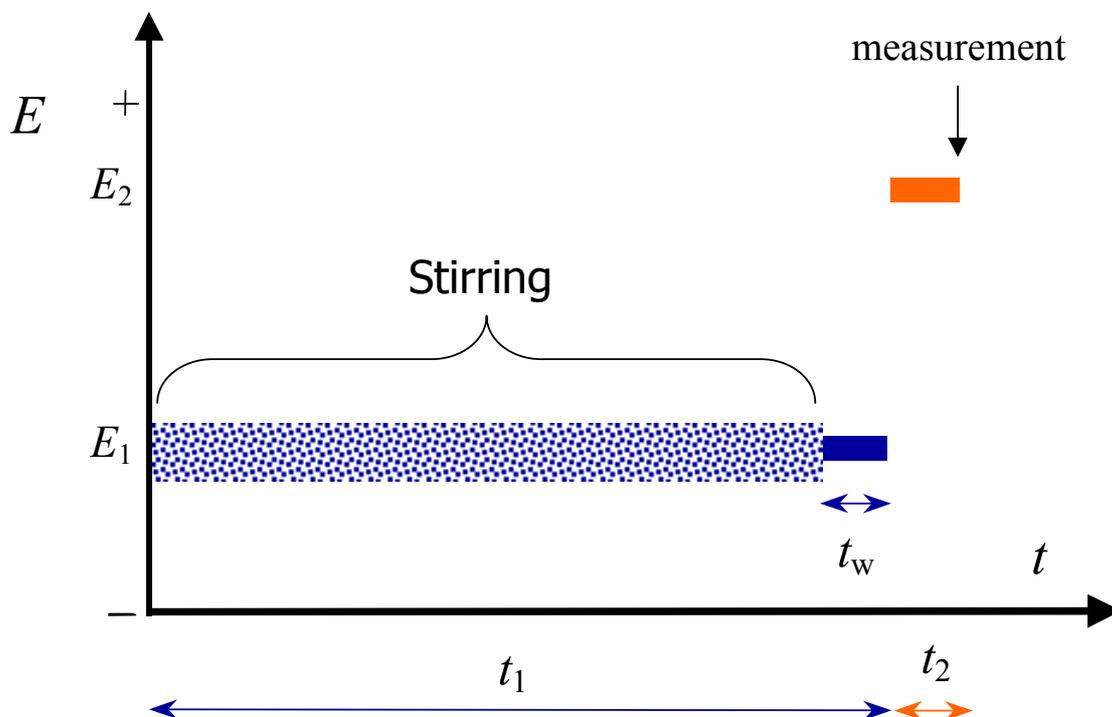


Fig 1: Schematic potential program for the simplest implementation of AGNES (one potential step along the first stage). The thicker line indicates that stirring is on along most of the deposition time (t_1). One key point of AGNES is that t_1 must be sufficiently long and the required preconcentration factor Y sufficiently small so that equilibrium is reached by the end of the first stage. A second important aspect is that E_2 must correspond to diffusion limited conditions for the reoxidation.

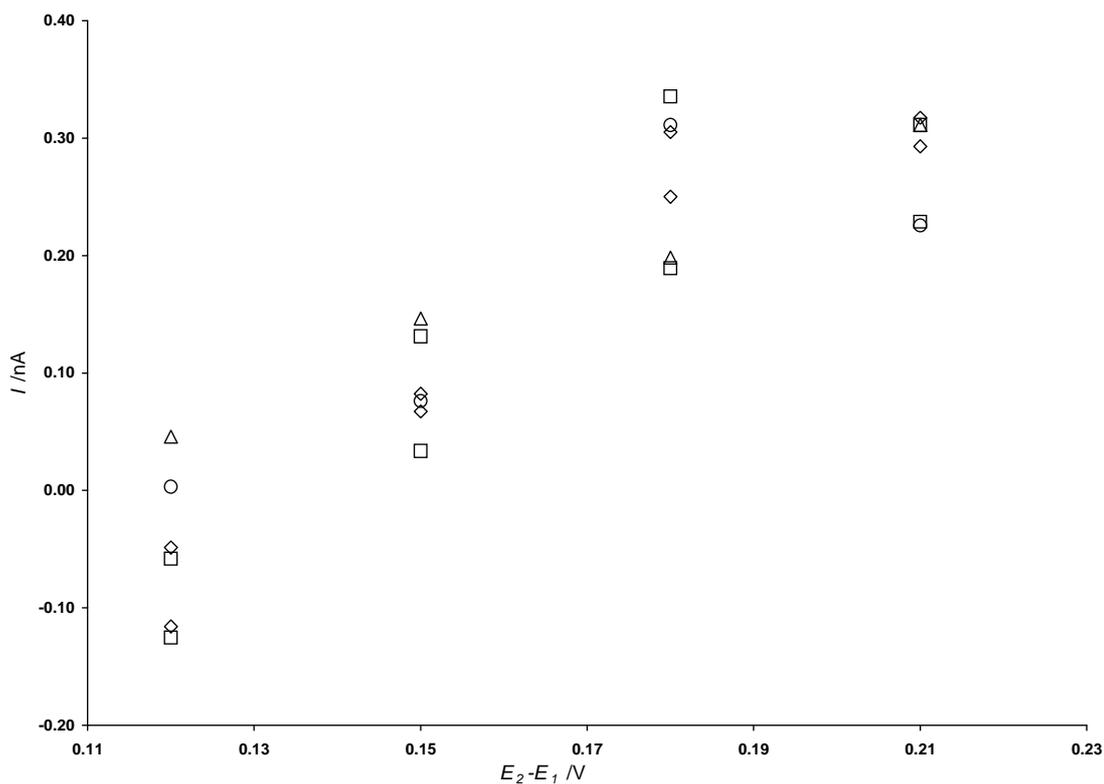


Fig 2: Currents measured at $t_2=0.2$ s for different potential differences (E_2-E_1) between the first potential step and the second potential step of the implementation of AGNES with only one potential step in the deposition stage (see Fig 1). Diamonds: $Y=0.01$; squares: $Y=0.0025$; triangles: $Y=0.01$ with added EDTA; circles: $Y=0.0025$ with added EDTA. The presence or absence of the ligand is not relevant in the measured shifted blank, while the value of E_2-E_1 is a crucial parameter in the shifted blank current.

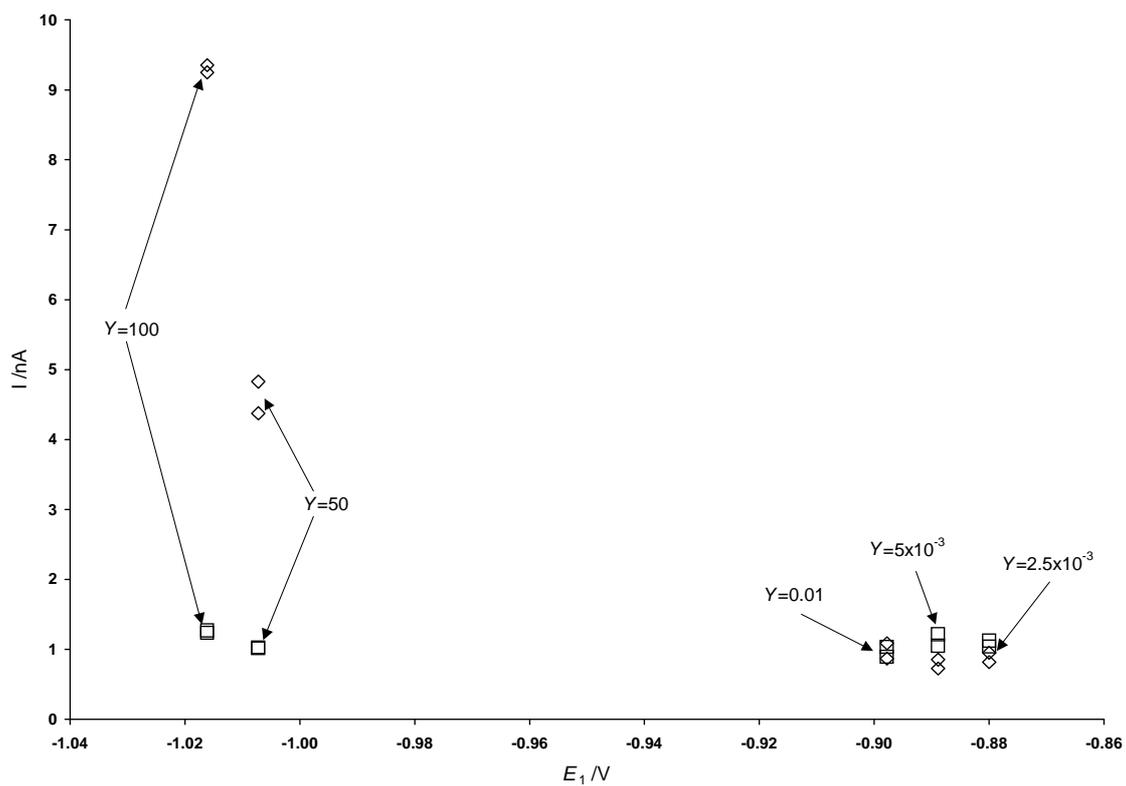


Fig 3: Current measured at $t_2=0.2$ s for different deposition potentials while keeping a fixed $E_2-E_1=0.1982$ V. Diamonds: KNO_3 0.1 M (without any EDTA); squares: same solution after adding EDTA 2×10^{-5} M.

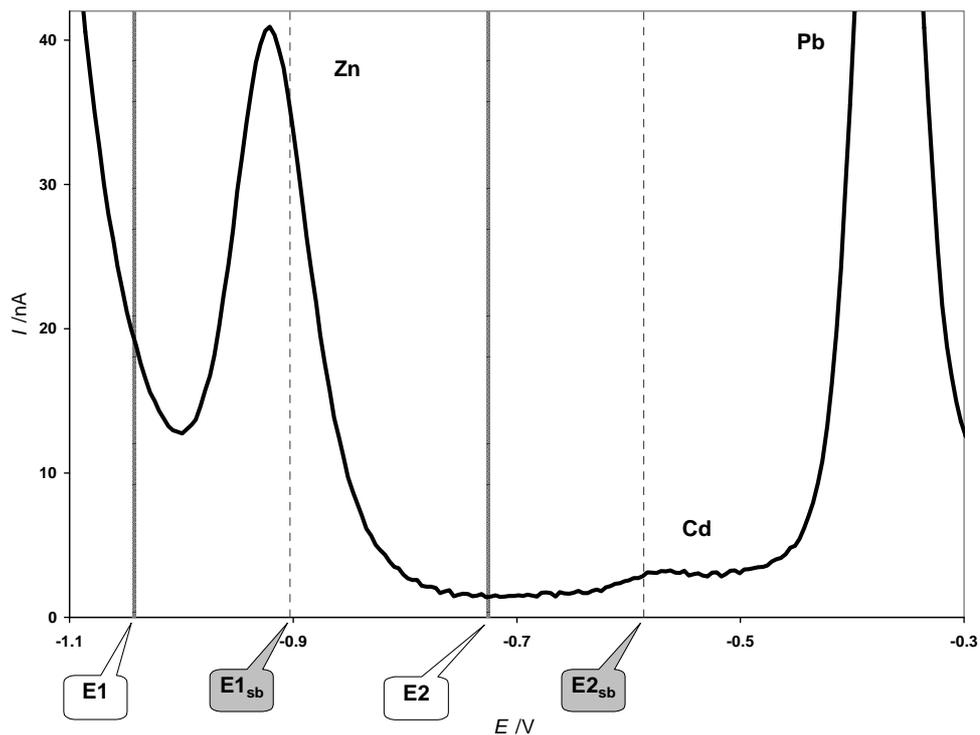


Fig 4: Anodic stripping voltammogram corresponding to a sample containing Zn, but also traces of Cd and Pb (non-analytes). The difference between potentials in the measurement (E_1 and E_2) must be the same as in the shifted blank ($E_{1, sb}$ and $E_{2, sb}$) and $E_{2, sb}$ should not produce the reoxidation of other non-analytes (Cd and Pb in this work).

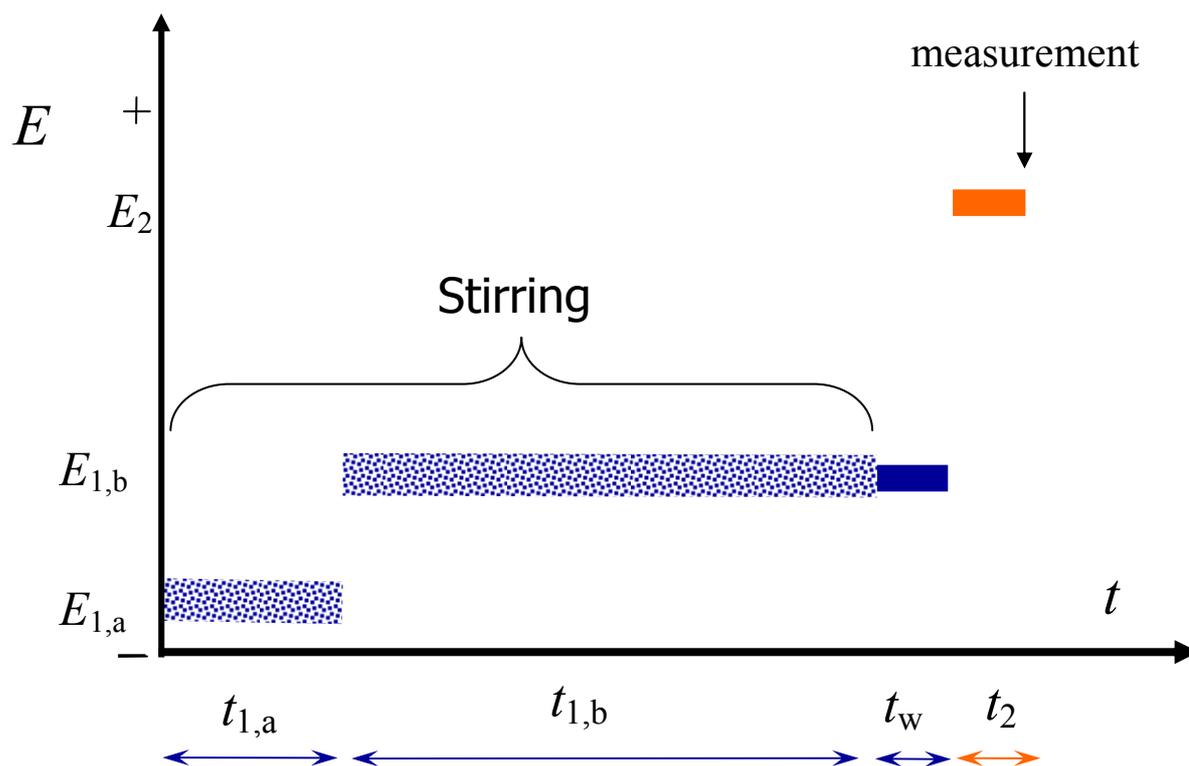


Fig 5: Potential program for AGNES with 2 potential steps. The total time of the first stage (t_1) comprises a short period under diffusion limited conditions ($t_{1,a}$), a "fine tuning" pre-concentration period ($t_{1,b}$) with the desired gain Y and a "waiting" period (t_w) without stirring. The aim of this program is to allow for shorter deposition times.

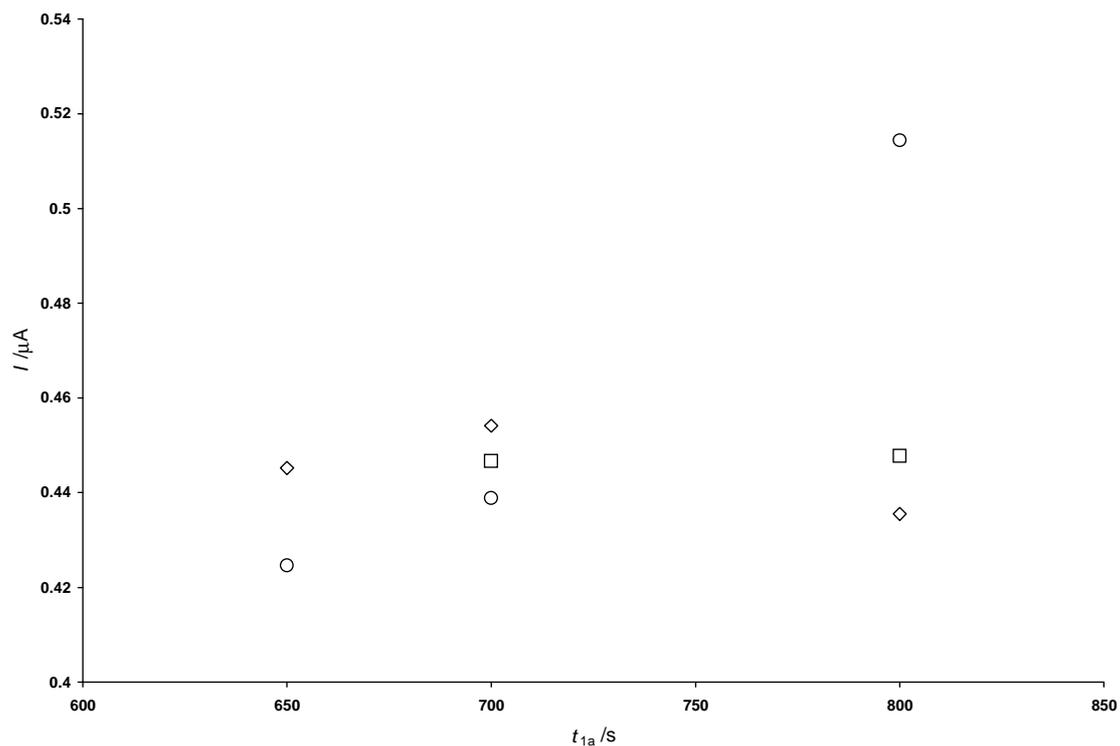


Fig 6: Currents measured at $t_2=0.25$ s for different combinations of $t_{1,a}$ and $t_{1,b}$ in a solution with $[\text{Zn}^{2+}]=3.71 \times 10^{-7}$ M in KNO_3 0.5 M . Markers: open circle $t_{1,b}=50$ s; open square $t_{1,b}=t_{1,a}$; open diamond $t_{1,b}= 3 \times t_{1,a}$

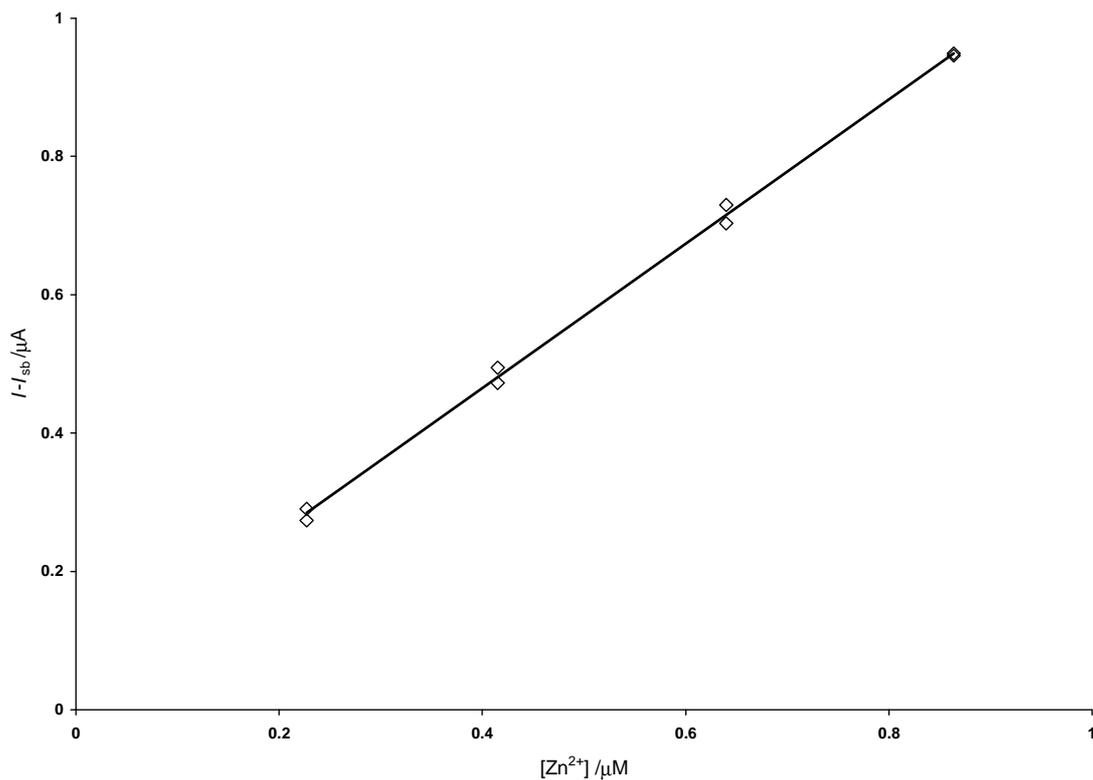


Fig 7: Calibration plot for Zn^{2+} in KNO_3 0.5 M. Parameters: $t_{1,a} = t_{1,b} = 700$ s; $Y_{1,a} = 10^{10}$; $Y_{1,b} = 500$; $Y_2 = 10^{-8}$. From the slope we derive $h = 1.04$ A M^{-1} to be used in a speciation test on Zn+NTA (see Fig 8).

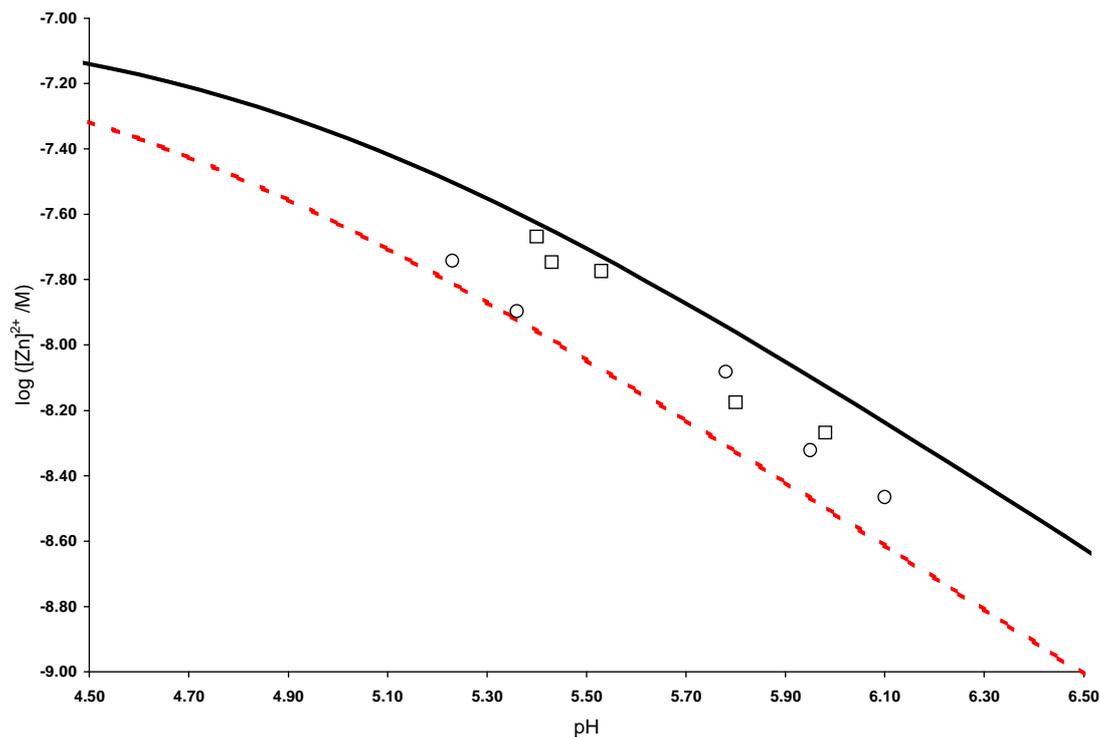


Fig 8 : Theoretical and experimental free Zn concentrations in a synthetic solution of Zn+NTA at different pH-values. Continuous line: MEDUSA calculations; dashed line: MINTEQ calculations; circle and square markers are experimental results obtained with AGNES in two different experiments carried out different days.

Reference List

- [1] M.A.Anderson, F.M.M.Morel, R.R.L.Guillard, *Nature* 276 (1978) 70.
- [2] W.G.Sunda, S.A.Huntsman, *Limnol. Oceanogr.* 37 (1992) 25.
- [3] Buffle, J. and Horvai, G. *In Situ Monitoring of Aquatic Systems. Chemical Analysis and Speciation. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems.*, John Wiley & Sons, Chichester, 2000.
- [4] J.Galceran, H.P.van Leeuwen, in H. P. van Leeuwen and W. Koester (Eds.), *Physicochemical kinetics and transport at chemical-biological surfaces. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems.*, John Wiley, Chichester, UK, 2004, Chapter 4, p. 147.
- [5] G.E.Batley, S.C.Apte, J.L.Stauber, *Australian Journal of Chemistry* 57 (2004) 903.
- [6] A.Tessier, J.Buffle, P.G.C.Campbell, in J. Buffle and R. R. DeVitre (Eds.), *Chemical and Biological Regulation of Aquatic Systems*, Lewis Publishers, Boca Raton, FL, 1994, Chapter 6, p. 197.
- [7] P.G.C.Campbell, O.Errecalde, C.Fortin, W.R.Hiriart-Baer, B.Vigneault, *Comp. Biochem. Physiol. C* 133 (2002) 189.
- [8] P.R.Paquin, J.W.Gorsuch, S.Apte, G.E.Batley, K.C.Bowles, P.G.C.Campbell, C.G.Delos, D.M.Di Toro, R.L.Dwyer, F.Galvez, et al. *Comp. Biochem. Physiol. C* 133 (2002) 3.
- [9] M.L.Tercier-Waeber, F.Confalonieri, G.Riccardi, A.Sina, S.Noel, J.Buffle, F.Graziottin, *Mar. Chem.* 97 (2005) 216.
- [10] M.Pesavento, R.Biesuz, C.Gnecco, E.Magi, *Anal. Chim. Acta* 449 (2001) 23.
- [11] R.Biesuz, G.Alberti, G.D'Agostino, E.Magi, M.Pesavento. [In Press] *Mar. Chem.*, 2006;
- [12] M.Pesavento, R.Biesuz, F.Dalla Riva, G.Alberti, *Polyhedron* 21 (2002) 1343.
- [13] L.Tomaszewski, J.Buffle, J.Galceran, *Anal. Chem.* 75 (2003) 893.
- [14] L.Sigg, F.Black, J.Buffle, J.Cao, R.Cleven, W.Davison, J.Galceran, P.Gunkel, E.Kalis, D.Kistler, et al. *Environ. Sci. Technol.* 40 (2006) 1934.
- [15] E.R.Unsworth, K.W.Warnken, H.Zhang, W.Davison, F.Black, J.Buffle, J.Cao, R.Cleven, J.Galceran, P.Gunkel, et al. *Environ. Sci. Technol.* 40 (2006) 1942.
- [16] L.E.Brand, W.G.Sunda, R.R.L.Guillard, *Limnol. Oceanogr.* 28 (1983) 1182.
- [17] F.M.M.Morel, J.R.Reinfelder, S.B.Roberts, C.P.Chamberlain, J.G.Lee, D.Yee, *Nature* 369 (1994) 740.
- [18] M.J.Ellwood, C.M.G.van den Berg, *Mar. Chem.* 68 (2000) 295.
- [19] M.J.Ellwood, *Mar. Chem.* 87 (2004) 37.
- [20] D.W.Crawford, M.S.Lipsen, D.A.Purdie, M.C.Lohan, P.J.Statham, F.A.Whitney, J.N.Putland, W.K.Johnson, N.Sutherland, T.D.Peterson, et al. *Limnol. Oceanogr.* 48 (2003) 1583.
- [21] A.L.B.Marques, G.O.Chierice, *Talanta* 38 (1991) 735.
- [22] C.M.G.van den Berg, *Talanta* 31 (1984) 1069.

- [23] K.W.Cha, C.I.Park, S.H.Park, *Talanta* 52 (2000) 983.
- [24] K.W.Bruland, *Limnol. Oceanogr.* 34 (1989) 269.
- [25] J.R.Donat, K.W.Bruland, *Mar. Chem.* 28 (1990) 301.
- [26] C.M.G.van den Berg, S.Dharmvanij, *Limnol. Oceanogr.* 29 (1984) 1025.
- [27] B.L.Lewis, G.W.Luther, H.Lane, T.M.Church, *Electroanal.* 7 (1995) 166.
- [28] K.Hirose, Y.Dokiya, Y.Sugimura, *Mar. Chem.* 11 (1982) 343.
- [29] A.R.Fakhari, M.Shamsipur, K.Ghanbari, *Anal. Chim. Acta* 460 (2002) 177.
- [30] R.B.Thompson, E.R.Jones, *Anal. Chem.* 65 (1993) 730.
- [31] J.Van den Bergh, B.Jakubowski, P.Burba, *Talanta* 55 (2001) 587.
- [32] J.Galceran, E.Companys, J.Puy, J.Cecilia, J.L.Garcés, *J. Electroanal. Chem.* 566 (2004) 95.
- [33] E.Companys, J.Cecilia, G.Codina, J.Puy, J.Galceran, *J. Electroanal. Chem.* 576 (2005) 21.
- [34] A.J.Bard, L.R.Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1980.
- [35] Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: version 3.0 user's manual. Washington, DC. U.S. Environmental Protection Agency, Office of Research and Development. 1991; EPA 600/3-91/021; U.S.
- [36] Medusa: make equilibrium diagrams using sophisticated algorithms. Windows program. [computer program]. Puigdomenech I. Royal Institute of Technology KTH, Stockholm, Sweden; 2001;
- [37] E.H.Oelkers, H.C.Helgeson, *Geochimica Et Cosmochimica Acta* 54 (1990) 727.
- [38] D.R.Turner, in A. Tessier and D. R. Turner (Eds.), *Metal Speciation and Bioavailability in Aquatic Systems*, John Wiley & Sons, Chichester, 1995, Chapter 4, p. 149.
- [39] L.A.Currie, *Pure Appl. Chem.* 67 (1995) 1699.
- [40] M.S.Shuman, G.P.Woodward, *Anal. Chem.* 48 (1976) 1979.
- [41] E.Y.Neiman, L.G.Petrova, V.I.Ignatov, G.M.Dolgopolova, *Anal. Chim. Acta* 113 (1980) 277.
- [42] F.Elbaz-Poulichet, C.Guieu, N.H.Morley, *Marine Pollution Bulletin* 42 (2001) 623.
- [43] K.Kremling, P.Streu, *Deep-Sea. Res. Part I* 48 (2001) 2541.
- [44] J.Buffle, *Complexation Reactions in Aquatic Systems. An Analytical Approach.*, Ellis Horwood Limited, Chichester, 1988.
- [45] E.P.Achterberg, C.Colombo, C.M.G.van den Berg, *Continental Shelf Research* 19 (1999) 537.
- [46] E.van Veen, S.Comber, M.Gardner, *Journal of Environmental Monitoring* 4 (2002) 116.

