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Building an effective concentration signature for Zn availability, from 4 techniques, in a stream

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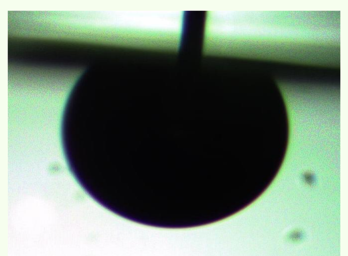
1. INTRODUCTION

Zn bioavailability in natural waters depends on its chemical speciation, so it is necessary to develop analytical techniques able to measure the free fraction or the labile ones. Four techniques: AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) (1), ASV (Anodic Stripping Voltammetry) (2), DGT (Diffusive Gradients in Thin films) (3) and Polymer Inclusion Membranes (PIMs) (4), are applied for this purpose to the water of the Osor Stream (Girona, Spain) affected by an abandoned mine. The Osor Stream is a tributary of the Ter River (a river of Mediterranean regime) with an average pH of 8.2. The Zn concentration downstream of the effluent area is between 200-400 µg L^{-1}. Organic complexation was found negligible.

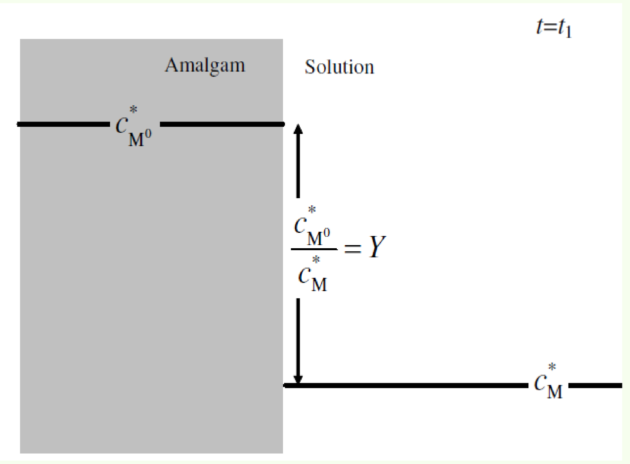
2. MATERIAL AND METHODS

○ Free Zn concentration from AGNES and PIM



AGNES, free

- **Principles of AGNES**



1. First stage aims at reaching absence of gradients in the concentration profiles and Nernstian equilibrium at the electrode.
2. Second stage aims at quantifying the accumulated Zn^0. The intensity and charge are proportional to the free concentration.

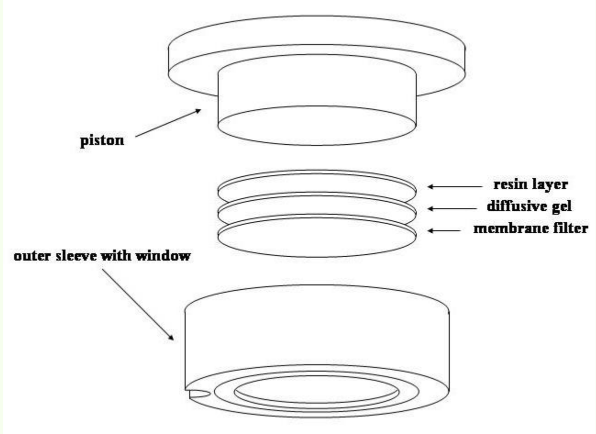
- **Principles of PIM**

PIM, free

PIM consists of a base polymer and a carrier or extractant that facilitates the selective transport for specific chemical species. We have worked with a PIM containing: 50% CTA, 40% D2EHPA and 10% NPOE (% in w/w). Volume of the *in-situ* device: 10 mL (0.01 M HNO_3).

○ Fluxes associated to different labile fractions provided by DGT and ASV

- **Principles of DGT**



The diffusive gel defines a diffusion domain and the resin gel layer contains a strong binding agent to accumulate the metals. Both gel layers are mounted as discs in a plastic molding and they are covered with a filter, which separates them from the solution.

DGT, labile

$$J = \frac{D_{Zn^{2+}} c_{DGT}}{\delta_{DGT}}$$

A concentration c_{DGT} can be defined from Fick's first law. This concentration can also be expressed in terms of the stability constant *K*' and the lability degree ξ:

$$c_{DGT} = \left[Zn^{2+}\right]\left(1 + K'\xi_{DGT}\right)$$

- **Principles of LASV**

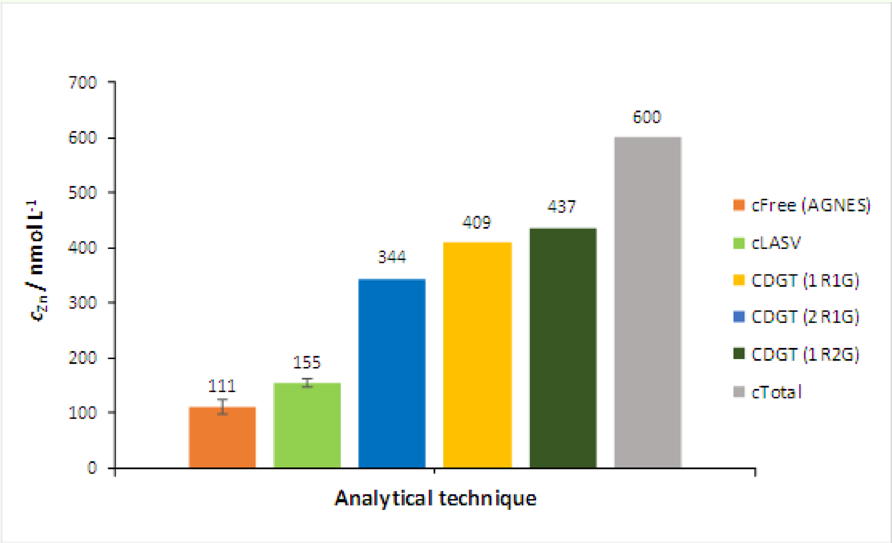
The amalgamated Zn^0 in the electrode (accumulated under diffusion limited conditions) is linearly stripped away for quantification purposes in the variant LASV. Parallel to DGT:

$$J = \frac{D_{Zn^{2+}} c_{LASV}}{\delta_{LASV}} \qquad c_{LASV} = \left[Zn^{2+}\right]\left(1 + K'\xi_{LASV}\right)$$

LASV, labile

3. RESULTS AND DISCUSSION

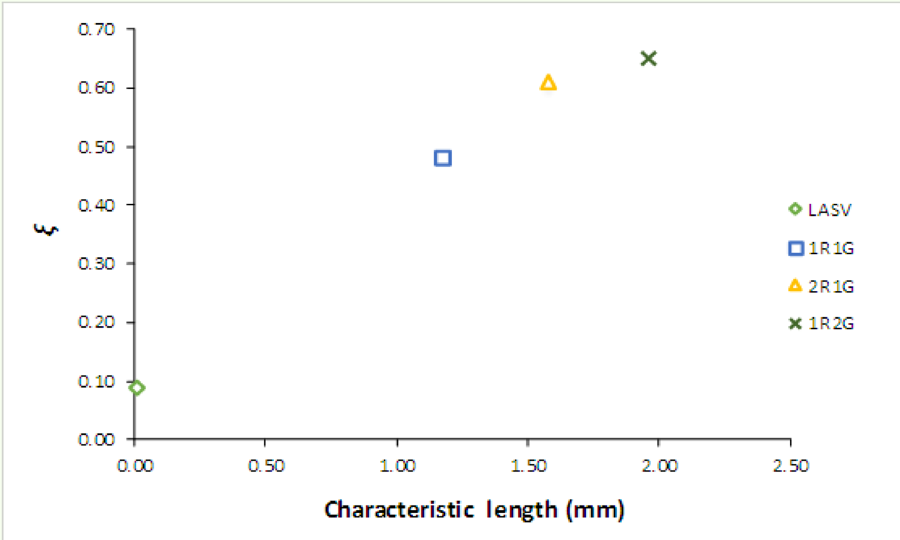
❑ Comparison of Zn concentrations from analytical techniques



The free fraction of Zn determined with AGNES is around 18.5% of the total concentration.
LASV labile concentration is less than that of DGT technique, as expected. The presence of complexes (such as Zn hydroxides) with low lability, justifies that c_{DGT} and c_{LASV} are lower than $c_{T,\,Zn}$.

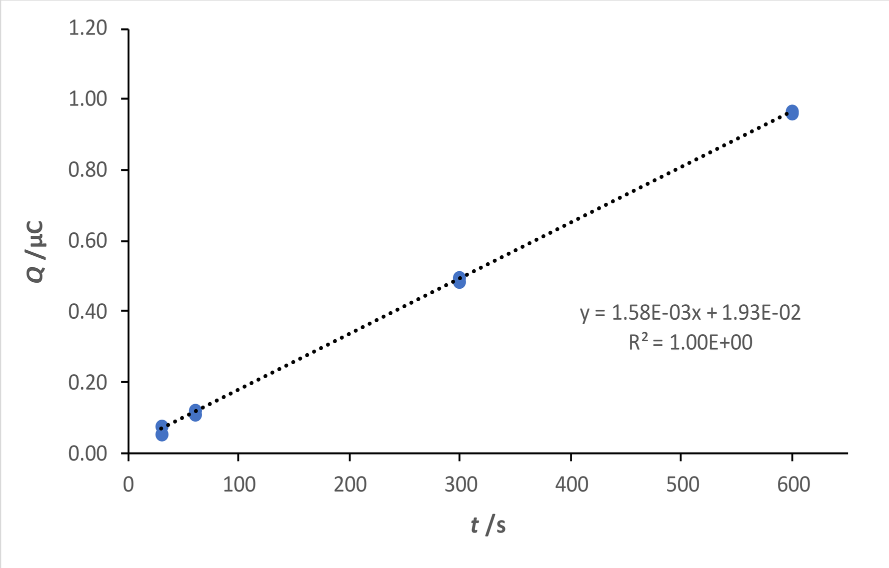
This effective concentration signature can provide an estimation, usually by interpolation, of the maximum available Zn that could be received by an organism in contact with this water from its diffusive characteristic length.

❑ Zn lability and mobility determined with LASV and DGT



The lability degree of zinc determined with the LASV technique (green triangle) is much lower than those of the DGT with different configurations, i.e. 1 or 2 resin disc(s) + 1 or 2 gel disc(s), due to a much smaller diffusion layer in LASV (δ_{LASV} =0.011 mm).

❑ Determination of c_{LASV}

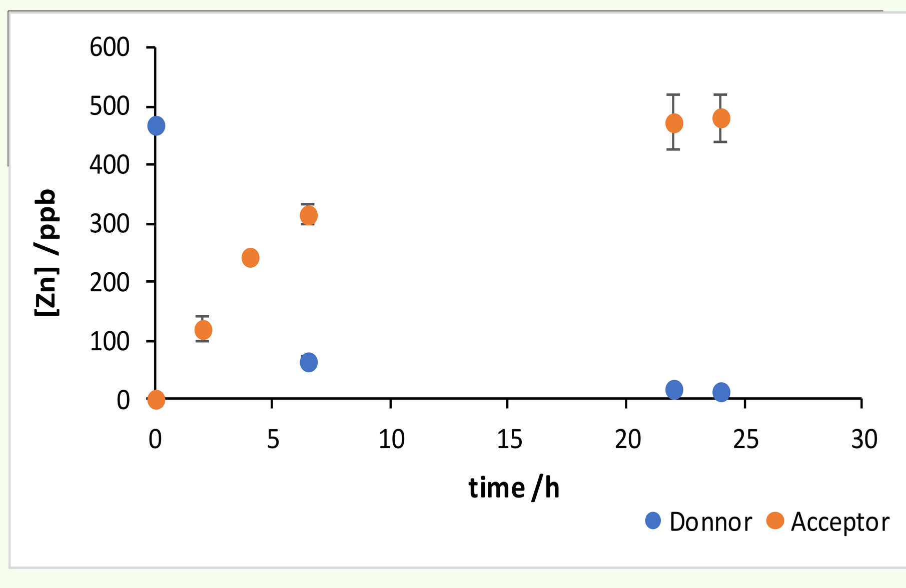


c_{LASV} is found from the slope in the plot *Q* vs deposition time using the expression,

$$Q = nFA\frac{D_{Zn^{2+}} c_{LASV}}{\delta_{LASV}}t$$

where the diffusion layer thickness δ_{LASV} is taken from a previous calibration.

❑ PIM calibration



A simple model with constant initial permeability P_0 was applied:

$$J = P_0\left[Zn^{2+}\right]$$

P_0 was obtained from a calibration experiment in a diffusion cell. The *in-situ* deployment of PIM provided free Zn concentrations for the first time.

4. CONCLUSIONS

- The use of several analytical techniques allows the combination of complementary information about the studied system in the effective concentration signature.
- As the characteristic length of the diffusion layer increases, the more labile the complex becomes, as it will have more time to dissociate.
- The lability degree of the pool of Zn inorganic complexes as seen by LASV technique was determined

5. REFERENCES

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