Universitat de Lleida

Availability of metals and nanoparticles in natural media

Alexandra Altier Infantes
Department of Chemistry, University of Lleida

XXXVI Reunión del Grupo de Electroquímica
XVII Encontro Ibérico de Electroquímica

Supervisor: Jaume Puy Llorens
Advisor: Carlos Rey Castro

Index

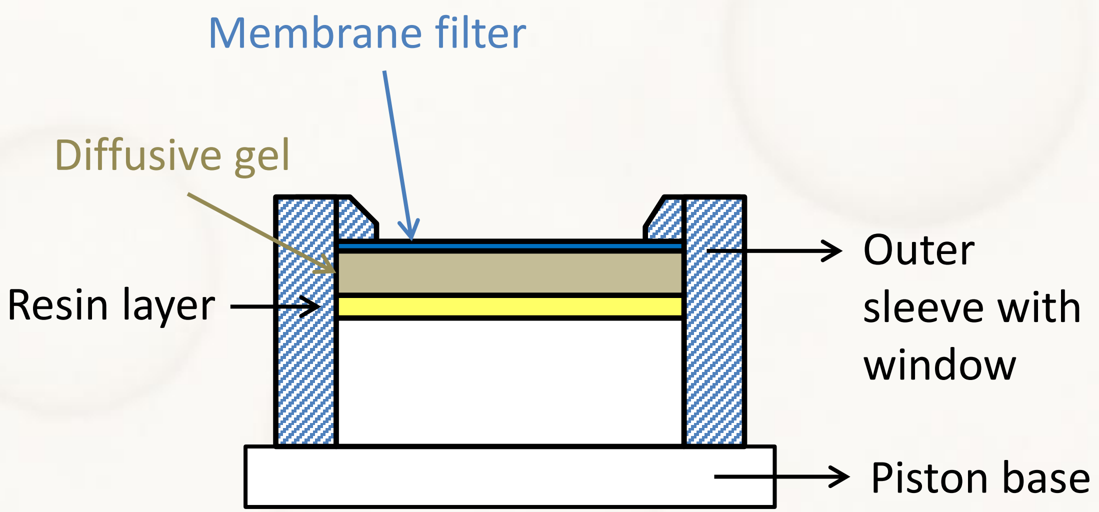
1. Introduction. Importance of speciation
2. Methodology
3. Results
4. Conclusions
5. Future work

Contamination with metals and nanoparticles

Speciation:

determination of the distribution of metal ions over different chemical and/or physico-chemical forms.

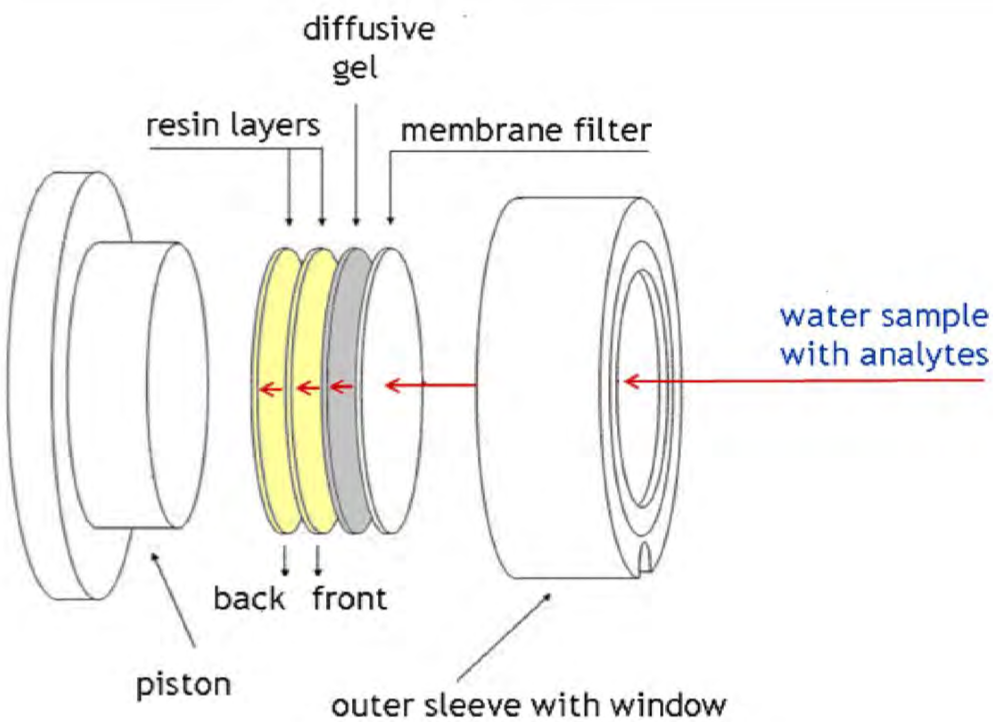
Diffusive Gradients in Thin films (DGT):
dynamic speciation technique for "in situ" measurements based on using a diffusive gel to accumulate metals in a resin layer (Chelex-100).

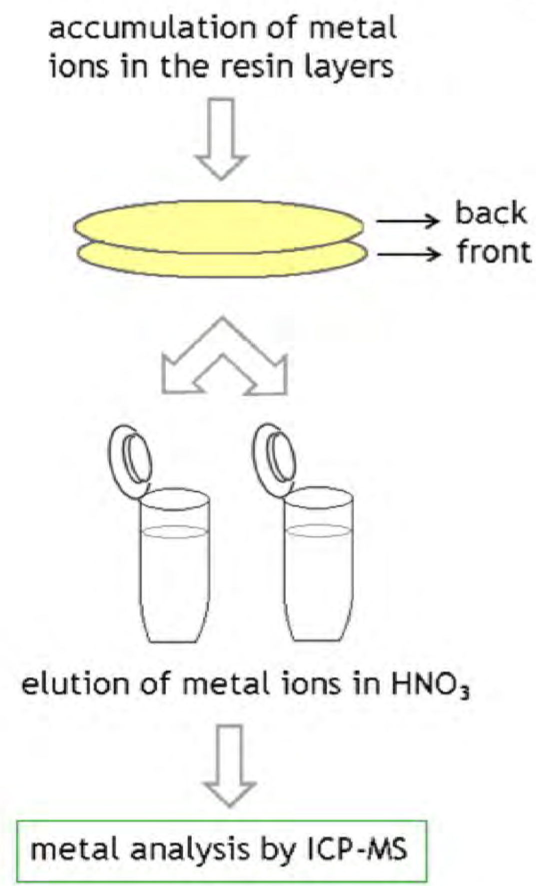


Scheme of a DGT in cross section

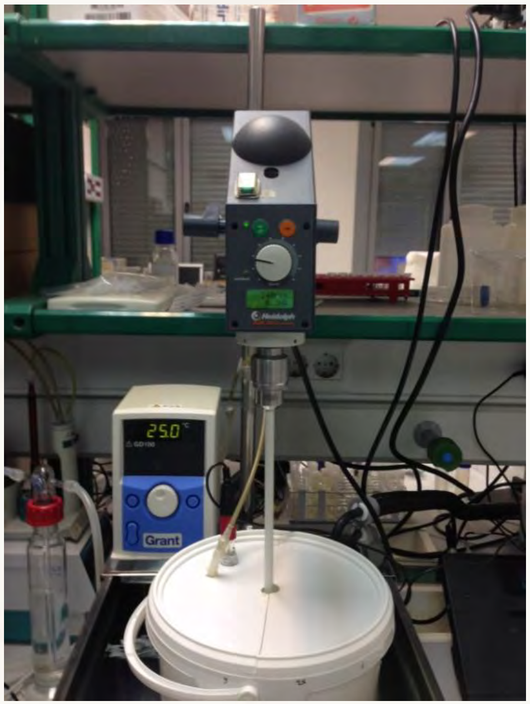
Photo of a *DGT device*

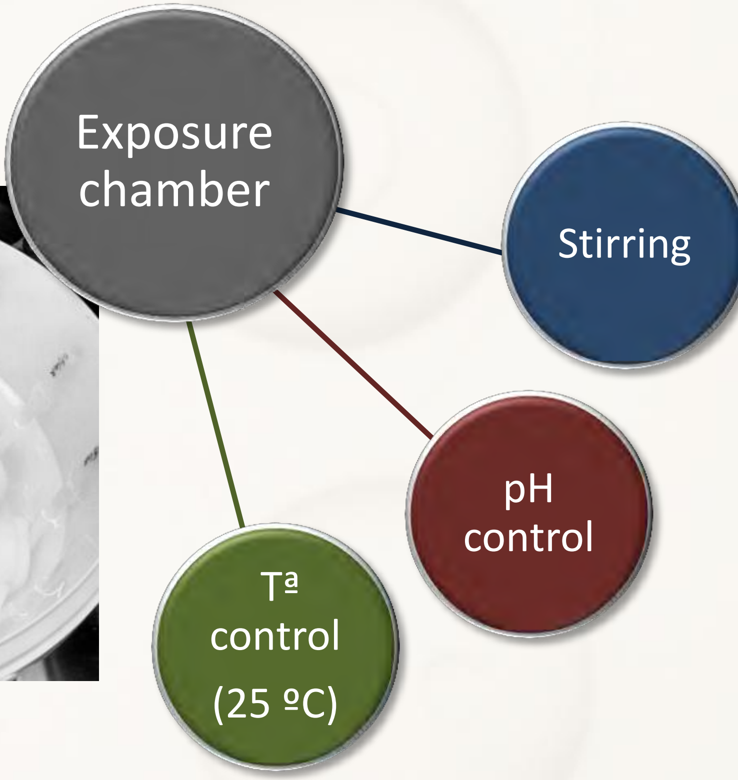
Davison and Zhang *Nature* 367 (1994) 546





Representation of the DGT, components, accumulation and elution of trace metal ions from Chelex-100 resin.

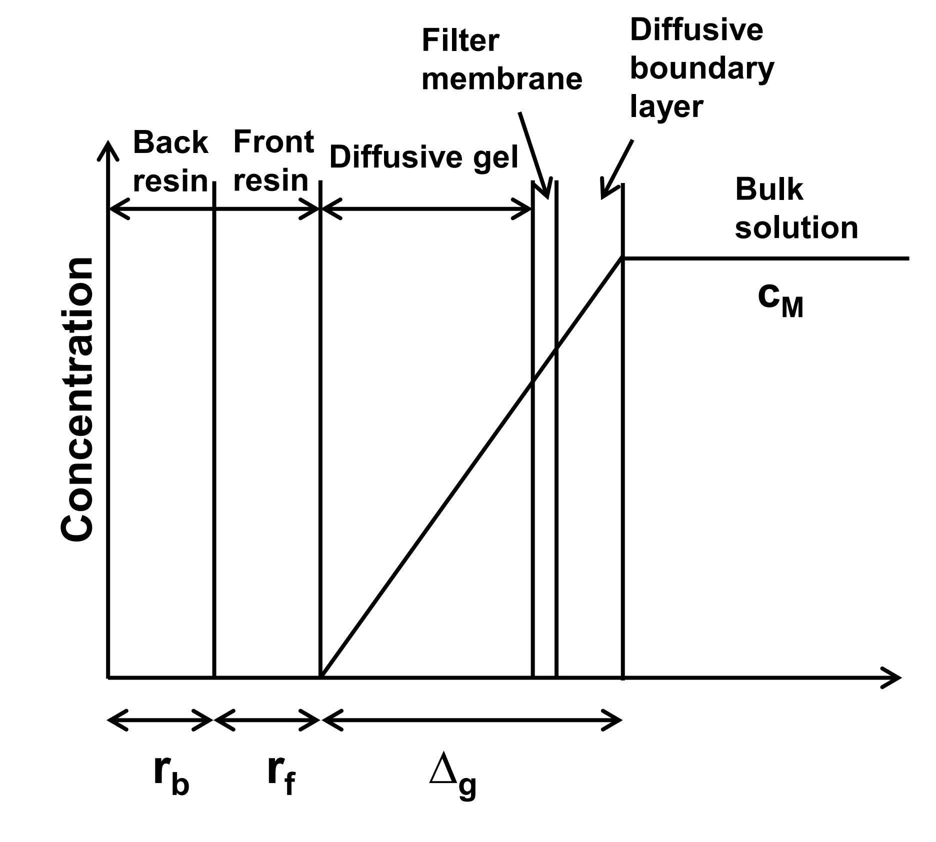




Picture equipment used for data collection

Introduction | **Methodology** | Results | Conclusions | Future work

- Simplest system: only metal is present



Schematic representation of the steady state concentration profile

$$n = \frac{c_e(V_e + V_r)}{f_e}$$

1º Fick law: $$\mathrm{J} = \mathrm{D}\,\frac{dc}{dx}$$

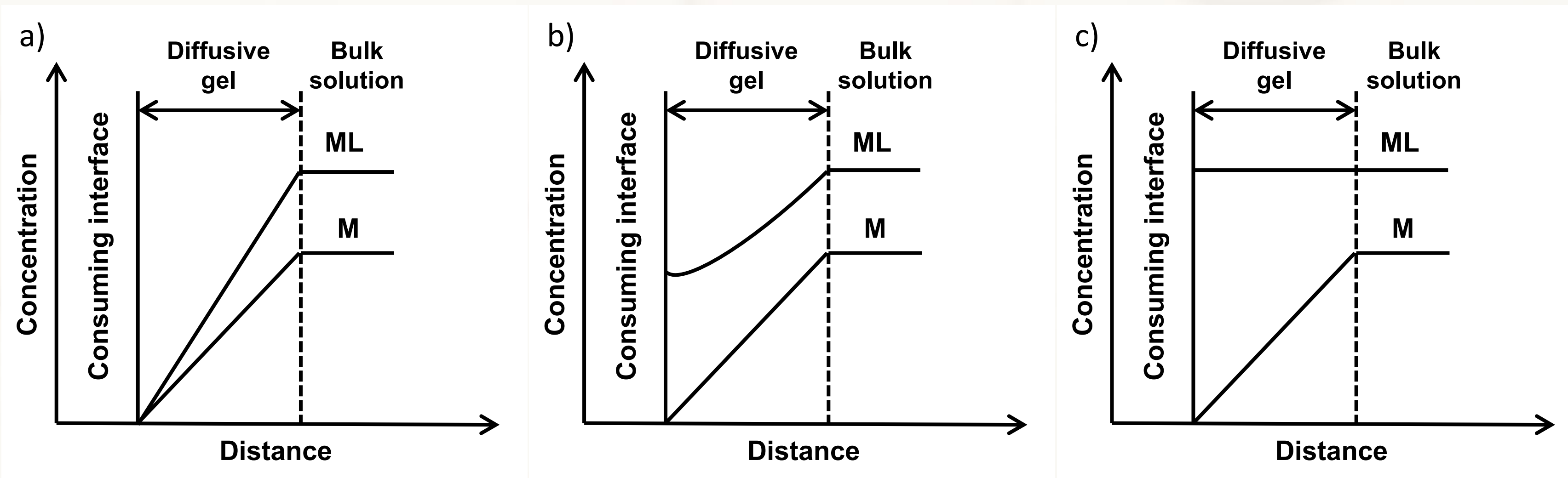
$$\mathrm{J} = \frac{n}{A \cdot t}$$

$$c_{\mathrm{DGT}} = \frac{n \cdot \Delta g}{D \cdot A \cdot t}$$

- ❑ Natural systems contain mixtures of ligands

Accumulations in DGT come mostly from transport and dissociation of complexes (ML).

How much a complex ML contributes to the process of accumulation of M in a chemical sensor?



Labile complex | Partially labile complex | Inert complex

Definition of lability degree:

$$\xi = \frac{J_{\mathrm{M}} - J_{\mathrm{libre}}}{J_{\mathrm{labil}} - J_{\mathrm{libre}}}$$

→ Complex real contribution

→ Maximum contribution

J_{M}: metal flux

J_{libre}: the diffusive transport of free metal present in the system

$J_{\mathrm{lábil}}$: the metal flux that comes into the system if the complex was fully labile

Advantages of DGT:

- *in situ* measurements:

Natural resources

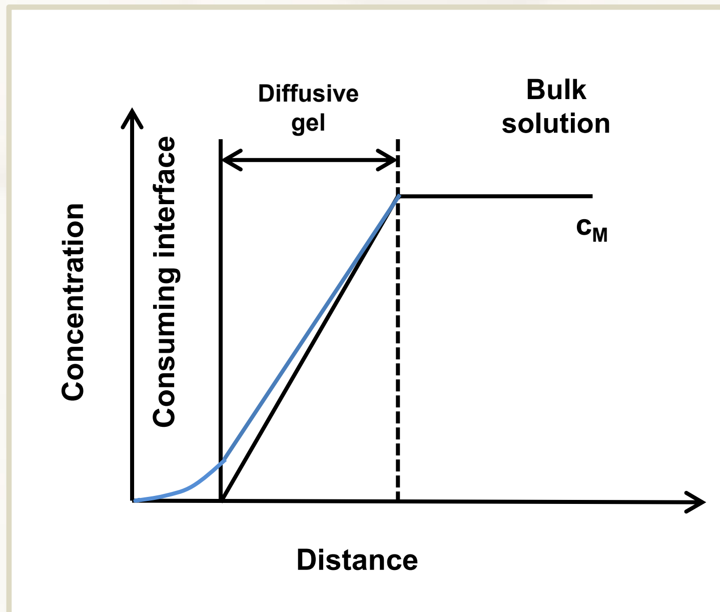
Solutions in the laboratory

- Preconcentration of metals
- Determination of a wide range of metal ions, anions, or organic species
- Inexpensive technique

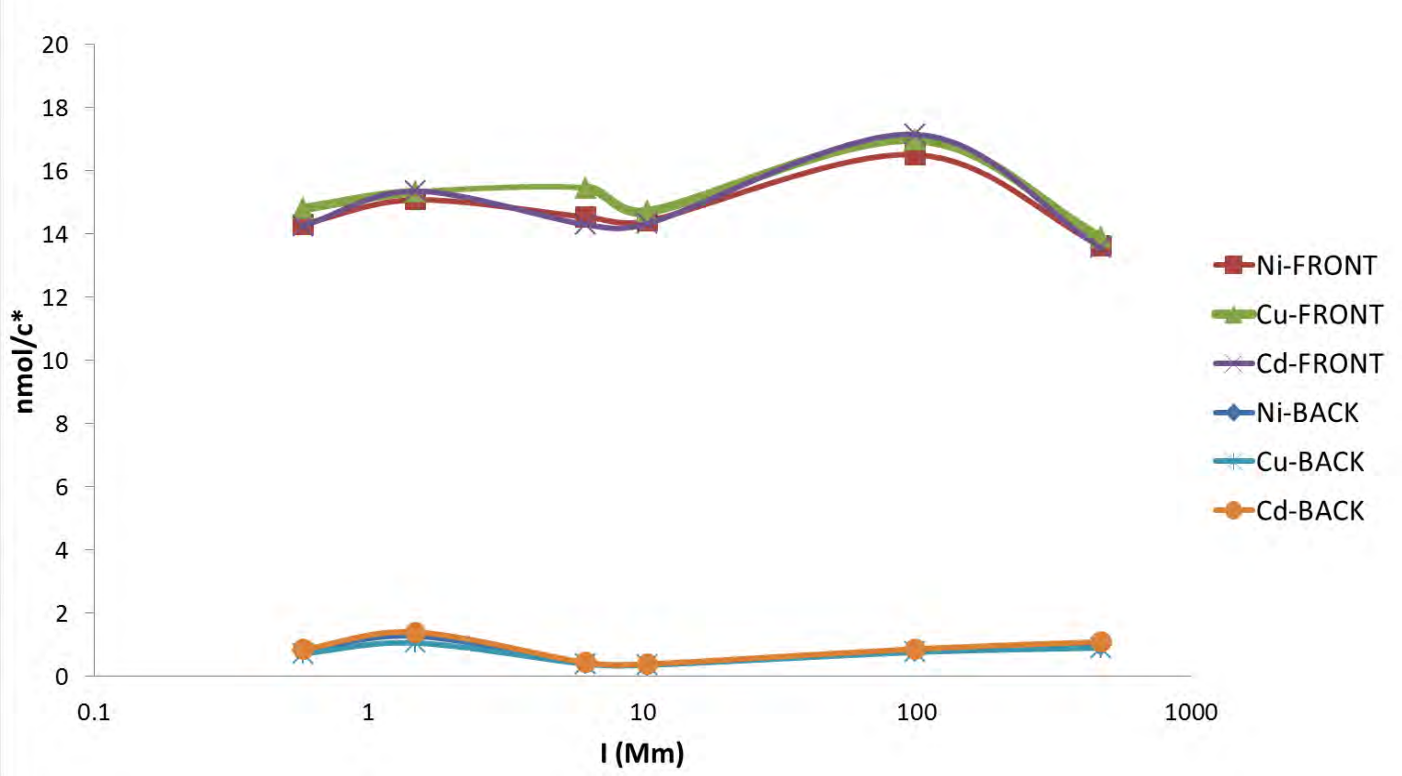
1. Study of the effect of ionic strength on metal accumulation on DGT

Experimental details	
Ca^{2+}, Mg^{2+}	$K_{a,R} \downarrow$
Ni^{2+}, Cu^{2+}, Cd^{2+}	$K_{a,R} \uparrow$
MOPS (M)	2.5×10^{-3}
I (mM)	0.4 - 500
pH	6.5
3 sensors	24h

$$M^{2+} + 2R^{-} \xrightarrow{K_{a,R}} MR$$

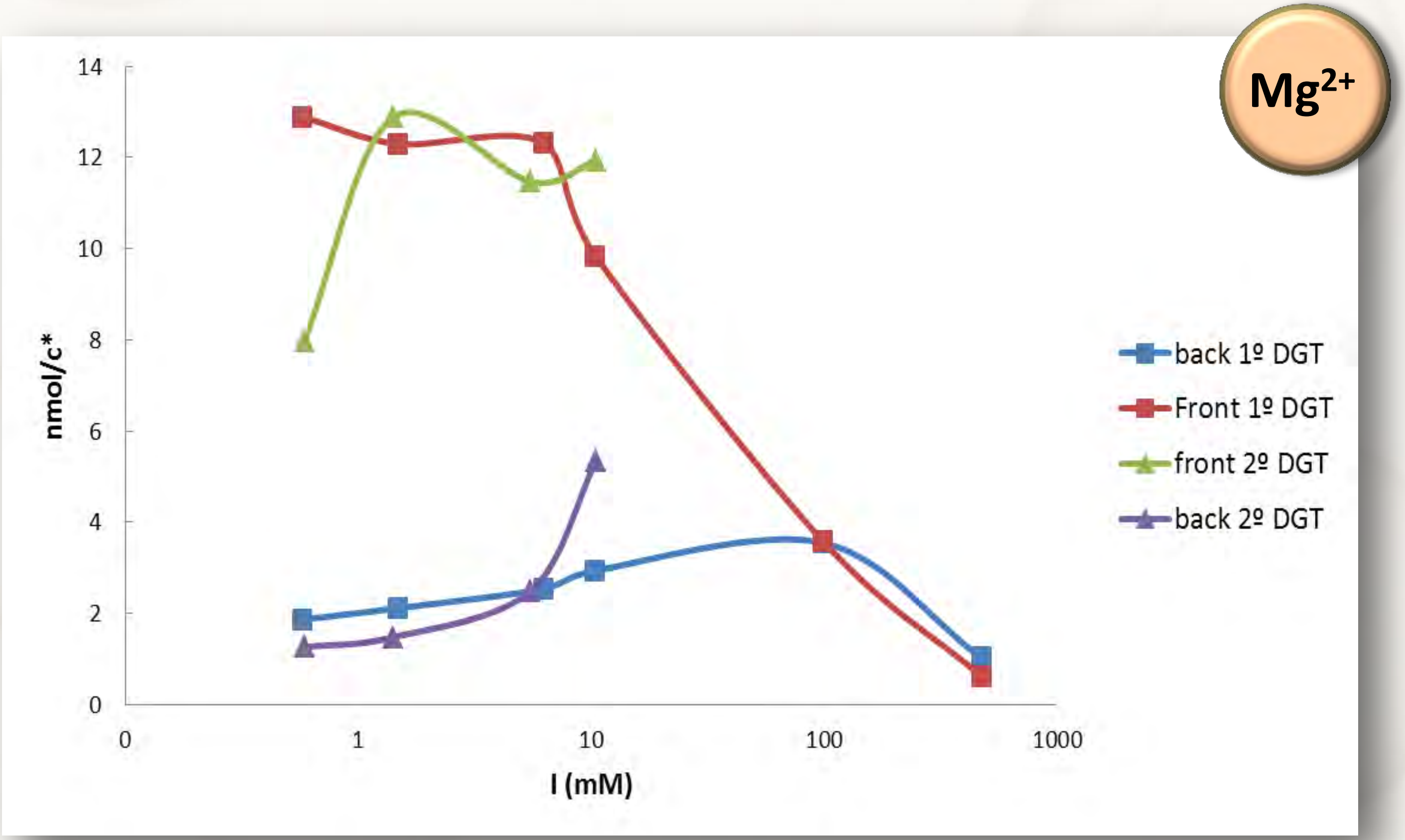


1. Study of the effect of ionic strength on metal accumulation on DGT



Total metal accumulation for Ni^{2+}, Cu^{2+} and Cd^{2+}

1. Study of the effect of ionic strength on metal accumulation on DGT



Total metal accumulation for Mg^{2+}

2. Study of the effect of ionic strength on metal accumulation in MNTA systems

Resin disc

$0.5c_{T,R}$

$c_{T,R}$ standard concentration

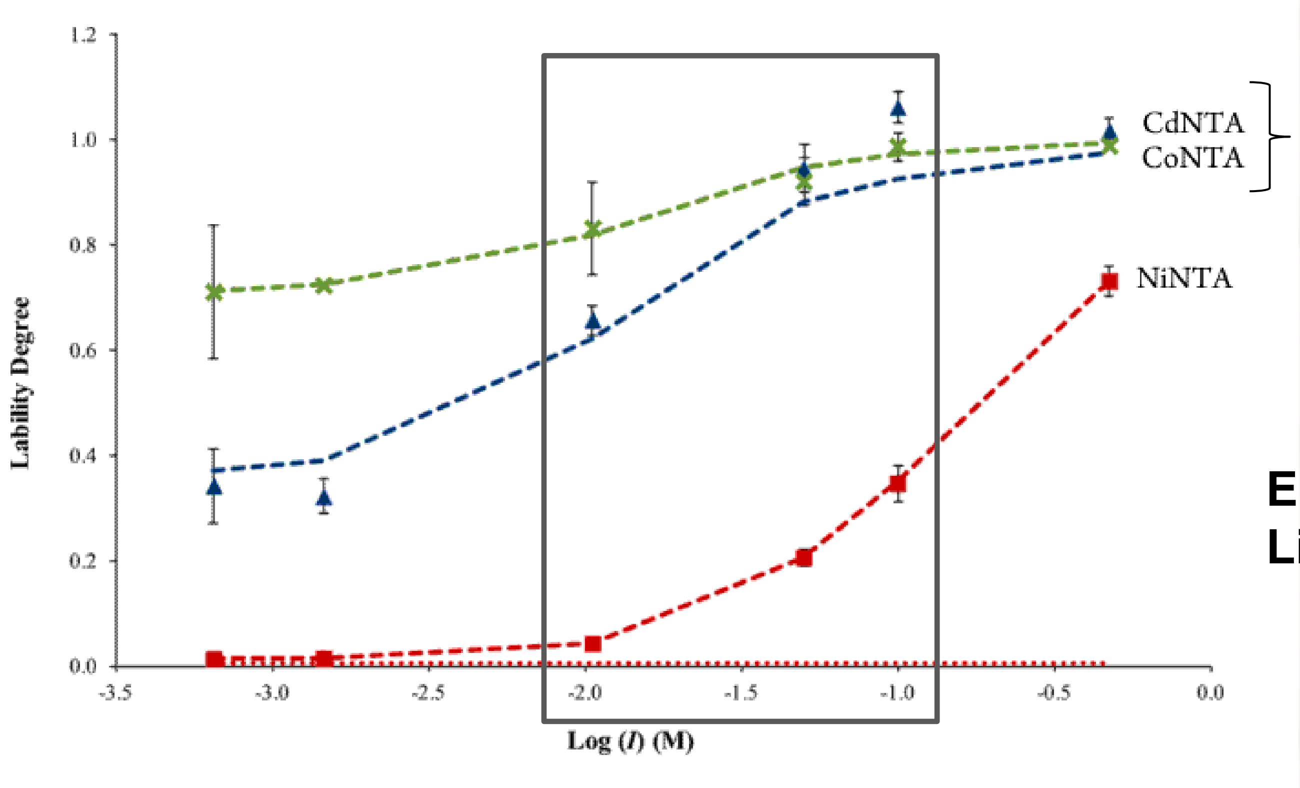
$1.5c_{T,R}$

$2c_{T,R}$

Experimental details ($mol\ L^{-1}$)	
Ni^{2+}	2.5×10^{-5}
Cd^{2+}, Co^{2+}	10^{-5}
Rb^{+}	5×10^{-4}
NTA	8×10^{-5}
MOPS	7×10^{-3}
pH	7.5
I	0.01, 0.05, 0.1

$$\mathbf{M^{2+} + NTA^{3-} \longrightarrow MNTA^{-}}$$

2. Study of the effect of ionic strength on metal accumulation in MNTA systems



Labile

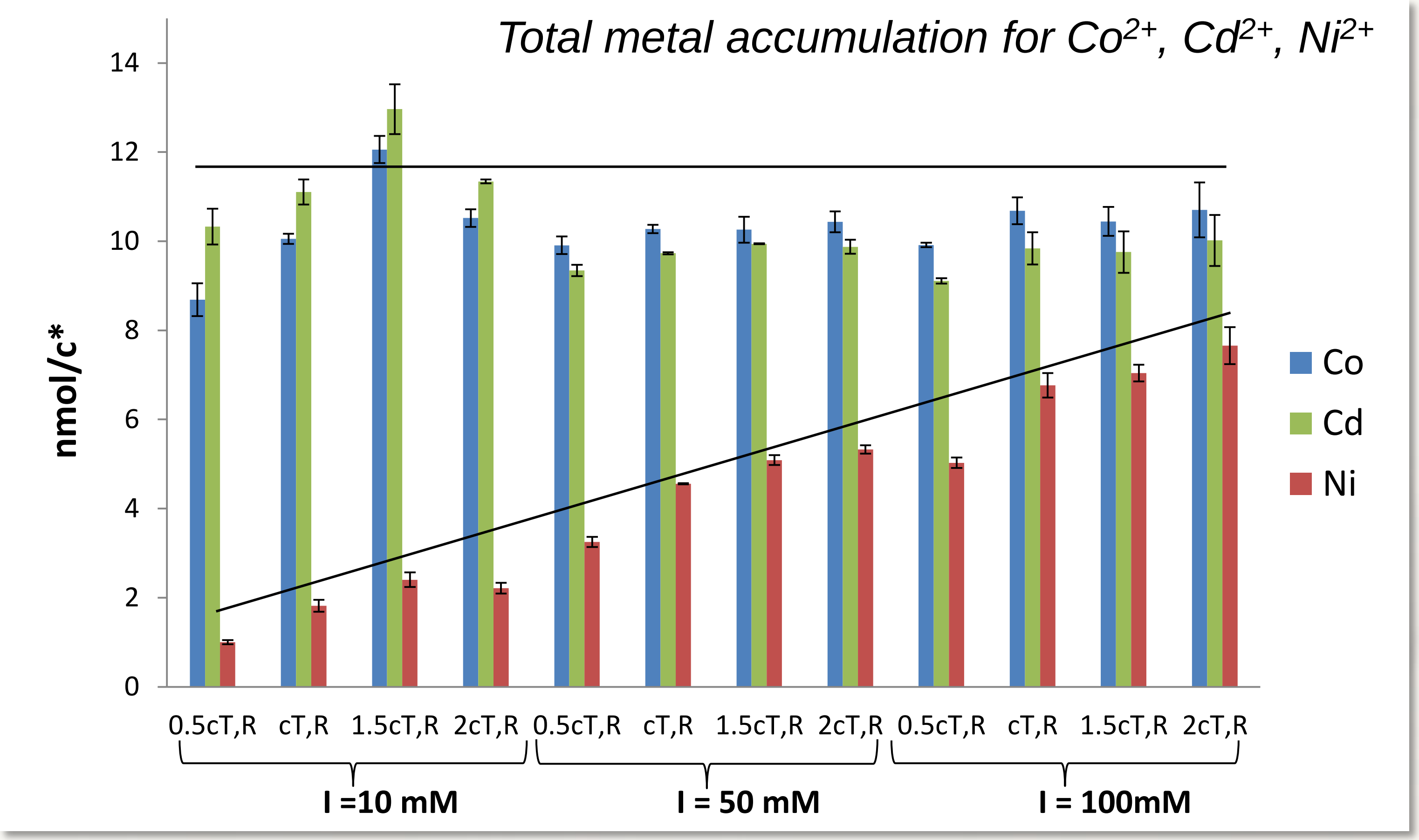
Partially labile

Electrostatic effects
Ligand assisted effects

Lability degree of CdNTA, CoNTA and NiNTA complexes at ionic strengths in the range from 0.1 mM to 0.5 M.

J. Puy *et al*. Anal. Chem. (2014)

2. Influence of resin concentration ($c_{T,R}$) on metal accumulation on DGT



2. Influence of resin concentration ($c_{T,R}$) on metal accumulation on DGT

1. Effect of $c_{T,R}$ on k_d

Ligand-assisted mechanism

$$2R^{-} + MNTA^{-} \longrightarrow R_2M + NTA^{3-}$$

$$k_{LA} \cdot [R^{2-}][MNTA^{-}] = k_d\,[MNTA^{-}]$$

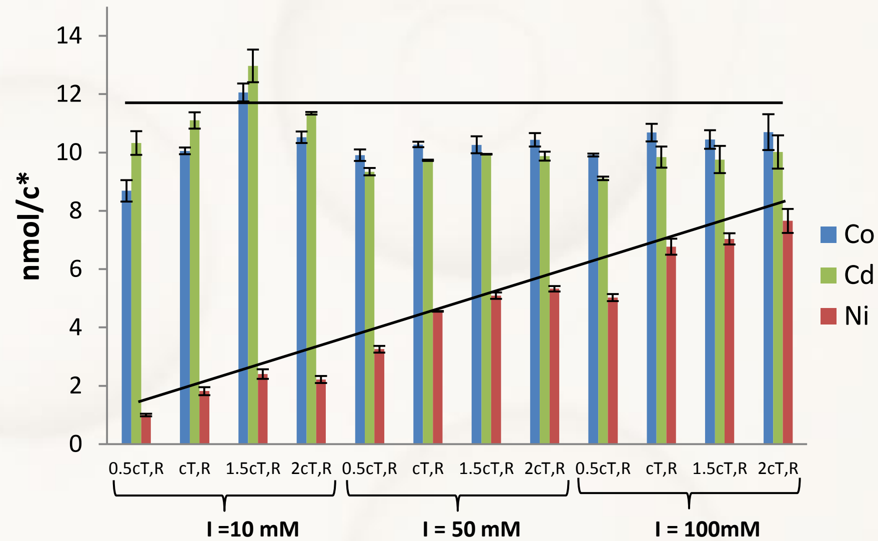
$$k_d = k_{LA} \cdot [R^{2-}]$$

$k_d \uparrow$

$0.5c_{T,R} \xrightarrow{\times 2} c_{T,R} \xrightarrow{\times 3/2} 1.5c_{T,R} \xrightarrow{\times 4/3} 2c_{T,R}$

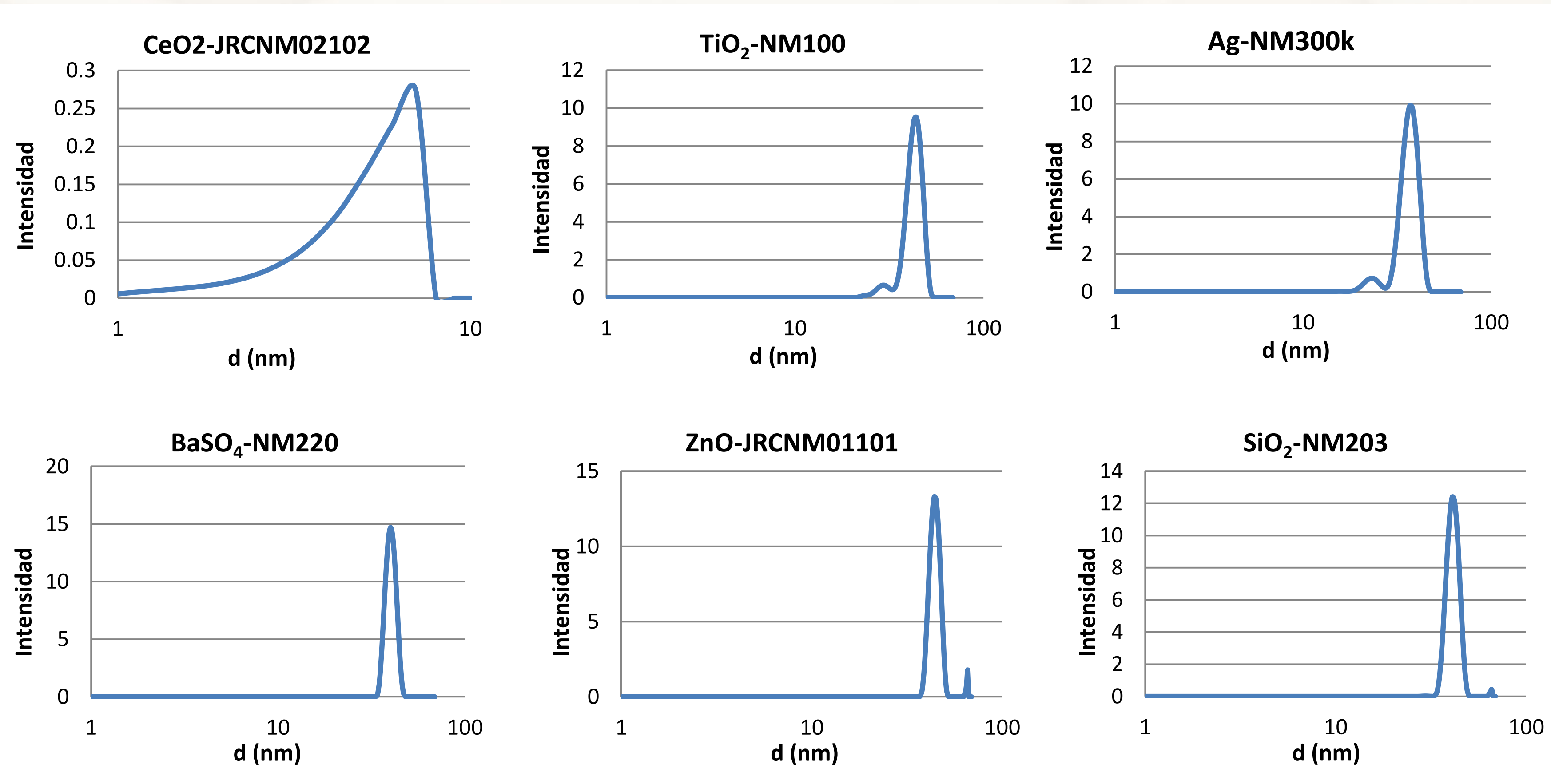
n_T →

Homogeneity →



2. Effect of homogeneous distribution

3. Characterization of nanomaterials



Intensity-weighed hydrodynamic size distribution of nanomaterials

- The binding of Mg^{2+} to the DGT seems to be kinetically limited at high ionic strength. Decreasing ionic strength below 0.006M, accumulation of Mg2+ proceeds at perfect sink conditions.

- Accumulations of metals from negatively charged partially labile complexes decrease as the ionic strength decreases. Electrostatic effects and a decrease of the dissociation rate constant can explain this behaviour.

- Accumulations increase as $c_{T,R}$ increases. Both, a dependece of the dissociation rate constant on $c_{T,R}$ as well as the settling of the resin beads can explain this bahaviour.

- Good reproducibility of the results obtained following the NANoREG Protocol – ECOTOX.

- The recognition of which species contribute to the metal biouptake or to the metal accumulation in a chemical sensor is the general aim of the present work.

- Important effects that have to be recognized and quantified are:
  - Electrostatic effects at low salt bakgrounds
  - Kinetic effects in the resin domain
  - Dependence of the kinetic constants on the ionic strength
  - Influence of the settling of the resin beads

- The project also aims at developping procedures to determine physicochemical parameters that characterise the metal accumulation in DGT devices.

- Special experiments or fitting strategies will be developped to avoid the simultaneous fitting of a large number of parameters

- Application of this framework to the metal accumulation in presence of dissolved organic matter is envisaged