

**AGNES: determining free Zn concentration in seawater**

César Huidobro<sup>1</sup>, Encarna Companys<sup>1</sup>, Jaume Puy<sup>1</sup>, Josep Galceran<sup>1</sup> and Giancarla Alberti<sup>2</sup>

<sup>1</sup>Departament de Química. Universitat de Lleida, Rovira Roure 191, 2519, Lleida, Spain

<sup>2</sup>Dipartimento di Chimica Generale, Università di Pavia, via Taramelli 12, 27100, Pavia, Italy

The free concentration of metals present in solution is a key datum in environmental studies, as recognised by the Free Ion Activity Model (FIAM) or the Biotic Ligand Model (BLM) which correlate the uptake of the element by the organisms with the concentration of the free metal.

AGNES (Absence of Gradients and Nernstian Equilibrium Stripping), a new electroanalytical technique (1) developed to determine free metal concentration in solution, can be an alternative to other existing techniques, specially in cases, such as Zn, where a commercial ion selective electrode (ISE) is not available. AGNES has been validated against ISE and against Resin Titration (2).

AGNES consists in the application of 2 stages: i) In the deposition stage, we apply a program of potentials aiming at preconcentrating the metal inside the amalgam until the system reaches Nernstian equilibrium with the solution and no concentration gradients in the amalgam or in the solution and ii) in the stripping stage, we determine the concentration of metal reduced in the amalgam. For that purpose, we apply a sufficiently less negative potential producing a stripping current under diffusion limited conditions. With this design, the technique avoids typical complications present in voltammetry such as electrodic adsorption, homogeneous and heterogeneous kinetics, etc. and the results are robust and extremely simple to interpret. The use of the simple potential program provides safe results, but can be prohibitively long for the determination of very low concentrations. So, we have designed various strategies to reduce the deposition time: a) reduction of the preconcentration factor (3); b) a deposition program with an additional potential step in reduction diffusion limited conditions (3); c) reduction of the electrode dimension (4), d) exploitation of the contribution of complex dissociation along the diffusion layer (2,3).

AGNES has been applied to determine free Zn concentration in two coastal seawater samples taken close to Barcelona and Tarragona (Catalonia, North Eastern Spain) finding values in the range of 1-3 nM, representing around 25% of total Zn (5). This determination required the development of a new blank, called the shifted blank, which is applied in the same solution with the same potential jump, but in another region of potentials. This technique can, in the near future, be crucial in helping to elucidate the role of the free zinc(II) concentration in natural waters.

[1] J. Galceran, E. Companys, J. Puy, J. Cecília, J.L. Garcés, J. Electroanal. Chem. 566 (2004) 95.

[2] G. Alberti, R. Biesuz, C. Huidobro, E. Companys, J. Puy, J. Galceran. A comparison between the determination of free Pb(II) by two techniques: AGNES and Resin Titration. Submitted to Anal. Chim. Acta, 2007.

[3] E. Companys, J. Cecília, G. Codina, J. Puy, J. Galceran, J. Electroanal. Chem. 576 (2005) 21.

[4] C. Huidobro, E. Companys, J. Puy, J. Galceran, J.P. Pinheiro, J. Electroanal. Chem., 606 (2007) 134-140.

[5] J. Galceran, C. Huidobro, E. Companys, G. Alberti, Talanta 71 (2007) 1795.