

Key Notes: Session 2

[KN 2.1]

Towards In-Situ Measurement of Metal Speciation and Spatial Distribution

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Even at low concentrations (10^{-12} - 10^{-7} M), metals may present a severe hazard to the normal function of the aquatic ecosystem, as they are not biodegradable, but involved in biogeochemical cycles and then distributed under different physicochemical forms (species). To understand and predict the rôle and fate of these various species (in terms of toxicity, bioavailability, bioaccumulation, coagulation, sedimentation, etc.), analytical instrumentation capable of performing *in situ* real-time monitoring of specific forms of elements in continuous and reproducible manner, on a wide spatial network and sometimes with high spatial resolution are required. The design of such tools is still a challenge for analytical chemists, since techniques that combine high sensitivity, speciation capability, integrity of the sample and unattended operation are a prerequisite.

Such developments became possible with the progress of microelectrodes. Gel integrated voltametric microelectrodes (GIME), based on microtechnology and photolithography, have been developed to meet these requirements, in particular to avoid the fouling of the electrode by natural organic matter and colloids. The so-called dynamic metal species, i.e. those with diffusion and chemical dissociation fast enough to give rise to a reduction current are specifically measured. Those species are the important ones for predicting metal bioavailability. A complete submersible voltametric instrument (the Voltametric In Situ Profiler = VIP) has been developed to perform in-depth measurements and a speciation of metals

with this reliable sensor, and can be used to measure the real-time concentration of Pb, Cd, Cu, Zn, Fe(II) and Mn(II). Such measurements enable one to minimize sample handling and, thus, possible artifacts. Examples and conditions of measurements will be given in various types of natural waters.

Field and in situ speciation can be considerably broadened to various metals, anions and organics, as well as to various types of metal species (free ions, lipophilic complexes, hydrophilic labile complexes), by integrating permeation liquid membrane systems to voltametry. This can be performed in various ways including microtechnology. The permeation liquid membrane then plays the rôle of a species-sensitive, preconcentration device, and enables real-time analysis of the aforementioned metal species in the pico to nanomolar range.

It will also be shown that microtechnology enables one to produce individually addressable gel-integrated microelectrode arrays, allowing simultaneous voltametric measurements on up to 64 GIME, for high spatial resolution (200 μ m) at the sediment-water interface. This allows the instantaneous recording of concentration profiles, and their possible evolution with time. Because GIME is selective to dynamic species, this system opens the door to the determination and understanding of the rôle of metal speciation on in situ dynamic processes such as metal fluxes at the sediment-water interface.

[KN 2.2]

Determination of Trace Metal Using Renewable Surface Biosensing Systems

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Understanding the sources and fates of environmental contaminants, regulating their discharge, or remediating polluted sites all require a detection of the presence of pollutants and continuous measurement of their concentrations. However, the environment is a massive sink where even large quantities of pollutants are diluted to a very low concentration. The matrix in which the components of interest must be measured is complex. Modern, sophisticated analytical instruments have made it possible to identify and measure specific components or their speciation in the environment at trace levels.

In this context, there are new challenging fields for an environmental analytical chemist such as a) the measurement of new environmental parameters, e.g. global parameters related to environmental toxicity due to trace metals, pesticides, etc.; b) continuous monitoring of these parameters; c) measurements compatible with in-field equipment; and d) low cost instrumentation.

For these challenges, biosensor analytical systems can be an alternative to classical concepts based on conventional analytical instrumentation. A biosensor is an analytical device consisting of an immobilized biological recognition material (such as enzyme, microorganism, antibody, DNA strand, etc.) in contact with a suitable transducer platform which converts the primary biochemical signal into a quantifiable secondary electric signal. This concept allows for simple, small, portable, fast response, robust, low cost, analytical instrumentation.

However, the feasibility of a biosensor is based on the stability of the immobilized biological material and the reversibility of the biological interaction. In most of the measurements concerned with trace metals and pesticides, with enzyme biosensors or with the detection of other xenobiotics using immunosensors, the primary biochemical signal is irreversible. Therefore, continuous measurements based on these interactions are complex. Several methodologies have been reported to overcome this problem, most of them involve the regeneration of the biosensing surface using «wet procedures», i.e. regeneration or reactivation solutions. Usually these procedures imply extreme conditions that may denaturalize the immobilized biological materials and, in any case, the analytical procedure suffers from robustness.

Different strategies for renewing sensing surfaces have been developed in our laboratories to resolve this drawback related to metal trace or pesticide detection using biosensing systems. One strategy consists in the use of biocomposite materials that act as impervious reservoirs for the active biological components. The decrease of biosensor sensitivity during continuous analysis is recovered by a simple surface smoothing procedure. Another alternative has been the development of screen-printed biosensors that allow for multi-repeated, disposable, single-use sensing surfaces. A third strategy is concerned with biologically modified magnetic particles. These particles can be injected in a flow system, then immobilised in and released from a flow-through transducer using a magnetic field. Following this approach, automated on-line bioanalysers for water toxicity monitoring have been developed in our laboratory.