



Determination of free Zn^{2+} concentration in synthetic and natural samples with AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) and DMT (Donnan Membrane Technique)

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ABSTRACT

The determination of free Zn^{2+} ion concentration is a key in the study of environmental systems like river water and soils, due to its impact on bioavailability and toxicity. AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) and DMT (Donnan Membrane Technique) are emerging techniques suited for the determination of free heavy metal concentrations, especially in the case of Zn^{2+} , given that there is no commercial Ion Selective Electrode. In this work, both techniques have been applied to synthetic samples (containing Zn and NTA) and natural samples (Rhine river water and soils), showing good agreement. pH fluctuations in DMT and N_2/CO_2 purging system used in AGNES did not affect considerably the measurements done in Rhine river water and soil samples. Results of DMT *in situ* of Rhine river water are comparable to those of AGNES in the lab. The comparison of this work provides a cross-validation for both techniques.

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1. Introduction

Heavy metals in the environment can lead to negative effects on plants and animals, and consequently on human health (van Straalen and Looke, 1997). The reliable determination of both the amount and the chemical speciation of heavy metals in environmental studies is essential for an accurate risk assessment. According to the free ion activity model (FIAM) (Campbell, 1995; Parker and Pedler, 1997), the bioavailability of heavy metals to organisms depends mostly on the free metal ion concentration (which is directly linked to activity). Moreover, the free ion concentration is a well-defined thermodynamic entity and its measured value can be compared to calculations done with modern geochemical speciation codes with the proviso that the composition of the sample is well characterized.

However, reliable measurement of free ion concentrations in the natural environment (often at trace levels) remains an analytical challenge (Davison et al., 2000; Pesavento et al., 2009). The co-existence of various chemical forms that are hard to distinguish from the free ions complicates the measurement. Nevertheless, free metal ion concentrations can be directly measured by a few techniques such as Ion

Selective Electrode (ISE) (Bakker and Pretsch, 2007), Permeation Liquid Membrane (PLM) (Parthasarathy et al., 2001), DMT (Temminghoff et al., 2000) or AGNES (Galceran et al., 2004). Each technique has its advantages and limitations.

The element zinc is introduced into soils and surface waters by atmospheric deposition, agrochemicals, manure, and aerial fallout from factories (Charlesworth et al., 2011). It occurs also naturally in the soil and water environment. Zn is an essential micro nutrient for plants and animals. Zn deficiency is considered as a wide-spread malnutrition problem that affects the growth of children (Penland, 2000). At elevated levels, Zn becomes toxic to terrestrial and aquatic organisms.

The use of an Ion Selective Electrode would be a simple way to determine the free Zn^{2+} concentration, but, up to date, there is no commercial ISE for Zn. Alternatively, both DMT and AGNES are able to determine free Zn^{2+} concentrations. DMT uses a cation exchange membrane to measure free ion concentrations based on Donnan membrane equilibrium, whereas AGNES is an electrochemical technique. Previous works of DMT and AGNES have addressed their implementation in different systems: synthetic solutions using various ligands (Alberti et al., 2007; Companys et al., 2007; Domingos et al., 2004; Galceran et al., 2010; Kalis et al., 2006a; Oste et al., 2002; Temminghoff et al., 2000), soils (Weng et al., 2001a), natural waters (river and seawater) (Galceran et al., 2007; Kalis et

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al., 2006b; Zavarise et al., 2010), wine (Comanys et al., 2008), multi-metal systems (Chito et al., 2010; Kalis et al., 2007a, 2007b), etc. However, there is, so far, no direct comparison of measurements using these two techniques (DMT and AGNES), which are based on very different physicochemical properties leading to equilibrium.

The aim of this work was to determine free Zn^{2+} concentration in three types of samples under similar conditions with AGNES and DMT and to establish a comparison between both techniques. Firstly, synthetic solutions containing Zn–NTA mixtures were analyzed with DMT and AGNES and compared with the predictions using the speciation code VMinteq. Then, Rhine river water was analyzed with DMT *in situ* and AGNES in the lab. Finally, extraction samples from 4 soils were analyzed in the lab with both techniques.

2. Theory

2.1. DMT (Donnan Membrane Technique)

This technique is based on the theory of Donnan membrane equilibrium (Donnan, 1925; Helfferich, 1969). Experimentally, a cation exchange membrane separates the sample solution (donor solution) from an acceptor solution. The negative electrostatic potential generated in the membrane by the deprotonated sulfonic acid groups favors transport of cations and strongly retards anion transport and practically only allows cation exchange through the membrane. The technique has been implemented in the lab and *in situ* (Kalis et al., 2006b; Oste et al., 2002; Weng et al., 2001a).

Fig. 1 shows the lab and field cells usually employed. In the lab cell, the donor side contains the solution with unknown concentration, while the acceptor side contains the supporting electrolyte ($Ca(NO_3)_2$ or $CaCl_2$) with an ionic strength similar to that of the donor solution. The donor and acceptor solutions are separated by the cation exchange membrane. The cell has been designed so that there is a direct contact of both solutions with the membrane and there is a continuous recirculation at each side. The field cell consists of one acceptor chamber enclosed by two cation exchange membranes and it is immersed in the donor solution.

A certain time is required to attain the Donnan membrane equilibrium. After the chosen time, samples are taken from both donor and acceptor side of the DMT and the total element concentrations are determined, for instance with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The salt difference between the two sides of the DMT can be corrected by measuring the concentration of a reference cation in the donor and acceptor solution. Ideally the reference cation has a total concentration that is approximately equal to the free concentration, because only weak complexes are formed and/or the concentration is high compared to the dissolved ligand. In this work calcium can be used as a reference cation. The correction is based on the Donnan membrane equilibrium principle that the cationic activities in the donor and acceptor sides (for any

given cation) are equal at Donnan membrane equilibrium (Helfferich, 1969). In the case of Zn, it reads:

$$\frac{[Zn^{2+}]_{don}}{[Zn^{2+}]_{acc}} = \frac{[Ca^{2+}]_{don}}{[Ca^{2+}]_{acc}} \quad (1)$$

In this work, the total Ca concentrations in the donor and acceptor have been taken as the free concentrations, given that the expected complexation by the relevant ligands can be considered as negligible.

2.2. AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) technique

AGNES is a stripping technique which consists in the application of two stages: i) preconcentration up to equilibrium and ii) stripping. In the first stage, a preconcentration factor or gain Y between the reduced metal concentration in the amalgam, $[Zn^0]$, and the free metal concentration in the solution, $[Zn^{2+}]$, is eventually reached. The simplest way to achieve this equilibrium goal consists in applying a deposition potential E_1 during a sufficiently long time, t_1 . In the second stage, the stripping takes place when a potential E_2 is applied under diffusion limited conditions (Galceran et al., 2004). In order to reduce the deposition time, the first stage can be split into two different sub-stages (a potential step at diffusion limited conditions $E_{1,a}$ for $t_{1,a}$, followed by a potential step $E_{1,b}$ corresponding to the desired concentration gain Y for $t_{1,b}$) (Comanys et al., 2005). The response function can be the intensity current (typically at $t_2 = 200$ ms) or the total faradaic charge measured in the stripping stage (Galceran et al., 2010; Parat et al., 2011a, 2011b).

When the current is the analytical response, the free metal concentration in the solution can be computed from the proportionality factor η (obtained from a calibration), the faradaic current (I) measured at t_2 and the gain Y , through:

$$[Zn^{2+}] = \frac{I}{Y\eta} \quad (2)$$

3. Experimental

3.1. Reagents

A membrane (BDH Laboratory Supplies, Poole, UK) of polystyrene and divinylbenzene with sulfonic acid groups was used as cation exchange membrane in DMT experiments. The ion-exchange capacity is 0.8 meq g^{-1} and the thickness of the membrane is 0.15–0.17 mm. All material used for the experimental set up of DMT was cleaned following the procedure described elsewhere (Kalis et al., 2006b).

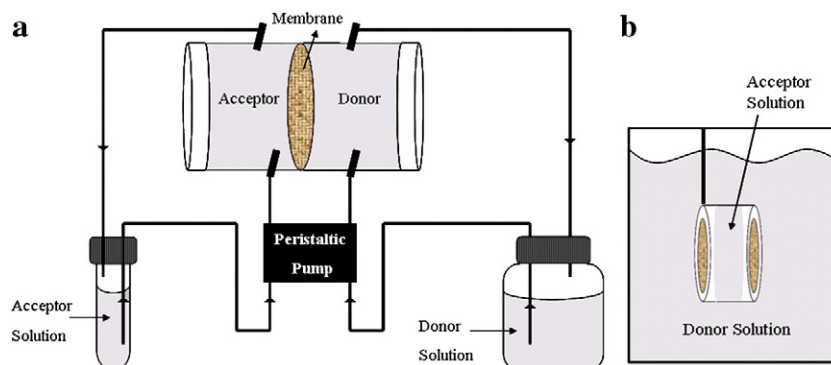


Fig. 1. Schematic representation of the DMT cell. (a) Lab cell. (b) Field cell.

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