

MULTI PHYSICAL-CHEMICAL PROFILER FOR REAL-TIME AUTOMATED IN SITU MONITORING OF SPECIFIC FRACTIONS OF TRACE METALS AND MASTER VARIABLES.

Mary-Lou Tercier-Waeber^{1,*}, Fabio Confalonieri², Giuliano Riccardi², Antonio Sina²,
Flavio Graziottin², Jacques Buffle¹

¹*CABE, Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, 30 Quai
E.-Ansermet, CH-1211 Geneva 4, Switzerland.*

²*Idronaut Srl, Via Monte Amiata 10,I-20047 Brugherio (MI), Italy.*

**Corresponding author: Mary-Lou Tercier-Waeber,*

Phone: +41-22-702.6048; FAX: +41-22-702.6069 ; E-mail: Marie-Louise.Tercier@cabe.unige.ch

Abstract. State of the art in the development of a novel Multi Physical-Chemical profiler (MPCP system) for simultaneous, autonomous, in situ measurements of three environmentally relevant specific fractions of trace metals as well as master variables in natural waters is presented. It has been designed using advanced voltammetric microsenors, microprocessor and telemetry technology. A detailed description of the system is given and examples of environmental applications for in situ measurements in sea water are reported. The results indicate that the system is reliable and that in situ measurements of the three specific fractions of trace metals can be achieved down to concentrations at the ppt level using Square Wave Anodic Stripping Voltammetry (SWASV).

1. INTRODUCTION

The development of new analytical tools capable of performing *in-situ* detailed monitoring of the temporal/spatial evolution of specific metal species and master variables is of prime importance. They will enable to better understand the role and the fate of trace metals in aquatic systems and to develop more accurate predictive models, based on biogeochemical processes, to evaluate the impact of human activity on coastal ecosystems.

A Multi Physical-Chemical Profiler (MPCP) developed by us to meet this challenge is presented. It has been designed to allow simultaneous in situ, autonomous monitoring of three specific fractions of Cu(II), Pb(II), Cd(II) and Zn(II) using Square Wave Anodic Stripping Voltammetry (SWASV), i.e: i) the free metal ion concentrations which are known to be related to biological uptake; ii) the dynamic Me species which are potentially available for organisms; iii) the total extractable metal concentrations which, by subtraction, yield concentrations of metal bound on particulate and colloidal species that can be release in case of important variation of the physico-chemical conditions, as well as master variables (pressure, temperature, pH, oxygen, conductivity, salinity, redox E, turbidity and chlorophyll a). It is based on unique gel integrated voltammetric microsenors, a submersible probe with three independent measuring channels, a submersible flow-injection system, conventional multiparameter and fluorescence probes and telemetry technology. The characteristics of the microsenors and main components of the probe are summarized. The MPCP environmental utility is illustrated with examples of environmental applications.

2. DESCRIPTION OF THE MPCP SYSTEM

The MPCP system is based on the Voltammetric In situ Profiling System (VIP System), which was developed during an European MAST-III project and is now commercialized by Idronaut [1]. The heart of the VIP probe is a gel integrated microelectrode (GIME) which consists of an 100-interconnected Hg-electroplated Ir-based microelectrode arrays covered with a 300 µm thick agarose antifouling gel [2]. The GIME sensor allows specific measurements of the concentrations of the dynamic fraction of the trace metals, defined as the sum of the free metal ions and the small labile complexes with a size of few nanometers [1, 2]. Developments of: i) a novel chelating resin-gel integrated microsensor (CGIME) for in

situ measurements of free metal ion concentrations; ii) a submersible flow-injection analysis system (FIA) for in situ sample pre-treatment and measurements of total extractable metal concentrations, iii) an improved submersible voltammetric probe, iv) a surface deck unit and v) a management software performed to improve the capability of the VIP probe are described below. The CGIME sensor consists of an 100-interconnected Hg-electroplated Ir-based microelectrode arrays covered with a 3.5 μm thin Microchelex chelating resin, itself covered with a 300 μm thick agarose antifouling gel. This sensor, under final laboratory characterisation, allows direct measurements of free metal ions in natural waters using SWASV [3]. The schematic diagram of the submersible FIA developed is given in Fig. 1b. It is based on the following analytical procedure: ligand exchange (using TRIEN) followed by acidification (HNO_3 suprapure) and heating of the pre-treated sample.

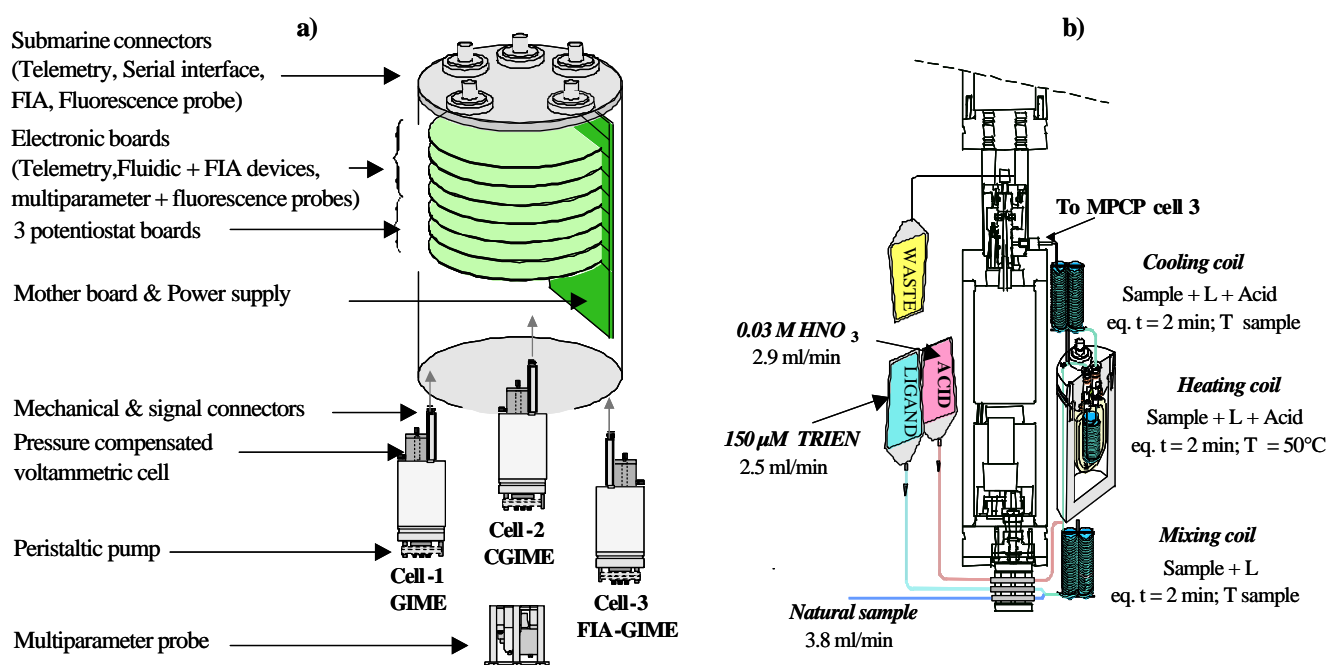


Figure 1. Schematic diagrams of the MPCP submersible a) voltammetric probe and b) FIA developed.

The submersible voltammetric probe is comprised of distinct specific modules (Fig. 1a): an electronic housing, three pressure compensated flow-through voltammetric cells [1] each one screwed on a pressure case base incorporating a sampling submersible peristaltic pump, and an integrated multiparameter probe. The electronic housing contains all the hardware and firmware necessary to manage: i) the simultaneous control of the fluidic system and the SWASV measurements of each cell, i.e. simultaneous measurements of dynamic metal concentrations (channel 1 – GIME), free metal ion concentrations (channel 2 – CGIME) and total extractable metal concentrations (channel 3 – GIME+FIA), ii) the interfacing of the integrated multiparameter probe and of an external fluorescence probe (for chlorophyll a monitoring), the data acquisition and transfer. The surface deck unit powers and interface, by telemetry, the measuring system with the PC. A management software allows the user to control and configure the MPCP probe operating parameters and functions, such as fluidic and electrochemical parameters, data acquisition and transfer, calibration and maintenance operations. The MPCP can be controlled either by an operator on board or in automatic mode following pre-programmed parameters.

3. ENVIRONMENTAL APPLICATIONS.

3.1 Reliability the MPCP three measuring channels.

The MPCP probe was first tested for in situ Cu(II), Pb(II) and Cd(II) measurements in Gullmar Fjord (Kristineberg Marine Station-Sweden, August 19-28, 2002). Three GIME sensors were integrated in the three voltammetric cells. The probe was first deployed from the pontoon of the station (1.5 m depth) and autonomous measurements performed every 1 hour over a total time of 5 hours. Relative standard

deviations of maximum 13%, 10% and 12% were found for the Cu(II), Pb(II) and Cd(II) average concentrations determined from i) each individual channel and ii) over the three channels. The MPCP probe integrating the 3 GIME sensors was also deployed from the *RV Arne Tiselius* vessel at various stations and depths (5 to 25 m) together with VIP probes. Concentrations of the dynamic fraction of the three metals monitored with the three MPCP individual channels and the VIP probes were found to be similar. These results demonstrate the stability and reliability of the SWASV voltammetric measurements made with the MPCP probe.

3.2 Characterisation and optimisation of the submersible MPCP FIA.

Preliminary tests of total extractable metal concentration measurements using the submersible FIA system coupled to the MPCP channel 3 were performed first in the laboratory using freshly collected Arve river samples (Geneva-Switzerland, May 2002) and Gullmar fjord sea water samples (Sweden, August 19-28, 2002) then, in situ, in coastal Adriatic sea (Adriatic cruise, October 27 to November 2, 2002). Total extractable metal concentrations obtained after a FIA pre-treatment time of 6 minutes were compared with trace metal concentrations measured in i) pH 2 acidified samples (acidification time for maximum metal release: 1 hours for sea water and 60 hours for river samples) and ii) pH 2 acidified + UV irradiated samples using the MPCP channel 2 and a VIP probe respectively. Typical results obtained for Cu(II) and Pb(II) in samples collected at two different stations and depths in Gullmar fjord are given in Fig. 2. The

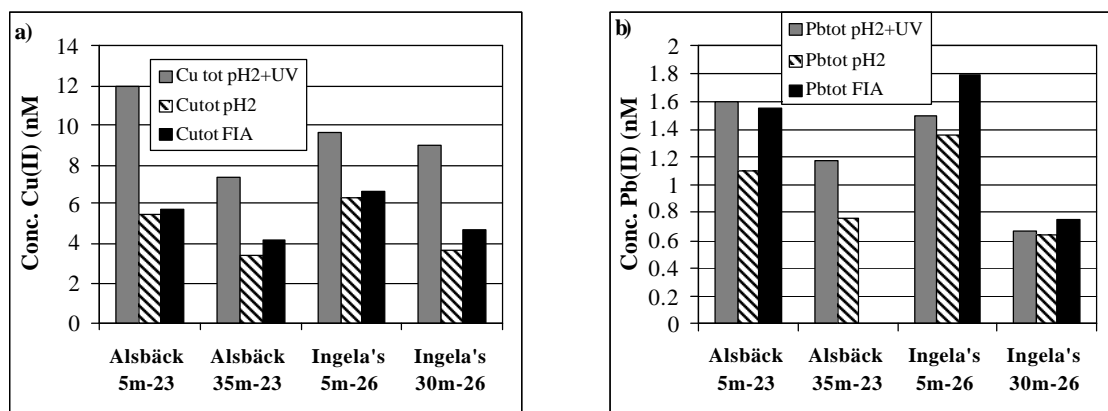


Figure 2. Comparison of a) Cu and b) Pb concentrations measured in pH 2 acidified + UV irradiated, pH 2 acidified and FIA pre-treated samples collected in Gullmar fjord (Sweden, August 23-26, 2002). SWASV conditions: pre-cleaning $E = 100$ mV; pre-cleaning $t = 60$ s; $E_{\text{dep}} = -950$ mV; $t_{\text{dep}} = 10$ min; $E_f = 100$ mV; SW amplitude = 25 mV; SW step = 8 mV; $f = 200$ Hz. FIA conditions as in Fig. 1b.

results in the laboratory and in situ were similar and showed that: Cu, Pb and Cd total extractable concentrations \cong Cu, Pb and Cd concentrations measured in pH 2 acidified samples; Pb and Cd total extractable concentrations similar to total Pb and Cd concentrations in pH 2+UV irradiated samples, and Cu total extractable concentrations < total Cu concentrations measured in pH 2+UV irradiated samples (typically 65 to 75 %). These results demonstrate the efficiency of the submersible FIA system and of its automatic control at depth. They also demonstrate the usefulness of the submersible FIA which allows fast in situ measurements of the total concentrations of the metals which may be released in case of important variation of the physico-chemical conditions of the media (e.g. problem of acidification), i.e. only Cu strongly bonded on some organic complexes, which can be dissociate under drastic chemical conditions, are not detected.

3.3 MPCP trace metal speciation in the Po plume.

The MPCP system (Fig. 3a) was used for measurements of Cu and Pb speciation and master variable at various stations and depths located in the Po river plume (Adriatic cruise, October 27 to November 2, 2002). This later extends along the Adriatic coast from the Po mouth down to the city of Ancona.

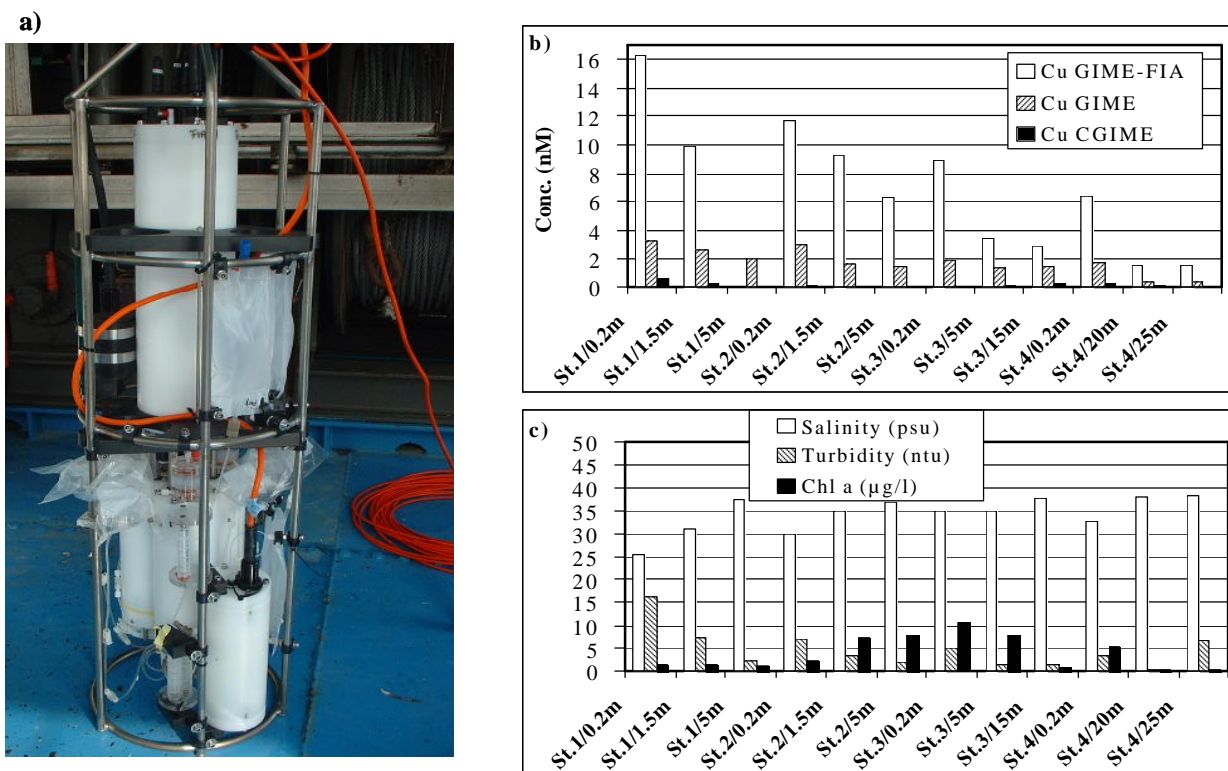


Figure 3. a) Picture of the MPCP system ready for deployment. b) Cu speciation and c) salinity, turbidity and chlorophyll a monitored at various stations and depths in the Po river plume (Adriatic cruise, Italy Oct. 27 – Nov. 2, 2002); SWASV conditions as in Fig. 2, excepted $E_{\text{dep}} = -1150$ mV and $t_{\text{dep}} = 20$ min for GIME measurements; FIA conditions as in Fig. 1b.

Measurements of concentrations of the dynamic and total extractable metal species as well as master variables were performed in situ while free metal concentration measurements with the CGIME sensor were performed on board ship in freshly Go-Flo collected samples [3]. Typical examples of results obtained for Cu are shown in Fig. 3b and for salinity, turbidity and chlorophyll a in Fig. 3c. Decrease, under various proportions, were observed for Cu and Pb (not shown) total extractable and dynamic concentrations as a function of both the Po mouth distance (distance between station 1 and 4 \cong 70 km) and the depth linked to the mixing of Po river and Adriatic sea waters (sea also salinity and turbidity data in Fig. 3c). Comparison of Cu CGIME measurements (Fig. 3b) and chlorophyll a concentrations (Fig. 3c) suggests that Cu(II) free metal ion concentration variations are not only related to water mixing but also to primary productivity. Of course more systematic studies are required for rigorous interpretation of these data. However, these preliminary tests highlight the potentiality of the MPCP system developed for efficient environmental monitoring and more rigorous interpretation of trace metal cycles in natural aquatic systems.

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