

## NOVEL PLM-VOLTAMMETRIC COUPLING DEVICES FOR TRACE METAL SPECIATION

P.Salaün<sup>1</sup>, N. Parthasarathy<sup>1</sup>, J. Buffle<sup>1</sup>,  
O. Guenat<sup>2</sup>, M. Koudelka-Hep<sup>2</sup>.

<sup>1</sup> University of Geneva, CABE, Switzerland <sup>2</sup> University of Neuchâtel, SAMLAB, Institute of Microtechnology, Switzerland

Trace metal elements are present under various forms in natural waters: they can be found as hydrated ions or complexed to inorganic or organic compounds. Each of these species behaves differently in terms of mobility, bioavailability and toxicity. Speciation studies to understand their role in environmental system is thus of primary interest. However, very few methods are available for this purpose as the trace metal concentration found in natural waters is often in the nM range, or even below, i.e. below detection limits of most techniques.

The coupling of the Permeation Liquid Membrane (PLM) technique and a sensitive voltammetric detection has been shown to be very promising in terms of both speciation and sensitivity purposes [1, 2]. The PLM is based on complexation and diffusion properties. It consists of an hydrophobic carrier dissolved in an organic solvent which transports selectively target metal ions from the sample (source) solution to a so-called strip solution through a thin hydrophobic membrane. The voltammetric detector can be placed either directly in the strip solution (Figure 1) or coupled on-line to the PLM system. In both cases, the electrode consists of array of Ir-based Hg-plated microelectrodes covered with a 1.5% LGL agarose gel containing 10% of C18 particles. These particles protect the mercury surface from the adsorption of organic species leached out from the PLM. The strip solution is a pyrophosphate solution which forms labile complexes with Pb, Cd, Cu or Zn (Figure 2) and allows measurements in presence of oxygen. In the case where the electrode is placed in the strip solution, the effective strip volume is c.a. 0.8  $\mu\text{l}$ . As predicted by theory, accumulation factor (ratio of the concentration in the strip solution and in the source solution) of up to 400 have been achieved for Pb (Figure 3) leading to detection limit of c.a. 2 pM when Square Wave Anodic Stripping Voltammetry (SWASV) is used as detection technique.

For on-line coupling, a  $\mu\text{l}$  volume microcell has been specially designed for performing real time measurements. The inter-electrode distance is 450  $\mu\text{m}$  thus insuring the non-overlapping of adjacent diffusion layers (Figure 4). The minimum volume required for reliable measurement is less than 50  $\mu\text{l}$  and this microcell has been used with different PLM systems. When used with the hollow-fiber PLM, detection limits down to the pM range for lead can be expected.

Description and capabilities of these devices in terms of trace metal speciation will be presented in this talk. Results obtained with both synthetic and natural waters will be given.

### References:

[1] N. Parthasarathy, P. Salaün, M. Pelletier and J. Buffle, "Permeation liquid membrane coupled to voltammetric detection for in-situ trace metal speciation studies", ACS Symposium series 811, Chapter 6, 102-124.

[2] J.Buffle, N. Parthasarathy, N.-K. Djane, L. Maatthiasson, IUPAC series on "Analytical and Physical chemistry of environmental systems", vol.6, chapter 10 (2000), Wiley, Chichester.

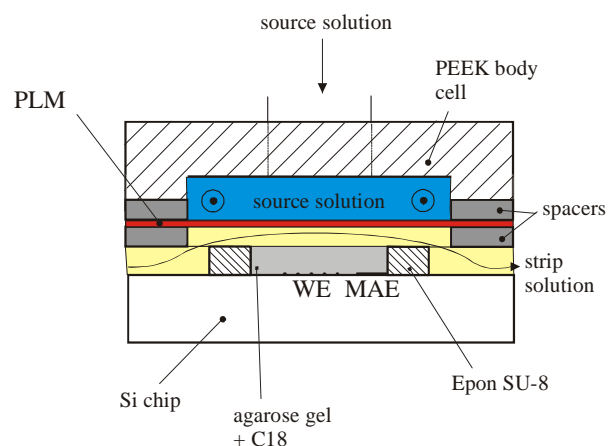


Fig.1: Schematic diagram of the integrated coupling of PLM and voltammetric detector (WE: working electrode, MAE: micro auxiliary electrode).

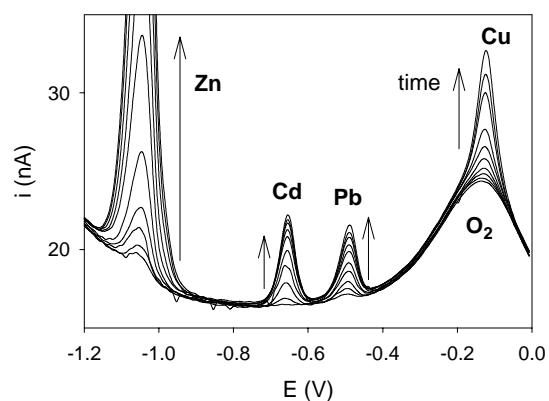


Fig. 2: Typical example of real-time measurement using the system presented in Figure 1.

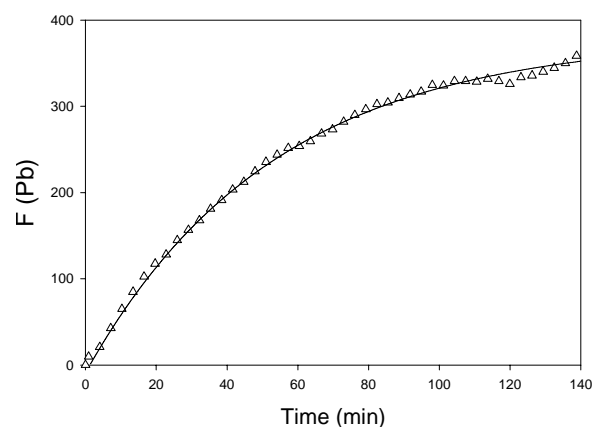


Fig. 3: Time evolution of the accumulation factor – symbols: experimental points, full line: fitted theoretical curve.

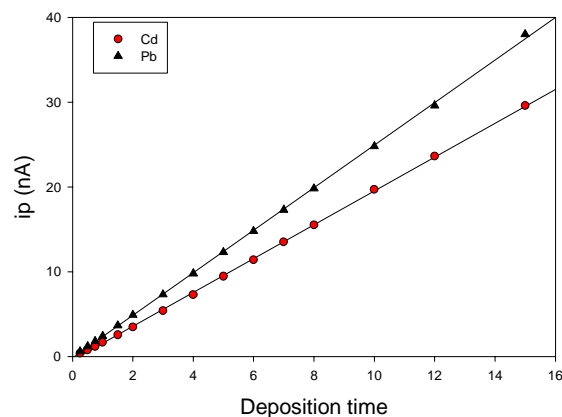


Fig. 4: Influence of the deposition time on the peak current intensity – Solution:  $\text{Na}_4\text{P}_2\text{O}_7$  ( $10^{-2}$  M), pH = 6.0,  $[\text{Pb}] = [\text{Cd}] = 100$  nM