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ISIDORE, a probe for *in situ* trace metal speciation based on Donnan membrane technique with related electrochemical detection part 1: Equilibrium measurements

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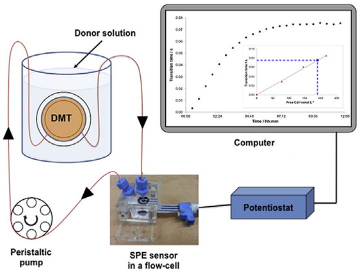
HIGHLIGHTS

- A new probe has been developed for on-site analyses of free metal ion.
- A screen-printed electrode has been hyphenated to a DMT device.
- Analysis time has been reduced to 6H against 36H when using a classical DMT device.
- This new probe has been successfully applied on a synthetic freshwater sample.

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents the development of a new probe (ISIDORE probe) based on the hyphenation of a Donnan Membrane Technique device (DMT) to a screen-printed electrode through a flow-cell to determine the free zinc, cadmium and lead ion concentration in natural samples, such as a freshwater river. The probe displays many advantages namely: (i) the detection can be performed on-site, which avoids all problems inherent to sampling, transport and storage; (ii) the low volume of the acceptor solution implies shorter equilibration times; (ii) the electrochemical detection system allows monitoring the free ion concentration in the acceptor solution without sampling.

1. Introduction

In natural waters metal ions react with a large variety of dissolved inorganic and organic ligands while also adsorbing onto colloids and suspended matter and interacting with living organisms, thus only a small portion of the total dissolved metal exists as free metal [1]. Therefore metal speciation effectively dictates the bioavailability, mobility and toxicity of the metal ions. Amongst the metal species the free metal is generally considered to be the most relevant since it is directly bioavailable [2].

Trace metal speciation analysis is not a simple task in such complex systems, and the sampling and handling of natural water

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samples can further induce changes in the distribution of species prior to measurement. On-site measurement avoids problems due to contamination during sampling and storage, instability of metal species during transport and storage prior to measurement.

The determination of total metal concentrations in natural waters, even at very low concentrations of trace metals (typically below 10^{-8} mol L^{-1}), is a comparatively simple task. It requires normally the acidification of the sample and storage in suitable plastic containers for later determination in the laboratory by means of inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry (ICP-OES).

Over the years, an extensive effort has been made to design chemical sensors for *in situ* measurements, hence there are several books on chemical sensors for aquatic measurements that describe various flow analysers as well as optical and electrochemical sensors [3].

Although numerous *in situ* methods have been proposed based generally on three different approaches [4,5], at this point there is no reliable on-site probe for trace metal speciation at concentration levels present in natural systems. The first approach is based on the deployment of *in situ* exposure devices in which the metal permeates a membrane and accumulates either in an inner solution like the Donnan Membrane Technique (DMT) [6], the Permeation Liquid Membrane (PLM) [7] or in a resin phase metals like the Diffusive Gradient in Thin film (DGT) [8]. After a suitable exposure in the field, which can take from a few hours to a few days the devices are collected, transported to the laboratory and measured either directly or after an extraction normally by ICP-MS. A second approach developed for *in situ* measurements is performed either by hyphenating a separation technique based on gel layer (GIME) [9,10], or by means of a permeation liquid membrane [11] with an electrochemical detection system. A third approach consists in applying a direct *in situ* electrochemical stripping speciation method like Absence Gradient Nernstian equilibrium stripping (AGNES) [12–14] or competitive ligand exchange (CLE/SV) [15].

Although DGT have gained some preponderance for *in situ* exposure devices, the interpretation of the dynamic signal is not straightforward [16–18]. Also recent insight in the interaction of humic matter with gel phases [19] poses some serious difficulties in the interpretation of the data obtained with gel-based devices like DGT or GIME.

The direct speciation measurement with AGNES appears as an interesting and reliable method to determine the free ion concentration in natural water such as freshwater [14]. However, at this moment AGNES detection limit is around 10^{-8} mol L^{-1} for the free metal, and the analytical signal strongly depends on the ionic strength and the presence of dissolved oxygen which makes it unsuitable for the monitoring on several hours where these parameters are likely to change [20].

In terms of portability for trace metal detection system, electrochemical devices are the most advantageous due to their small size and low energy demand hence the possibility of being battery powered. Additionally stripping electrochemical methods coupled with the correct electrode/flow systems present some of the lowest detection limits available for trace metal determination, often as low as a few nmol L^{-1} [21]. In terms of on-site applications, screen-printed sensors have been increasingly investigated due to their performance, small size which makes them easy to deploy *in situ* and their potential to be mass-produced at very low costs [22–24]. They have been extensively reviewed in the field of trace metal detection [25–31].

At present, DMT seems the best combination of signal interpretation, robustness and ease of operation of *in situ* exposure techniques. Nevertheless in its present configuration it needs a long exposure time, usually 36–48 h, and the inner solution still needs to be transported to the laboratory for measurement. We propose to overcome some of these problems by reducing the acceptor volume of the field DMT device and circulating it through a flow cell screen-printed stripping electrochemical sensor. The objective of this hyphenation is to perform an on-line electrochemical detection of trace metal accumulation in the acceptor solution and thus to shorten the analysis time and avoid bringing the acceptor solution to the laboratory for analysis.

This work presents the development of this new *in-situ* probe based on Donnan membrane technique related to an electrochemical detection system probe (ISIDORE probe) and its optimization regarding the environmental analysis.

2. Donnan membrane technique (DMT)

The common experimental protocol for DMT devices relies on waiting long enough for the equilibrium situation and measuring the total metal in the acceptor side which is equal to the free metal in the donor (or sample) side.

This technique is based on the Donnan membrane equilibrium principle [32], which says that, at the Donnan membrane equilibrium, the activity ratios (corrected for charge) of the ions in the solution on the two sides are equal (Eq. (1)):

$$\left(\frac{a_{i,\ \mathrm{donor}}}{a_{i,\ \mathrm{acceptor}}}\right)^{\frac{1}{z_i}} = \left(\frac{a_{j,\ \mathrm{donor}}}{a_{j,\ \mathrm{acceptor}}}\right)^{\frac{1}{z_j}} \tag{1}$$

with $a_{i,\mathrm{donor}}$ the activity of ion i in donor solution in mol L^{-1}, $a_{i,\mathrm{acceptor}}$ the activity of ion i in acceptor solution in mol L^{-1},$a_{j,\mathrm{donor}}$ the activity of ion j in donor solution in mol L^{-1}, $a_{j,\mathrm{acceptor}}$ the activity of ion j in acceptor solution in mol L^{-1}, z_i the charge of ion i and z_j the charge of ion j.

In these devices the charged membrane can be taken as a Donnan phase where the metal concentration will be higher than in both solutions. Additionally it is assumed that the electrolyte concentration is equal in both acceptor and donor so that there is no electrostatic potential gradient in the membrane, even if there are strong gradients at the donor/membrane and the membrane/acceptor interfaces. It is also assumed that both of the acceptor and donor solutions are stirred in such a way that the transport of ions between the solution and membrane will be controlled by diffusion in the solution film at the membrane interface (diffusion layer) [33].

The mathematical description of the device can be formulated as two diffusion layers (one in the acceptor and other in the donor side) separated by a negatively charged membrane that can be traversed by cationic species. The commonest use of the DMT is to wait for the equilibrium distribution of ions over donor and acceptor.

Although the investigation of the fluxes is outside the scope of this manuscript we are interested in studying this aspect in the future since the flux analysis may be significantly faster than the equilibrium one and additionally provides information in the dynamic nature of the complexes in solution as demonstrated by Weng et al. [33] and Marang et al. [34].

3. Material & methods

3.1. Reagents

Zn 1000 mg L^{-1} stock solution was obtained from Merck. KNO_3 (Trace Select), HNO_3 (69–70%, Baker Instra-Analysed for trace metal analysis), NaOH (Baker Analysed), HCl (Baker Instra-Analysed for trace metal analysis) were purchased from Aldrich. Acetic acid