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DEVELOPMENT OF AN AUTOMATED BUOY SUPPORTED MULTI-CHEMICAL PROFILER FOR REAL-TIME IN SITU TRACE METAL MEASUREMENTS AND SPECIATION IN AQUATIC SYSTEMS

PARTICIPANTS

IDRONAUT s.r.l. (I)
UNIVERSITY OF GENEVA (CH), Analytical and Biophysical Environmental Chemistry
UNIVERSITY OF GOTEBORG (SE), Department of Analytical and Marine Chemistry
UNIVERSITY OF PLYMOUTH (UK), Department of Environmental Sciences
UNIVERSITY OF ANCONA (I), Institute of Marine Sciences
UNIVERSITY OF NEUCHATEL (CH), Institute of Microtechnology

Contact: F. Graziottin, tel. +39-039-87956; fax: +39-039-883382; e-mail: dronaut@idronaut.it

INTRODUCTION

Coastal ecosystems are threatened by anthropogenic activities and in particular by chemical pollution. Assessment of the impact of chemical pollutants are presently very difficult, because their speciation (i.e. the distribution of the various chemical forms of a given compound) cannot be determined accurately enough or at sufficiently frequent time intervals. Development of novel analytical tools allowing real-time monitoring, as well as detailed temporal/spatial evolution of the distribution of specific chemical species, is thus of prime interest. They will enable us to develop much better predictive models based on biogeochemical processes, to evaluate the impact of human activity on the ecosystem, and therefore to optimise industrial/social developments.
The overall objective of the IMTEC European project [IMTEC: In situ automated Monitoring of Trace metal speciation in Estuaries and Coastal zones in relation to the biogeochemical processes; contract EVK3-CT-2000-00036] is to develop an automated buoy supported Multi-Chemical Profiler (MCP) for real-time, in situ trace metal speciation measurements in natural aquatic ecosystems. The MCP, coupled to other probes for simultaneous measurements of master variables, will be extensively deployed for: a) systematic tests of the new developments under real conditions, b) biogeochemical studies and c) pollution control monitoring in three complementary coastal ecosystems [i.e.: i) fjord systems in west Sweden, ii) micro-tidal estuaries in south west England and iii) the Po estuary and its coastal plume]. These tests will allow us to validate the new developments in real environmental conditions and to study: i) the impact of phytoplankton production on trace metal speciation, ii) the distribution and fate [residence time and transport] of the specific trace metal species as a function of the physico-chemical conditions of the three ecosystems.

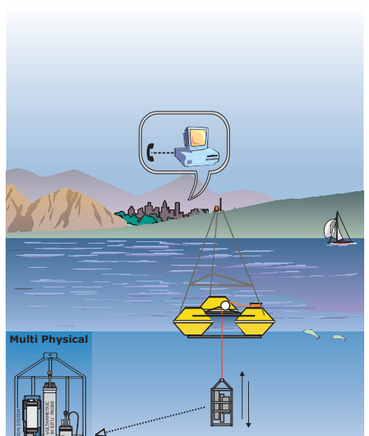
THE BUOY SUPPORTED MULTI-CHEMICAL PROFILER (MCP System)

ANALYTICAL AND TECHNICAL DEVELOPMENTS

The MCP will be based on the Voltammetric In situ Profiling System (VIP System), which was developed during an European MAST-III project and is now commercialised by Idronaut. The VIP probe is based on a gel integrated microelectrode (GIME) which allows the specific measurement of the concentrations of the dynamic fraction of trace metals, defined as the sum of the free metal ions and the small labile complexes with size of few nanometers.

The following analytical and technical developments are under way in the IMTEC project to improve the capability of the VIP probe:

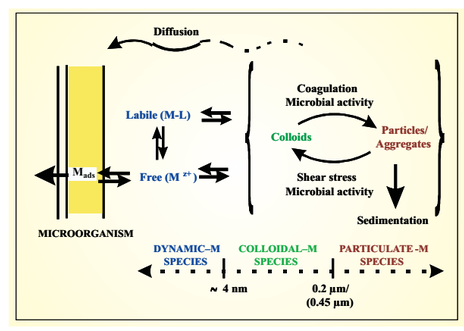
- Development of a novel chelating resin-gel integrated microsensor (CGIME) for
  - **In situ measurements of free metal ion concentrations**
- Development of a submersible FIA system coupled to the VIP for
  - **In situ measurements of total extractable metal concentrations**
- Development of an improved VIP voltammetric probe based on 3 flow-through cells and three individual potentiostats (MCP voltammetric probe) for
  - **Simultaneous in situ measurements of three specific fractions of trace metals, i.e.:**
    - **free metal ions (VIP cell with CGIME)**
      - **dynamic metal species (VIP cell with GIME)**
        - **total extractable metal concentrations (VIP cell with FIA-GIME)**
- Incorporation of the MCP voltammetric probe with probes for measurements of master variables into a, buoy supported, automated monitoring system which can be controlled from a land station



ENVIRONMENTAL FEATURES OF METAL SPECIATION

Analytical tools allowing measurement of specific fractions of trace metals in a continuous and reproducible manner, on a wide spatial network, is required both to get deeper insight into natural processes occurring in natural aquatic media and to understand the relationship between anthropogenic releases and their long term impact on man and the environment.
The environmental interest of the metal species that will be measured by the MCP voltammetric probe are:

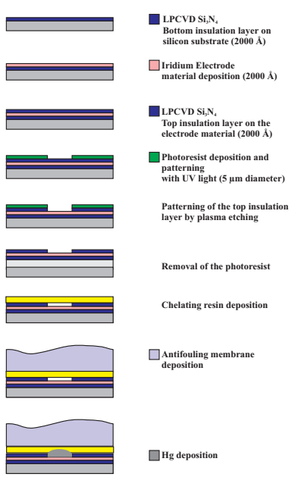
- the concentration (activity) of **free metal ions** which has in many instances been shown to be related to biological uptake;
- the **dynamic species** which are potentially available for organisms;
- the **particulate and colloidal species** (total extractable conc. minus dynamic species) which play important role in transport properties and residence time.

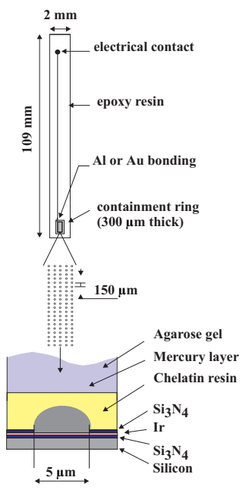


MCP SYSTEM MAIN COMPONENTS

CHELATING RESIN-GEL INTEGRATED MICROSENSOR (CGIME)

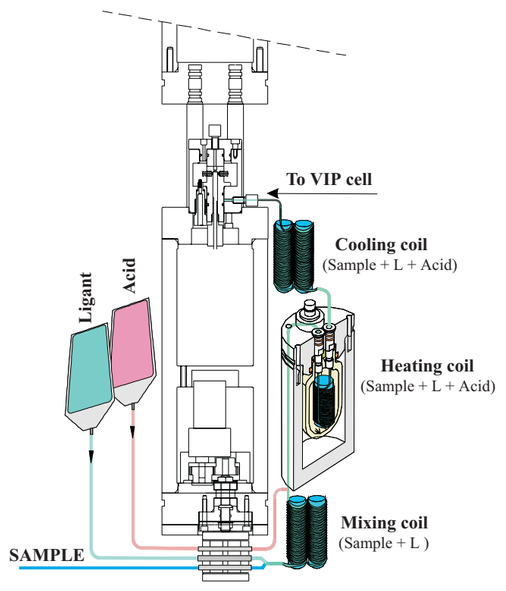
The CGIME is based on the GIME and the diffusion gradients in thin-films (DGT) technique principles.
Basically the surface of the interconnected Ir-based microelectrode array is covered with a thin (10-20 µm)layer of chelating resin, itself covered by a thick (300 µm) non complexing agarose gel. The Hg layers are electrochemically deposited through both layers. During equilibration with the test water, metals accumulate on the resin in proportion to free metal ion concentrations. After equilibration, the natural sample is replaced by an acidic solution, using a simple flow-injection system. The metal accumulated on the resin are released by the acid, and immediately measured by the voltammetric microsensor.





SUBMERSIBLE FIA PROTOTYPE

A first prototype of a submersible FIA system has been developed and coupled to one of the cells of the MCP voltammetric probe. It is based on an analytical pre-treatment procedure involving ligand competition followed by acidification and heating of the sample



THE MCP VOLTAMMETRIC PROBE AND ITS FLUIDIC SYSTEM

The MCP probe is provided with three complete measurement systems (cells, pumps, fluidic components, etc.) that allow the operator to perform simultaneously the sample preparation and the measurements on all the three voltammetric systems. The MCP probe hardware is composed of a compact and advanced electronic package, which has a network of dedicated smart controllers able to simultaneously manage the three required voltammetric cells. A main intelligent unit co-ordinates the simultaneous sample preparation activities and the measurements on the three cells. The MCP electronics is completed by the telemetry, the high voltage power supply module, by the pumps, valves and heater drivers and by the power supply board.
The operator can easily manage any activity of the MCP probe by means of the real time communication with the Windows based management software. The management program allows in particular:

- handling of the communications with the MCP probe
- configuration of the measurement method for each cell
- automatic storage of the acquired data
- graphical representation of the collected voltammogramms
- background and baseline current subtraction
- search and weight of the peaks
- calculation of the trace metal concentrations after T effect correction.

THE SUBMERSIBLE UNIT OF THE MCP PROFILER

The MCP voltammetric probe may also operated through **an external or integrated Ocean Seven 316 multiparameter probe.** This allows simultaneous measurements of master variables : pressure, temperature, conductivity, salinity, oxygen, pH, redox E, fluorescence and turbidity, which are required for trace metal data interpretation.

The main components of the submersible unit of the MCP system, i.e. the voltammetric probe, the multiparameter probe, the FIA system and the reagent and waste containers, are integrated in a titanium protective cage which simplifies the field deployment and protects the MCP submersible unit. The MCP system mechanical and fluidic components can withstand pressure up to 15 bars which allows deployment of the system down to 150 meters.

The MCP system can be integrated to a **Idronaut Buoy Profiler** or to any other existing platform to perform autonomous, continuous monitoring and profiling for an extended period of time. In such case, control of the system and data transfer can be performed from a land station via cellular phone.

ACKNOWLEDGMENTS:
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