PhD program

Determination of the speciation and bioavailability of Indium with electroanalytical techniques

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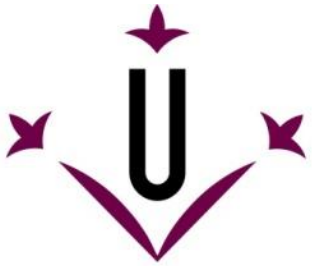

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Outline

- Motivation and state of the art
- Objectives
- Methodology
- Results
- Conclusion
- Acknowledgement

Motivation and state of art

Why Indium?

- Amalgamating element
- Negative redox potential
- Trivalent ion

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Standard technique

Ion selective electrodes

- X Non commercial electrodes
- X LOQ= 10^{-7} mol L^{-1}

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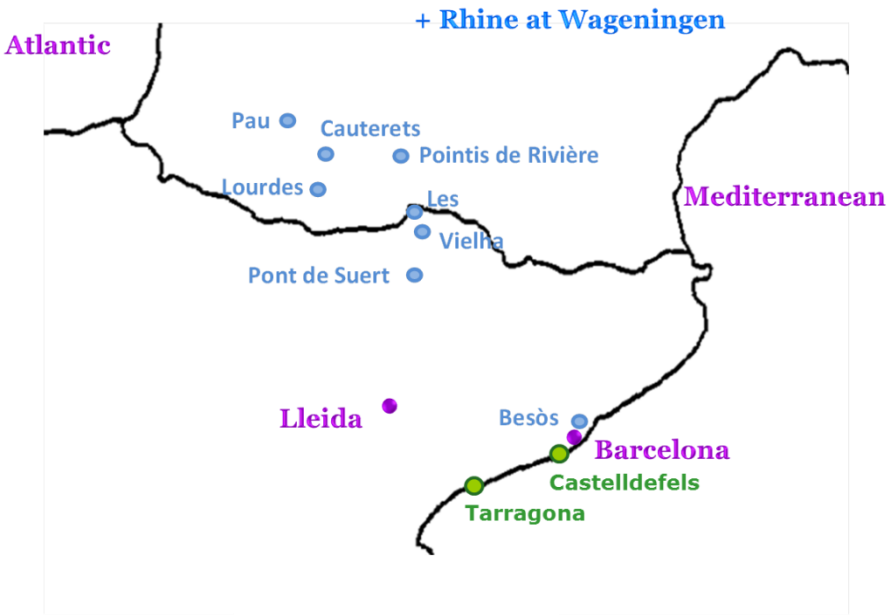
Technique: AGNES

River and seawater

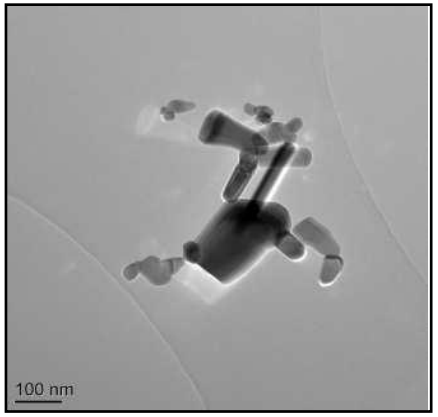


Galceran et al. Talanta 71 (2007) 1795
Zavarise et al. Anal. Bioanal.Chem. 397 (2010) 389
Chito et al. Sci. Total Environ. 421-422 (2012) 238
Parat et al. Environ.Chem. 12 (2015) 329

Soil extracts

Chito *et al*. **Sci. Total Environ.** 421-422 *(*2012) 238

ZnO nanoparticles



David *et al*. **J. Phys. Chem.C** 116 (2012) 11758
Adam *et al.* **Nanotoxicology** 8 (2014) 709
Mu *et al.* **Chem.Res.Toxicol.** 27 (2014) 558
Galceran *et al.* **JEC** 722-723 (2014) 110

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Research question

Can AGNES measure the free concentrations of Indium in various samples?

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Aims and Objectives

Main Goal:

Exploring AGNES potential in determining free concentation of Indium

- ✓ **Aim 1**: AGNES at optimal pH compare to other standard techniques
- ✓ **Aim 2**: AGNES at higher pH values in systems with precipitation
- ✓ **Aim 3**: AGNES applied to Indium nanoparticles

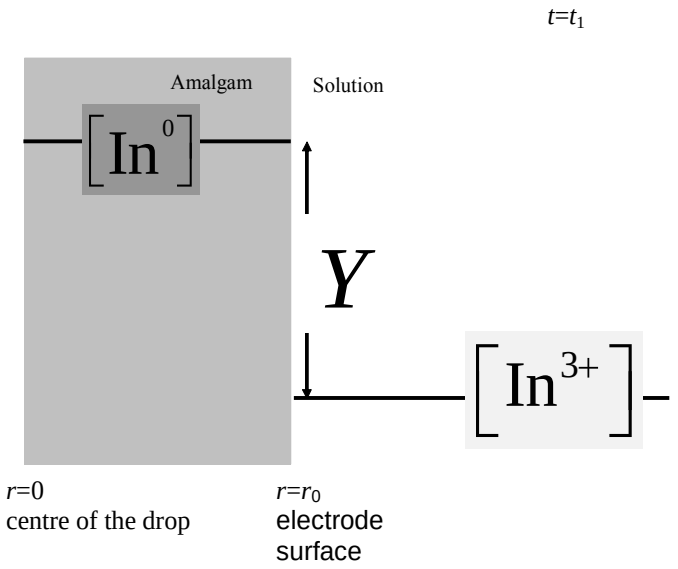
Methodology (first stage)

AGNES (Absence of Gradients and Nernstian Equilibrium Stripping)

Nernst equation:

$$Y = \frac{\left[\mathrm{In}^{0}\right]}{\left[\mathrm{In}^{3+}\right]} = \exp\left[-\frac{3F}{RT}\left(E_1 - E^{o'}\right)\right]$$

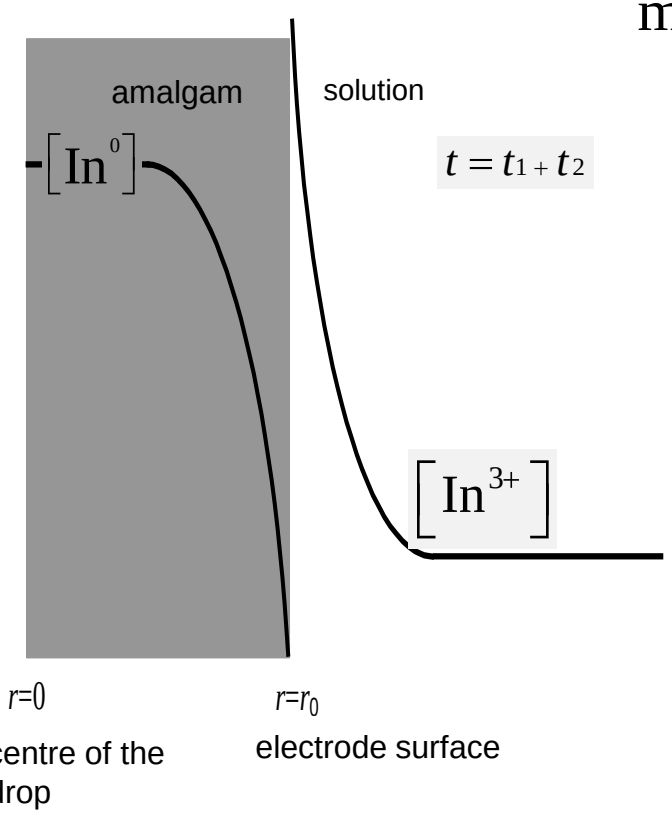
(preconcentration):



E_1 along t_1: $\mathrm{In}^{+3} + 3\mathrm{e}^{-} \rightarrow \mathrm{In(Hg)}$

Methodology (second stage)

$$In^0 - 3e^- \rightarrow In^{3+}$$



$$\text{moles in amalgam} = V_{Hg}[In^0]$$

$$Q = nFV_{Hg}[In^0]$$

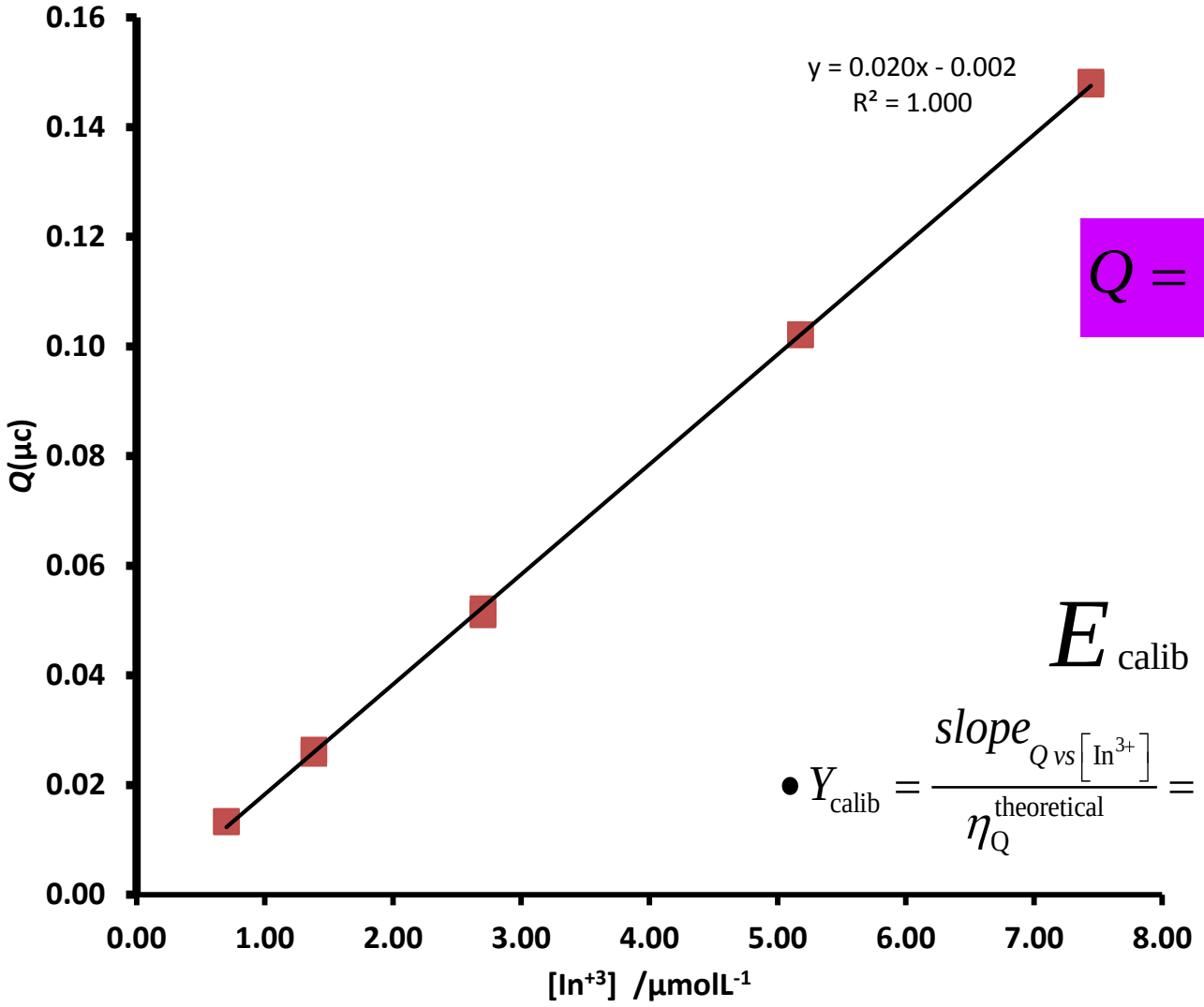
$$\eta_Q \equiv nFV_{Hg}$$

$$Q = \eta_Q[In^0]$$

$$[In^0] = Y[In^{3+}]$$

$$Q = \eta_Q \; Y[In^{3+}]$$

Calibration



$$Q = Y\,\eta_Q\,\left[\mathrm{In}^{3+}\right]$$

$$E_{\text{calib}} = -0.4996\,\text{V}$$

- $$Y_{\text{calib}} = \frac{slope_{Q\,vs\,\left[\mathrm{In}^{3+}\right]}}{\eta_Q^{\text{theoretical}}} = \frac{slope_{Q\,vs\,\left[\mathrm{In}^{3+}\right]}}{0.0034} = 5.90$$

$$\eta_Q^{theoretical} = n\,F\,V_{\text{Hg}} = 3\,F\,\tfrac{4}{3}\,\pi\,r_0^3\,1000 = 0.0034\ \text{C M}^{-1}$$

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Calibration

$$E_{\text{calib}} \quad \Leftrightarrow \quad Y_{\text{calib}}$$

$$E_j = E_{\text{calib}} - \frac{RT}{3F} \ln \frac{Y_j}{Y_{\text{calib}}}$$

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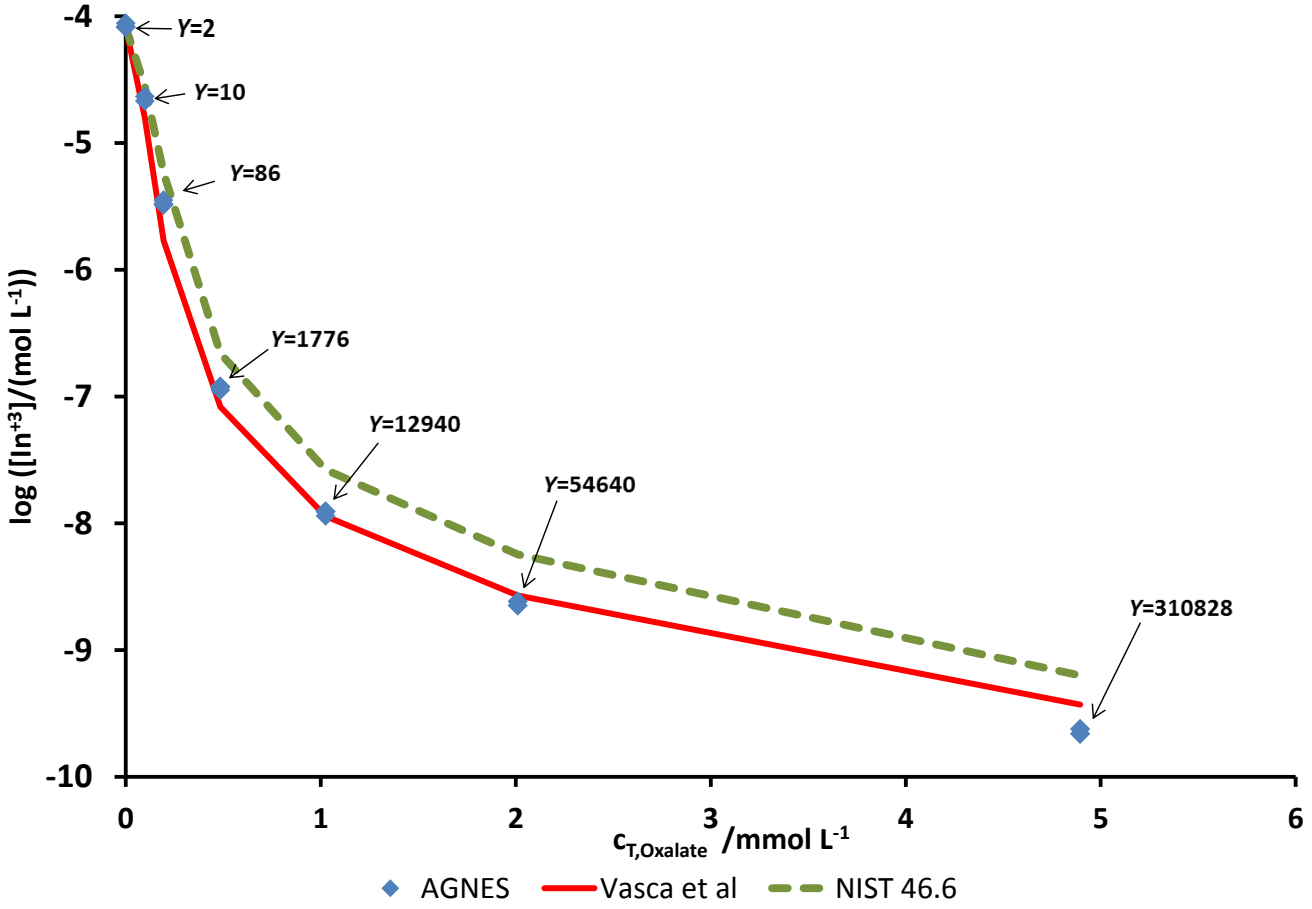
Speciation of In with Oxalate



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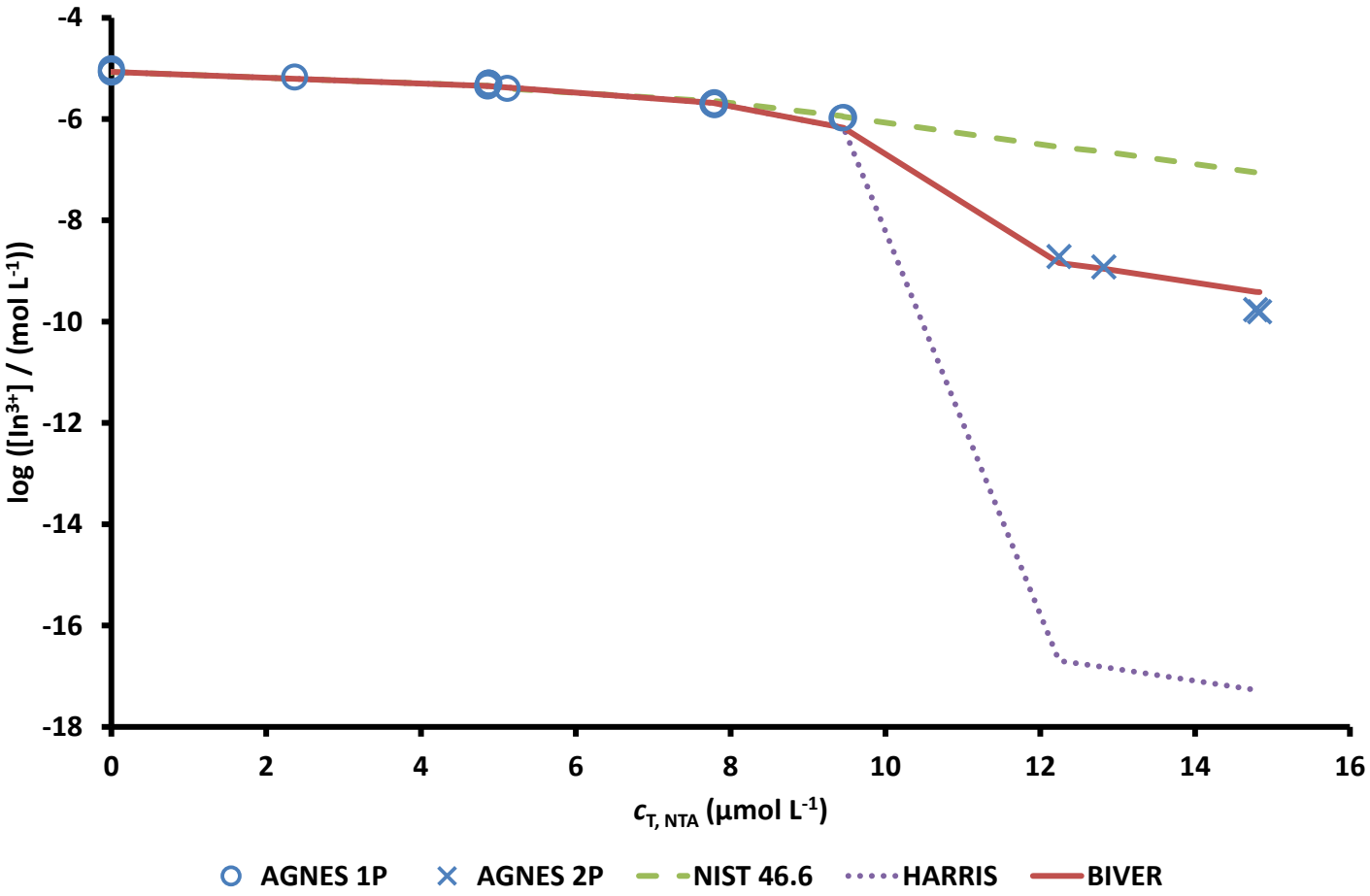
Speciation of In with NTA



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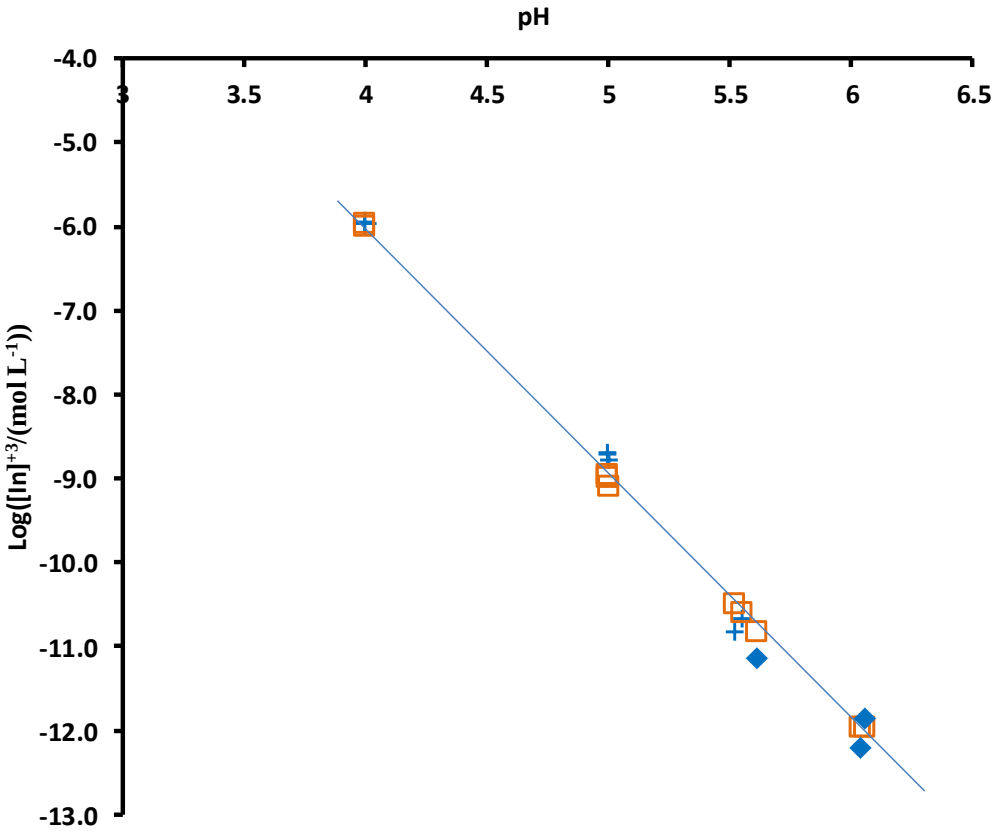
Precipitated systems



$$K_{sp} = \left[In^{3+} \right] \left[OH^{-} \right]^{3}$$

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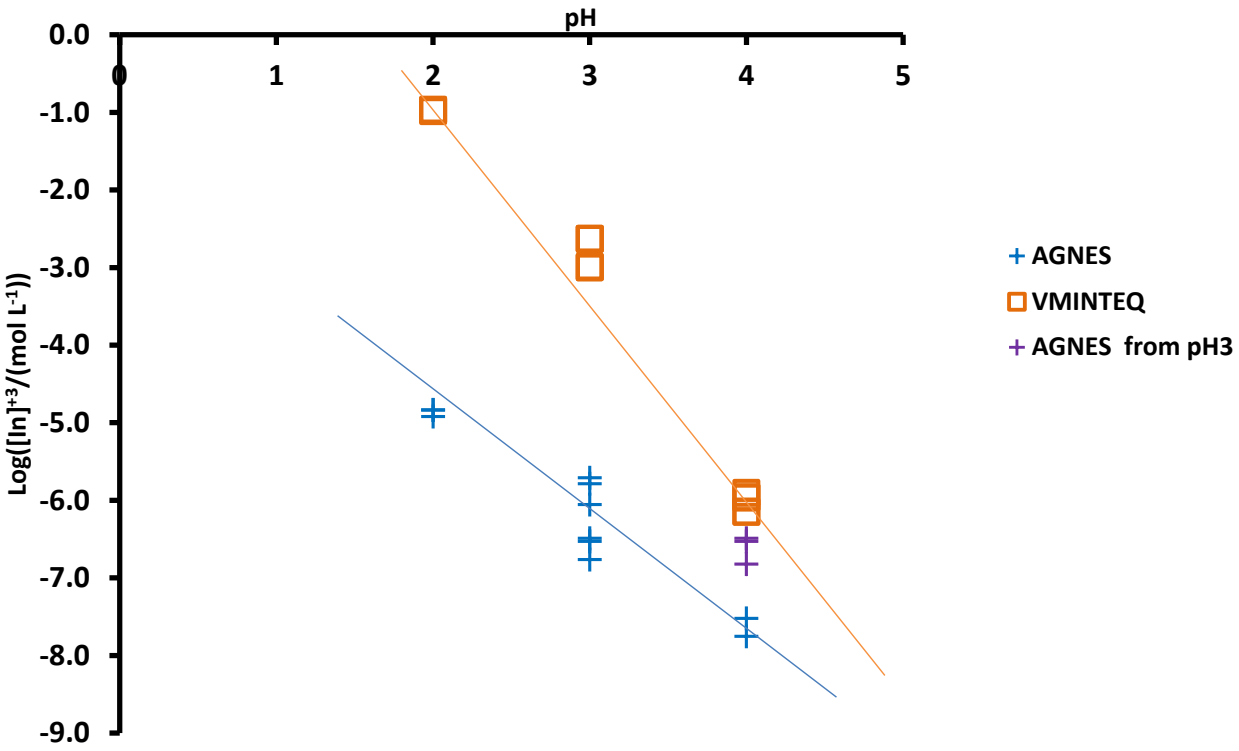
Nanoparticles



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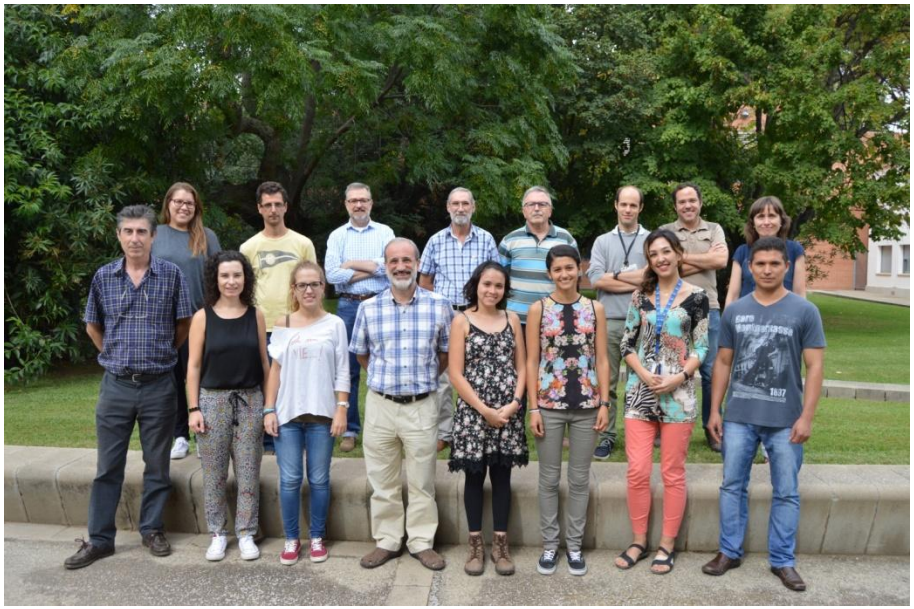
Conclusion

Key findings:

- A new calibration method was implemented.
- Speciation at optimal pH was carried out for both inert and labile complexes.
- Stability constants reported in NIST 46.6 were less accurate than others recently published by Biver (In-NTA) and Vasca (In-Ox).
- Lability and mobility of Oxalate allows a decrease of deposition time to 25s from the expected 3 x 10^6s.
- Determination was successfully carried out for precipitated systems at picomolar range.
- In dispersions of Indium nano particles (In_2O_3), a change of a pH from 3 to 4 caused $[In^{3+}]$ at higher pH to be shifted to its equilibrium value with In hydroxides.

Acknowledgement



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