# Final Report – In-Situ Monitoring of Environmental Trace Metal Pollutants (19-300)

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**Project Summary**

The overarching objective of this project was to develop new sustainable methodologies relying primarily on electrochemical principles for *in situ* environmental monitoring of trace metals in water systems (lakes and seas) using thin layer polymeric receptor-based membranes interrogated with controlled potential or current protocols.

**Background**

Most environmental researchers have "assumed defeat" and prefer extracting samples from water resources, either manually or mechanically, at different depths and/or locations. Once the samples are extracted, certain additives and preservatives are added to the prefiltered samples on the sampling platform. Then, the samples are ready to be transported to centralized laboratories under controlled temperature and ultraclean conditions. In the laboratory unit, some additional pretreatments are required (e.g., adjustment of pH and ionic strength, desalination in the case of seawater samples, centrifuging, among others) before the trace metal analysis, which consists of using costly instrumentation such as atomic absorption/emission spectroscopy (AAS/AES), inductively coupled plasma mass spectrometry (ICP–MS) among others operated by a trained laboratory assistant (U.S. Environmental Protection Agency, Method 1640).

While the multistep protocol and its associated methodologies are widely used by researchers, governmental agencies and industries; there is a challenging fundamental question that will be addressed through the proposal and relates to **how reliable is such extracted chemical information in the environmental context**? *A priori*, a straight answer seems to be extremely difficult because there are no alternative paths, but I identified three negative issues in the preexisting protocol that clearly impede evolving in a sustainable direction with tangible outcomes. The first one is related to the difficulty of preserving the sample from any alteration, such as pollution, degradation, destabilization, and adsorption that directly or indirectly modify concentration levels, chemical distribution (free and total), ultimately resulting in wrong chemical information. The second lies in the impossibility to "observe" biogeochemical processes in an appropriate timeframe (from seconds to minutes) with the classical protocol, which ranges from days to weeks. The last one is related to the inability to use that chemical information as strategic alarms to prevent or revert major risk that may have a disastrous impact on the sustainability of natural resources. Accordingly, this project was motivated by these weaknesses together with the formulated fundamental question; and it is expected that new electrochemical *in situ* approaches will advance these points bringing useful chemical information to environmentalists, industries (e.g., mining, textiles) and public and/or private agencies in charge of checking environmental pollutant levels in water ecosystems.

**Representative results**

In alignment to the general objective, we develop a new electroanalytical sensing concept for the detection of trace metals using as an example $Ag^+$. The working mechanism of the developed electrochemical principle is depicted in **Figure 1**. In an initial state (**case 1**), the electrode is just immersed in the $NaNO_3$ solution and then a constant potential of $E_{app}= 0$ V is applied for 10 min to reduce any $POT^+$ present in the electrode to its neutral form POT, accompanied by a releasing of $TFPB^-$ (labeled as $R^-$ in the scheme) back to the membrane, which is denoted as *m* in the figure. Since there is no $Ag^+$ in the solution, this extra part of negative charges brought to the membrane is compensated by $Na^+$ intake from the solution (accumulation step). In the stripping step, an application of a linear sweep potential (from 0 V to 1.2 V) forces POT to be oxidized to $POT^+$, which is then doped with the $TFPB^-$ and originates $Na^+$ release to the solution to keep the electroneutrality of the system. This $Na^+$ transfer at the membrane–sample interface is manifested as a voltammetric peak.
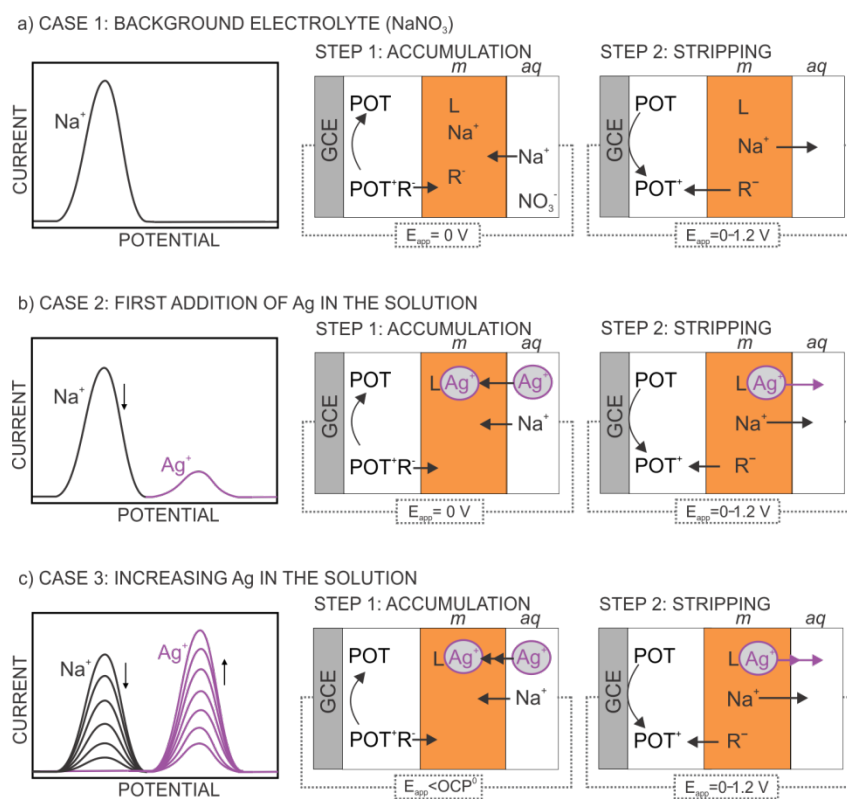


Figure 1 – Working mechanism of the concept put forward herein. Figure adapted from Doctoral thesis by Kequan Xu, Electrochemical detection of trace metals: from traditional techniques to new ultrathin membrane electrodes.

Next, traces of $Ag^+$ are added to the solution and the same protocol is applied. However, in the accumulation step, there is a competition of $Ag^+$ *versus* $Na^+$ to enter the membrane. The amount of each ion finally being accumulated depends on the $Na^+/Ag^+$ molar ratio in the sample solution together with the selectivity of the ionophore towards these two ions. Since the ionophore is very selective to $Ag^+$, nanomolar $Ag^+$ concentration in the solution can be accumulated into the

membrane in the presence of a high amount of $Na^+$ (such as 10 mM), which leads to both $Na^+$ and $Ag^+$ peaks appearing in the stripping voltammogram. Then, for a continuous increasing amount of $Ag^+$ in the solution (**case 3**), the intake of $Ag^+$ over $Na^+$ in the membrane is favored. As a result, the stripping peak for $Ag^+$ becomes higher compared to that of $Na^+$, which decreases correspondingly.

The principle put forward herein was validated in several samples as follows:

***Table 1.*** *Silver detection in artificial and real samples by the developed electrode. Table adapted from Doctoral thesis by Kequan Xu: Electrochemical detection of trace metals: from traditional techniques to new ultrathin membrane electrodes.*

| Matrix | Ag (nM) | Electrode | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | $I_{peak}$ | | | charge | | |
| | | $c_{Ag}$ (nM) | RSD | % Recovery | $c_{Ag}$ (nM) | RSD | % Recovery |
| 10mM NaNO$_3$ | 10 | 9.69 | 0.04 | 96.9 | 10.18 | 0.29 | 101.8 |
| | 50 | 50.30 | 0.01 | 100.6 | 43.92 | 0.79 | 87.8 |
| | 100 | – | – | – | – | – | – |
| | 500 | – | – | – | – | – | – |
| Tap water | 0 | – | – | – | – | – | – |
| | 10 | 15.41 | 0.01 | 154.0 | 7.62 | 0.38 | 76.2 |
| | 50 | 50.26 | 0.04 | 100.5 | 58.42 | 0.11 | 116.8 |
| Lake water | 0 | – | – | – | – | – | – |
| | 10 | 16.75 | 0.33 | 167.5 | – | – | – |
| | 50 | 43.33 | 0.18 | 86.6 | – | – | – |

**Conclusions**

These results pave the way towards individual electrodes for each metal that is desired to be analyzed. The newly developed accumulation/stripping methodology together with the use of membranes with controlled ionophore/NaTFPB molar ratio are expected to allow for (sub)nanomolar detection of any metal as far as a selective ionophore is available.

**Most important outcomes**

-Doctoral thesis by Kequan Xu, Electrochemical detection of trace metals: from traditional techniques to new ultrathin membrane electrodes. Supervisor: Gaston Crespo

-Selective Ion Capturing via Carbon Nanotubes Charging.
A Wiorek, M Cuartero, GA Crespo, Analytical Chemistry 94 (21), 7455-7459.