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Editorial: Environmental Electrochemistry

What's in that water?

Electrochemistry is playing an important role for the environment, either directly by monitoring levels of various element/molecules in soils, air, water, food or by removing contaminants in waste waters, or indirectly by providing alternative clean energy sources to fossil fuels or improving various industrial processes in terms of their environmental impact¹⁻⁴. This first environmental issue of Current Opinion in Electrochemistry is directed towards the monitoring aspect in aquatic media, to inform on the biogeochemistry and cycling of the analytes of interest and/or check that their concentrations levels are in compliance with relevant regulations. Contributions here cover the detection of arsenic, mercury, iron and the so-called technology critical elements (TCEs), highlights speciation studies and methods and provide critical evaluations of recently developed sensors, namely screen printed, bismuth, potentiometric (membrane) and carbon allotropes electrodes.

With pressures of increased population and associated anthropogenic activities as well as climate change, it can be argued that there has never been a greater need for high resolution monitoring, both spatially and temporally, in coastal waters, rivers, lakes but also in open ocean conditions. Similar to the idiom: “Seeing is believing”, one can say “Measuring is understanding”. For instance,

what is the impact of flooding on the levels of pharmaceuticals and bacteria such as *E.Coli* in coastal waters; what is the effect of dredging and storms on sediment resuspension and metal release? There are a multitude of physical processes that are intermittent, difficult to predict, and as such, difficult to monitor. With advances in engineering, data handling and sensor development, real time monitoring in aquatic systems might become routine analysis for a number of important analytes (e.g. nutrients, metals, pesticides, toxins) in the near future. And no doubt that electrochemistry will play a very important part in contributing to such task; electro-analytical devices are sensitive, selective, can be miniaturised and adapted into flow systems to perform fully automated analysis at the site of interest (called on-site analysis) or even directly in the water column of e.g. a lake or an estuary (in-situ analysis).

Ideally, measurements should take place directly in the water column and there are several reasons for this: sampling can be difficult to achieve, is expensive with a low time and spatial resolution; it is also prone to contamination problems and can modify the physical and/or chemical speciation of the species of interest by changing their physico-chemical environment (e.g. temperature, pressure, redox-potential, adsorption, precipitation, etc...). This is particularly true for the detection of metals that can be found in a variety of forms, from being present as the hydrated free metal ion to being complexed by inorganic/organic ligands and/or adsorbed onto particulates. Understand the cycling of a species of interest in the water column is largely dependent on its speciation. Although there are now a multitude of movable and fixed platforms (e.g. gliders, autonomous underwater vehicles, buoys, etc...) with submersible probes for routine measurements of temperature, salinity, turbidity chlorophyll and/or oxygen, performing electroanalytical in-situ measurement for a number of analytes (e.g. nutrients, metals, oxygen, pesticides, toxins.....) for a significant amount of time is a real challenge. At the heart of that challenge is the electroanalytical sensor: its robustness and long-term stability should be high and any potential interference well controlled to maintain a stable electroactive surface; internal calibration of the sensor must be performed to control any change in sensitivity (sensor drift) that might occur over long period of time (days, weeks). Adding to this the potential need for chemicals (e.g. acid), interference removal (e.g. oxygen, organic matter, particulates) and/or problems related to pressure, it is obvious that achieving this in the water column is a real challenge. Although early pioneering works have in part met this challenge (see e.g. ^{5,6}), in-situ analysis is still in its infancy and largely depends on the performance of the sensor. In this issue, recent advances in the use of membrane electrode for in-situ potentiometric determination of a variety of analytes (e.g. nutrients, carbonate) are critically reviewed by **Baker**.

The development of new electrodes for the determination of an ever-increasing list of analytes at relevant environmental concentrations is a very active area of research. Historically, the mercury drop electrode has been the most popular electrode for trace elements and although developed for laboratory based measurements, it was used for in-situ analysis of trace elements in a lake⁷ almost 30 years ago or more recently, for on-site monitoring of sulfidic species⁸ and metal⁹. However, its known toxicity is a major limiting factor for a wider use by the analytical community and there is thus a strong need to develop analytical methods at alternative electrode substrates, i.e. non-toxic ones. Amongst them, gold, carbon, silver, platinum, bismuth are being thoroughly tested in a variety of configuration (e.g. disk, films, microarrays, nanoparticles). Bismuth is in no doubt the most popular one, due to its high hydrogen overvoltage and overall similar behaviour to mercury. In this issue, **Jovanovski et al.** gives us an exciting historical account of the bismuth

electrodes from its introduction in 2000, as well as focusing on studies published in the last 3 years for the detection of metals and organics at bismuth electrodes.

Functionalisation of the electrode surface through a variety of methods, including with nanoparticles of various size, shapes and composition is also a major area of research. Due to the intrinsic properties of nanoparticles in terms of electrocatalysis, large surface area, increased electron transfer, electrodes are achieving lower detection limits while expanding their linear range and continuously improving their specificity and long term stability. Common nanomaterials include bismuth, gold or carbon. **Villareal et al.** report here on the large variety of carbon nano-materials and their application for environmental monitoring through various electroanalytical methods.

At the other end of the requirement for long-term stability, screen-printed electrodes (SPEs) are mass-produced, cheap, reproducible, convivial to use and well suited for single analysis making them attractive for on-site analysis. There is an extensive on-going research on developing new electro-analytical method at SPEs and this is nicely shown by **Li et al.** who report on their recent use for the detection of trace metals, herbicides and phenolic compounds.

Detection and speciation of specific metals:

There are specific toxic elements that are of serious concerns for human health, arsenic and mercury being amongst them. **Guo et al.** presents here recent advances made on the voltammetric detection of arsenic; this priority carcinogenic element contaminates groundwater in every continent, subjecting millions of people throughout the world to unsafe levels (e.g. ¹⁰). Arsenic detection by voltammetry has been and still is a subject of strong interest for the analytical community. Its detection is challenging because of its existence under different inorganic and organic forms, all having different electrochemical activity.

Mercury is present in aquatic media at what can be considered as very low concentration (pM levels) and thus its detection is a real challenge in terms of detection limits. **Yerga and Costa-Garcia** highlight the current research on its detection and the limitations associated with the 2 main types of electrodes: functionalised with nanostructures and DNA-based.

Mountserratt and Cobelo-Garcia present an account of the electrochemical methods that have been reported for the detection of technology critical elements (TCEs), those elements that are increasingly used in every-day technology but that have not benefited from much research, mostly because their concentration in the environment is very low. Now that the production of these elements (e.g. Ga, Tl, Pt group elements) is increasing significantly, a proper assessment of their environmental cycle, mobility and toxicity need to be undertaken. This task is currently benefiting from a COST action (COST TD1407 – Network on Technology Critical Elements: from Environmental Processes to Human Health Threats) ¹¹.

Another element that encompasses the capabilities of electrochemical methods is iron. Iron, or more exactly its lack of it, is known to limit primary productivity in large areas of the world's oceans, thus affecting levels of carbon dioxide in the atmosphere and contributing significantly to the overall greenhouse effect and climate change. This crucial role has been one of the "fer de lance" in the development of the on-going international GEOTRACES program¹² that aims to measure the concentration of trace elements in the oceans and unveil their chemical speciation. **Laglera and**

Monticelli present the recent electrochemical studies that have reported on the determination of iron, for its total concentration and/or its speciation.

Finally, speciation studies are required to understand under which chemical forms the analyte of interest is present, which help to assess potential toxicity or better understand their cycling through the environment. There are numerous electrochemical methods that can give speciation information; here, **Galceran et. al** give a comprehensive account of the advantage and disadvantage of AGNES (Absence of Gradient and Nernstian Equilibrium Stripping), method specifically designed to measure the free metal ion concentration. CLE-CSV (Competitive Ligand Exchange – CSV) and SSCP (Stripping Scanned Chronopotentiometry), two other speciation methods, are also presented.

Constant improvements in stability, sensitivity, specificity together with ease-of-use and cost effectiveness of the sensors all contribute in expanding the appeal of electrochemical methods to the research and wider community. Mostly seen as a “flimsy” technique that required too much knowledge and highly-skilled operator only a decade ago, the increase in number of companies selling electroanalytical devices show that the perception of electroanalysis is changing. With a constant ability to improve through new methods and/or new analytes (see e.g.¹³, a recent paper for the detection of low levels of anti-depressants in water by Ion Transfer Stripping Voltammetry ITSV), the future of electroanalysis for environmental monitoring definitely looks bright, not only in laboratory but more importantly for on-site and in-situ applications.

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