Project of Doctoral thesis for Marjan Heidarkhan Tehrani

Doctoral program: Electrochemistry and Science 1309

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Title:

Determination of the speciation and bioavailability of Indium with electroanalytical techniques

Aims:

Nowadays researchers are becoming more interested in improving methods for determining free concentrations of metals. Indeed, it has been revealed that if these metals arrive to the environment, they might cause serious ecotoxicological and health problems.

Indium is one of those rare elements in the earth crust that is mostly present in electronic devices. It has a vast application interest in many industries. It can be used as a semiconductor, vacuum seal, thermal conductor, in alkaline batteries, or it could be added to dental amalgam alloys. Since it is being widely used, it is very important to use a proper technique to determine its free concentrations.

For this purpose, we basically investigate whether the new electroanalytical technique Absence of Gradients and Nernstian Equilibrium Stripping, (AGNES), designed by Lleida Electrochemical Group (LEG), would be able to access to Indium free concentrations.

The knowledge of the free metal ion concentration is key to the hegemonic paradigms of ecotoxicity (FIAM and BLM), as the speciation of an element modulates its toxic effect. The new electroanalytical technique, AGNES, has proved suitable for the determination of the free metal ion concentration of Zn, Cd and Pb ions.

In this thesis, we aim at extending the development of AGNES to determine free concentrations of Indium (III) in aqueous solutions.

Materials and Methods:

The key technique in this thesis is AGNES, which is applied with standard instrumentation in LEG's lab (potentiostats and stands). New strategies are developed to tackle different challenges.

Systems were probed include: In solutions with ligands such as NTA and Oxalate, hydroxides and nanoparticles.

First year:

At the beginning, I reviewed the literature on Indium speciation and to address the question of what are the relevant stability constants for different complexes with Indium (Tuck 1983; wood and Samson, 2006). Our work was especially devoted to the speciation of Indium and the hydrolysis of its metal ion, including improvements made to AGNES to determine free concentrations of Indium ions. Application of AGNES at different pH values, especially, pH 3 was checked.

The slight irreversibility of indium led us to suggest a new calibration procedure based on fixing the proportionality factor (η). By taking the slope of the calibration and dividing it by that fixed η value, we were able to calculate the Y of the calibration and also to compute any needed Y from any used deposition potential.

We conducted several trajectory tests to check the attainment of equilibrium and determine the required deposition time using different gains at a series of times. After normalizing the trajectories, a collapse was observed, which was consistent with AGNES properties such as the proportionality between the gain and the charge. We concluded that in these simple programs the deposition time would be 10 times the desired gain.

Additionally, stability constants in the literature such as Indium-Nitriloaceticacid (In-NTA) (Harris et al, 1994 and Biver et al , 2008) and Indium Oxalate (Pingarron et al, 1984 and Vasca et al, 2003) were checked. I tested NTA and Oxalate and finally obtained satisfactory preliminary results that led to my first manuscript. In May 2015, I attended SETAC conference in Barcelona, and presented my preliminary results on Indium. I also presented my work in the regular seminars in our research group.

Second year:

I continued my work on determining the free concentrations of Indium by increasing the pH of the solutions. We designed experimental strategies to determine extremely low concentrations of Indium through.

In parallel I performed advanced speciation measurements, including In-NTA and In-Ox complexes to. We compared the measurements of AGNES with those predicted by the existing speciation models to discriminate between the suitability of different published set of constants. These results were added to my first manuscript.

Then, I continued my measurements of the lability degree of Indium-Hydroxides by varying the pH. We also devised a new method, called ADLC (accumulation under diffusion limited conditions), in order to be able to calculate the lability degree.

Some parts of these results were presented in Vigo 13-15 July 2015 and another part in SETAC conference held in Nantes 2016. In September 2016, I participated in the conference "Interfaces against pollutions" held in Lleida where I performed as one of the members of the

local organizing committee. At that time, I had enough data to put together my second Manuscript.

Third year:

Part of our findings on indium and precipitated solutions will be presented in ICOBTE 2017 in Zurich. More experiments on the precipitated solutions at pH 5.6 with MES and Oxalate and other one at pH 5.6 with MES have been performed. We also followed the dissolution of In_2O_3 nanoparticles (NP) by measuring the free concentration with AGNES technique at various times and different media.

These experiments consist in working with synthetic seawater solutions at pH 8 and solutions that only contain KNO_3 0.1 M at pH 2, 3 and 4 and with added In_2O_3 NP and following the kinetics of dissolution in the given medium.

We submitted a manuscript to the journal Science of the Total Environment, and positive comments from the reviewers have been received. Also the plan is to read my thesis approximately by mid November 2017.

Lleida
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