

VAMP - Voltammetric Autonomous Measuring Probes for trace metals in the water column (500m, max. depth) and at water-sediment interfaces (6000m, max. depth)

M.-L. Tercier-Waeber, C. Belmont-Hébert, J. Buffle,

(CABE), Dept. of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, 30 Quai E.-Ansermet, 1211 Geneva 4, Switzerland

F. Graziottin, F. Confalonieri, G. Riccardi, A. Sina,

Idronaut Srl, Via Monte Amiata 10, 20047 Brugherio (MI), Italy

G.C. Fiaccabrino, M. Koudelka-Hep,

Institute of Microtechnology, University of Neuchatel, Jaquet-Droz 1, 2007 Neuchatel, Switzerland

D. Turner.

Department of Analytical and Marine Chemistry, 41296 Goteborg, Sweden

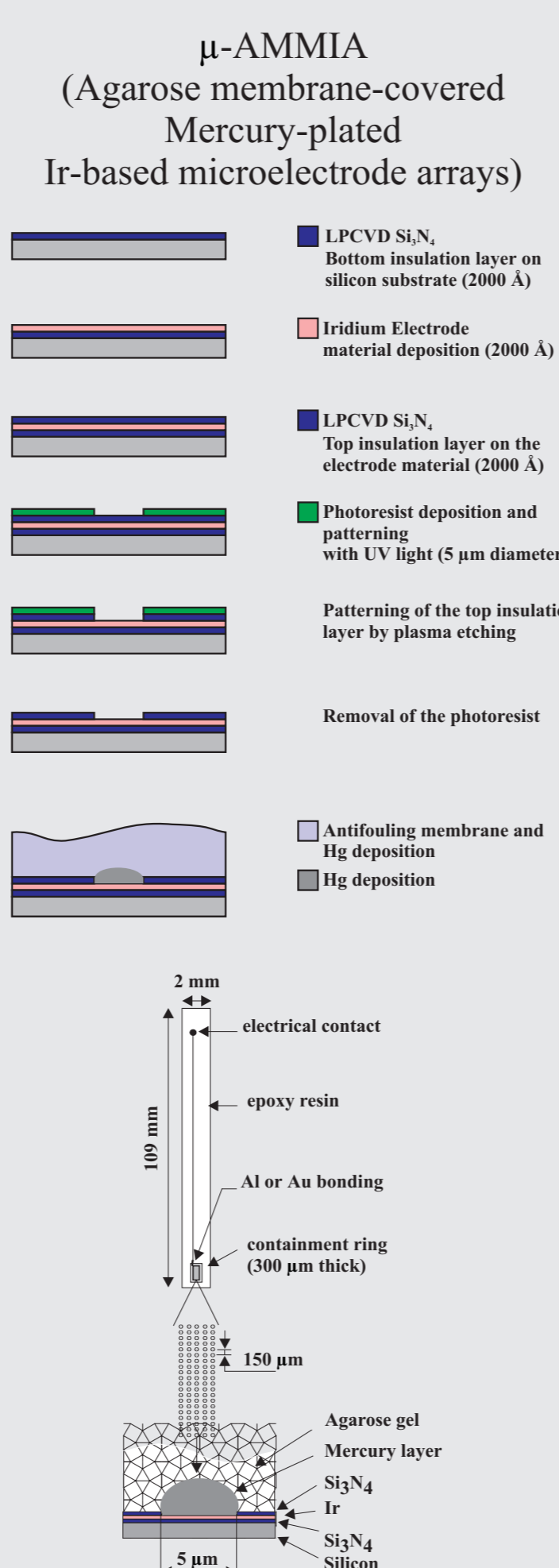
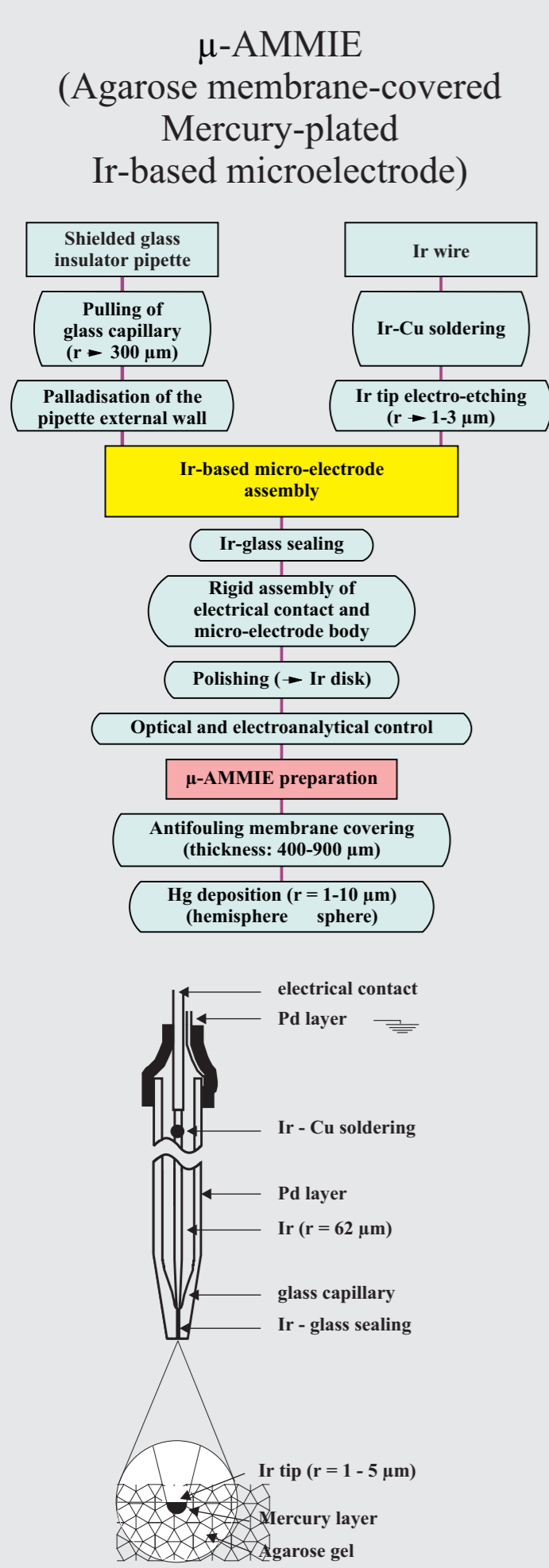
CONTENT OF THE PROJECT

The aim of the VAMP project is to develop, by means of several new technologies, voltammetric sensors and probes allowing in-situ automatic measurements of trace concentration profiles i) in the water column - sub project 1 and ii) at the sediment-water interface - Sub project 2.

Indeed new analytical instrumentation capable of performing in-situ, real-time monitoring of specific forms of trace elements in 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 design of such tool is still a challenge for analytical chemists since techniques that combine high sensitivity, speciation capability, integrity of the samples and unattended operation are prerequisite. During the first two years of our European MAST III project, a novel Voltammetric In-situ Profiling System (VIP System), based on advanced microprocessor and telemetry technology, were developed to meet this challenge. The heart of the submersible voltammetric probe is a novel gel integrated either single or array microelectrode. These microsensors were specifically developed, under well controlled conditions, to enable reproducible and reliable measurements of trace elements in complex media without physical and chemical interferences of the test solution. The VIP System allows direct in-situ monitoring of the mobile fractions of Cu(II), Pb(II), Cd(II) and Zn(II) as well as Mn(II) and Fe(II) using either Square Wave Anodic Stripping Voltammetry (SWASV) or Square Wave Cathodic Sweep Voltammetry (SWCSV) down to 500 meters depth. Key aspects of this development and application of the VIP System for real-time measurements in lake and sea waters are presented.

NOVEL GEL INTEGRATED MICROSENSORS

Fabrication steps and schematic diagrams.

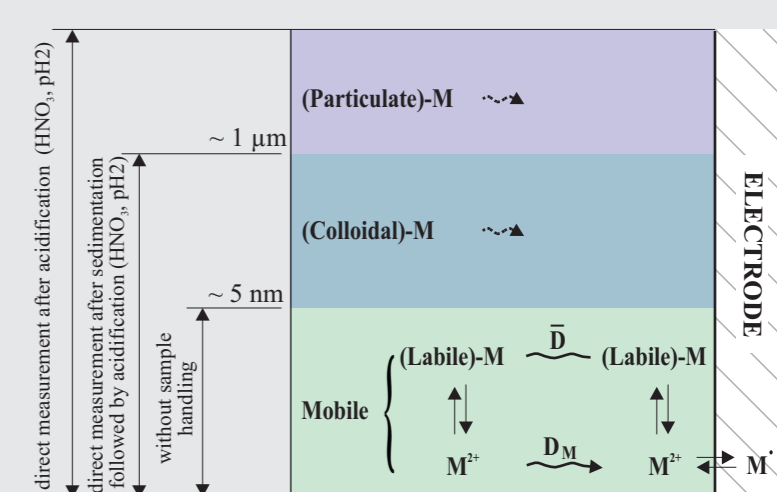


Main features and selectivity

Measurements with the gel integrated microsensors consists of two successive steps: equilibration of the agarose gel with the test solution (typically 5 min for a gel thickness of 300 μm) and voltammetric analysis inside the gel.

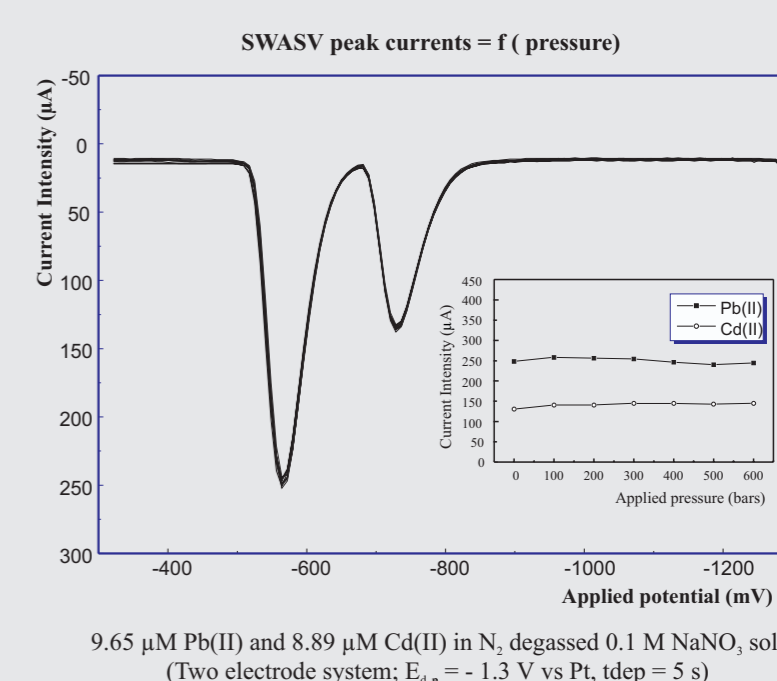
The key features of this kind of sensors are:

- the gel acts as a dialysis membrane, i.e. it allows selective penetration of small ions and molecules by diffusion but is impervious colloidal and particulate fouling material,
- analysis inside the gel is independent of ill-controlled hydrodynamic currents and thus based on well controlled molecular diffusion,
- direct voltammetric measurements, without added electrolyte, can be performed in low ionic strength natural waters,
- voltammetric currents measured at micro-sized electrodes are directly proportional to the diffusion coefficient values and negligible for species larger than a few nanometers. Thus combination of VIP System in-situ measurements with complementary measurements of total concentrations in raw and filtered samples allows the determination of three key environmental fractions of trace element species: i) the mobile species (≤ of a few nm) by direct in-situ measurements in unperturbed samples, ii) the colloidal species (total concentration in filtered samples minus mobile fraction) and iii) the particulate species (> 1 μm; difference in total concentration between raw and filtered samples). Distinction between these three fractions is important since the mobile species are the species the most readily bioavailable while colloidal and particulate fractions play different roles in



Other important characteristics of the gel integrated microsensors for in-situ monitoring are:

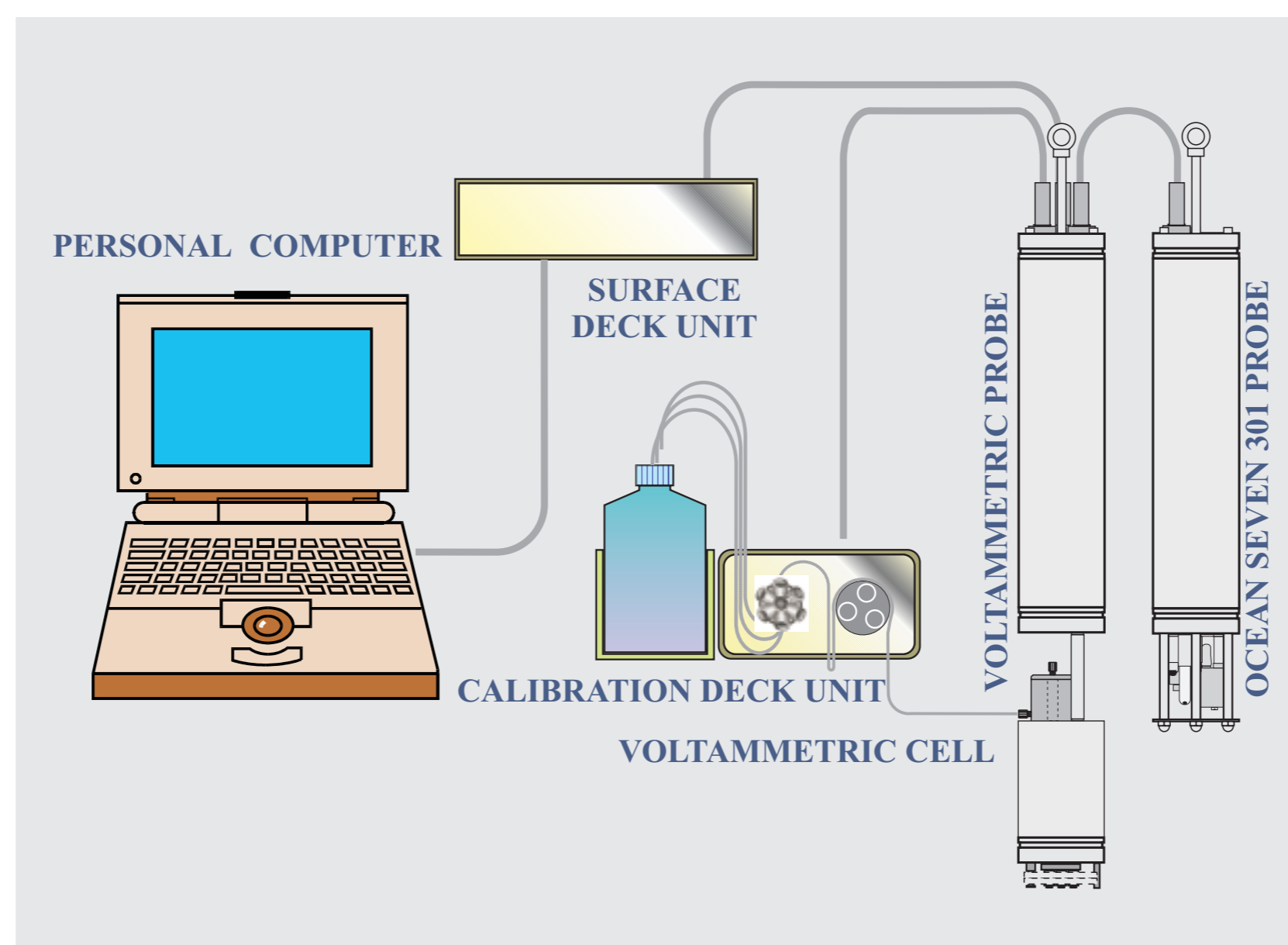
- effects of temperature variation (4 to 25°C) on the voltammetric current intensity follows the Arrhenius equation and thus can be corrected readily,
- pressures in the range 1 to 600 bars have been found to have no effect on the sensor response.



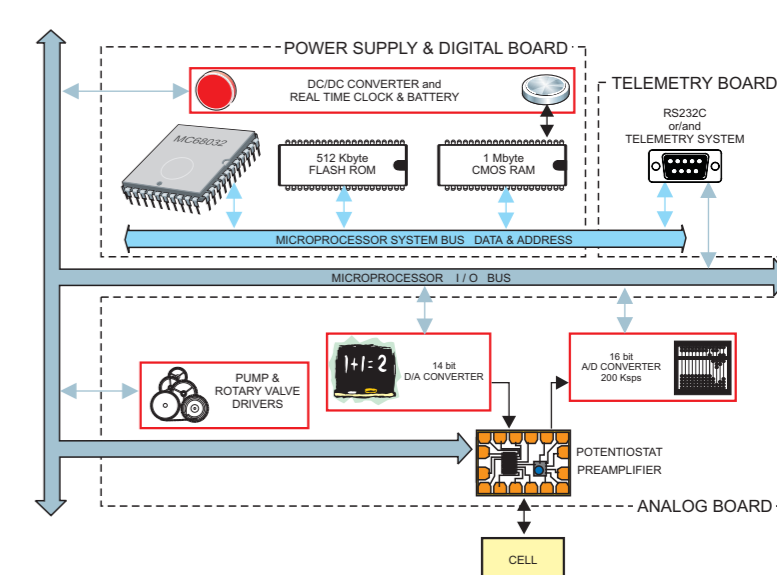
THE NOVEL VOLTAMMETRIC IN-SITU PROFILING SYSTEM (VIP System)

The VIP System consists of: a submersible Voltammetric Probe, an Idronaut Ocean Seven 301 Multiparameter submersible Probe, a Calibration Deck Unit, a Surface Deck Unit and a IBM compatible PC

- The calibration deck unit enables in the laboratory, on shore or on boat performance of: i) the renewal of the microsensor Hg layer, ii) the calibration of the probe, and iii) the measurements of standard and collected natural samples.
- The surface deck unit powers and interfaces, by telemetry, the measuring system with a Personal Computer. This unit permits an autonomy of about 35 hours and can be recharged either in a continuous mode using a solar captor or after use.
- The Ocean Seven 301 probe controls the exact position of the voltammetric probe in depth and the simultaneous measurement of: temperature, conductivity, salinity, dissolved oxygen, pH and Redox potential.

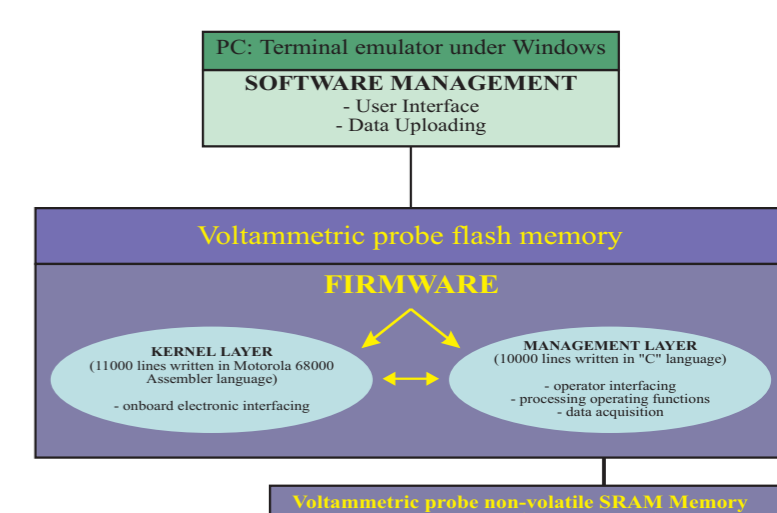


The electronic housing contains all the hardware and firmware necessary to manage: i) the voltammetric measurements, ii) the interfacing of the Multiparameter Probe Ocean Seven 301 (via an RS232C interface), the calibration deck unit and the submersible peristaltic pump, and finally iii) data transfer by telemetry.

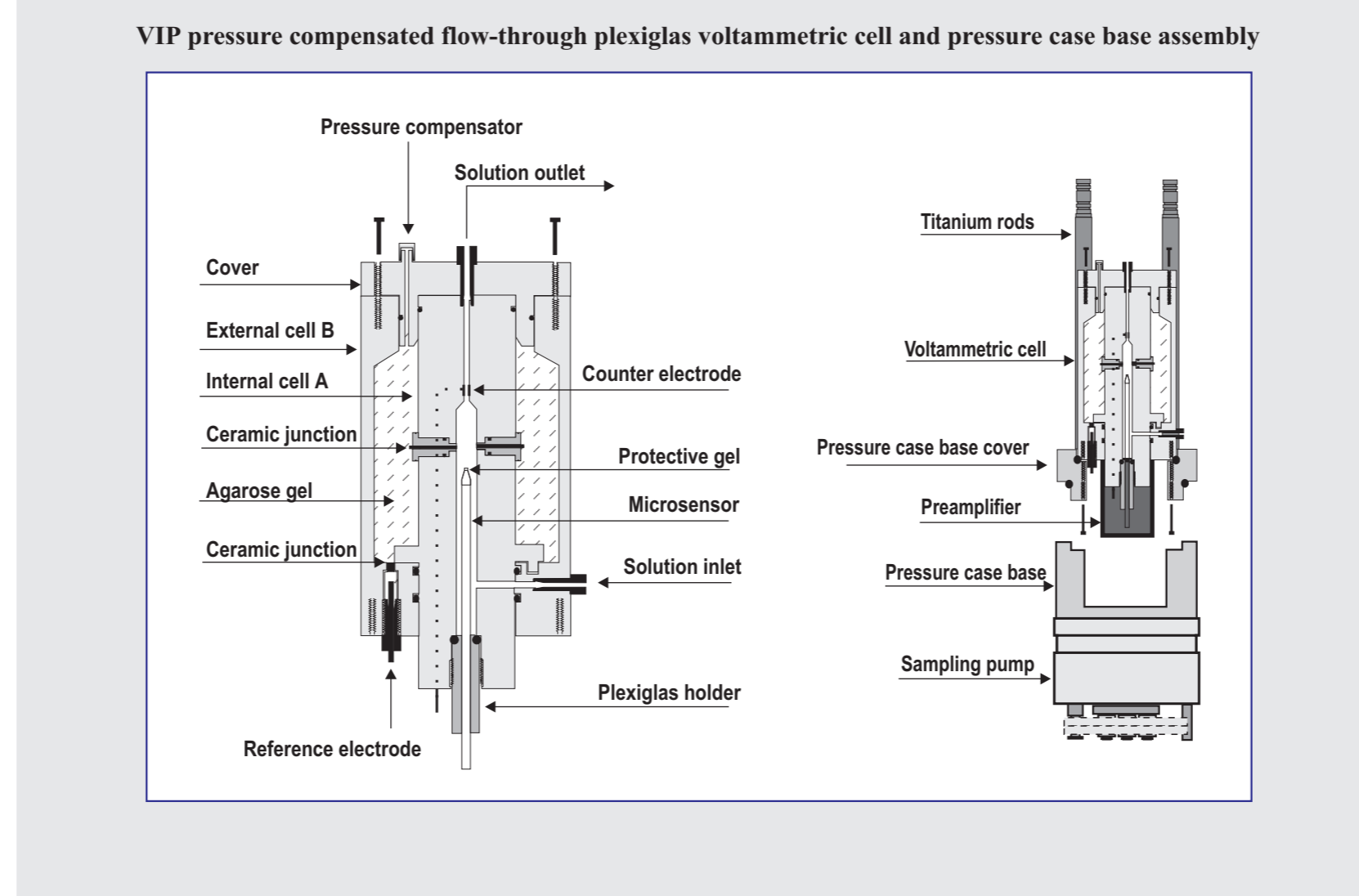


The interface between the Personal Computer and the Voltammetric Probe is carried out using the Terminal Emulator under Windows™.

The VIP System software is divided into management software and firmware. The firmware, stored in a flash memory, allows the user to execute the processing operating functions and the data acquisition. The management software allows the user, through menus and pop-up data entry windows, to control and configure the voltammetric probe operating parameters and functions such as: electrochemical parameters, data acquisition, calibration and maintenance operations. Data files are stored in a non-volatile memory having its own battery which guarantee high data retention and protection.



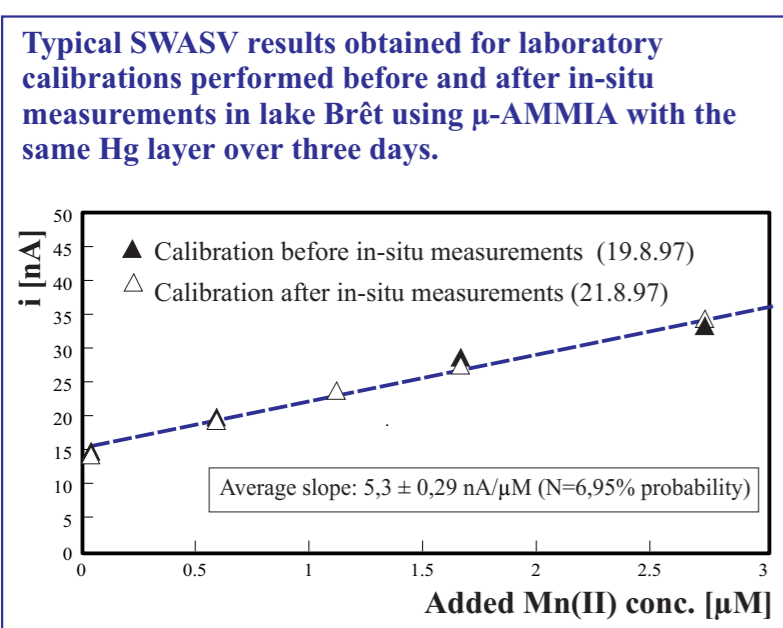
The submersible Voltammetric Probe (dimensions: 86 cm length, 10 cm in diameter; weight: 8 kg in air, 4 kg in water) is comprised of distinct specific modules: an electronic probe housing, a pressure compensated flow-through plexiglas voltammetric cell (internal volume = 1.5 ml) with a platinum ring auxiliary electrode and a home-made Ag/AgCl/KCl saturated gel reference electrode, a pressure case base incorporating the preamplifier for the voltammetric microsensor and a submersible peristaltic pump for sampling.



EXAMPLES OF ENVIRONMENTAL APPLICATIONS OF THE VIP SYSTEM.

In-situ Mn(II) profiling in anoxic lake waters.

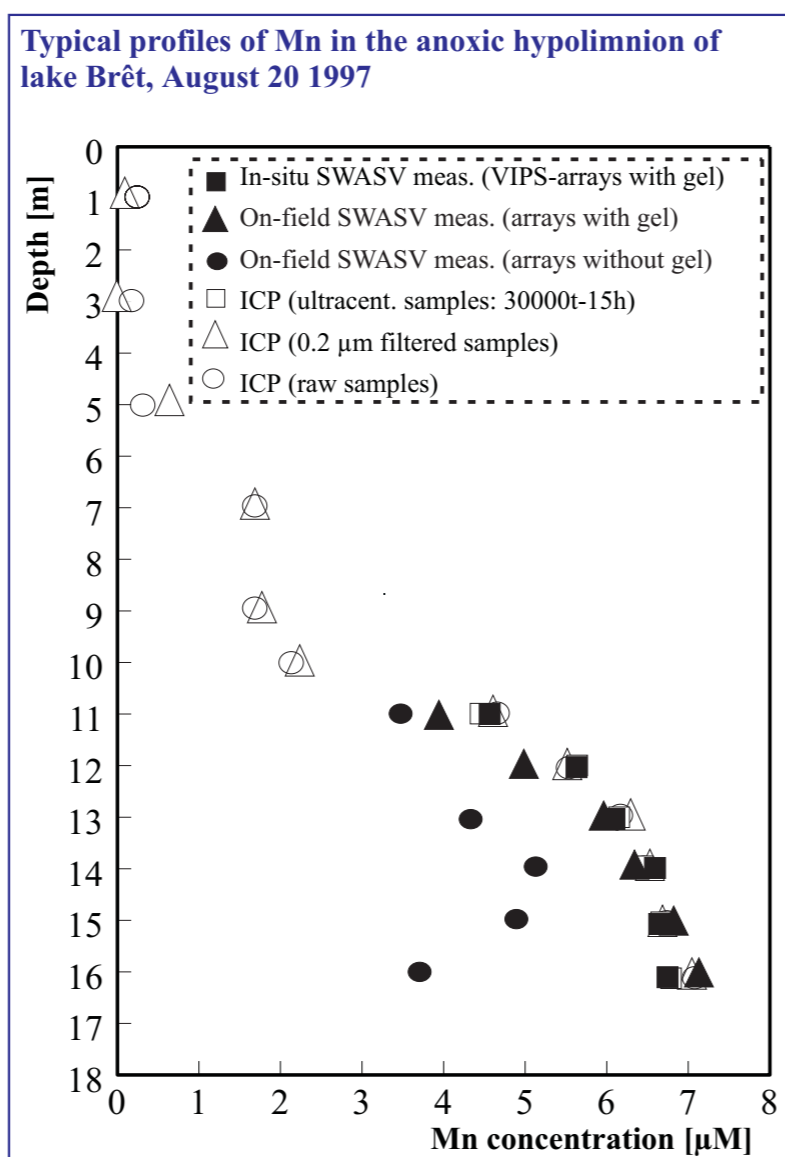
The VIP System was first applied for Mn(II) concentration profile measurements within the anoxic hypolimnion of lake Brêt (Switzerland). The main objective of these field tests were to check the validity and reliability of the measurements performed with the VIP System in real conditions. Throughout the field tests, μ -AMMIE or μ -AMMIA with the same mercury layers were used to calibrate the submersible voltammetric probe the day before and after each deployment as well as for in-situ measurements (i.e. no renewal of the mercury semidrops over three days).



The results showed:

- excellent stability of the gel integrated microsensor for at least three days,
- no memory effect from in-situ measurements performed between both laboratory calibrations,
- excellent reproducibility, with low standard deviation, of the slopes obtained for the different calibrations.

Concentration profiles obtained from *in-situ* voltammetric measurements were compared with on-field voltammetric measurements, performed at a constant temperature of 20°C, using a microsensor with and without a protective gel layer. Samples were also drawn to allow laboratory Mn measurements in acidified (pH 2) raw samples, acidified samples filtered on 0.2 μ m pore size membranes and acidified samples ultracentrifuged at 30000 rpm for 15 hours (which caused elimination of the species with a size > 5 nm assuming a density of 2) using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for comparison purpose.



The results obtained for the Mn profiles in lake Brêt have shown:

- excellent agreement between Mn(II) concentration profiles determined from *in-situ* voltammetric measurements, after temperature effect correction using the following equation $\ln(i) = 29.68 - 7091 \cdot 1/T$, and in-field voltammetric measurements performed at a constant temperature of 20°C using microsensors with gel,
- excellent agreement between Mn(II) concentration profiles determined from voltammetric measurements using a microsensor with gel (mobile species with size of few nm) and ICP laboratory measurements of ultracentrifugated acidified samples (species ≤ 5 nm),
- systematic lower concentrations for the unprotected microsensor due to adsorption onto the sensor surface of lake born iron hydroxide particles which then hinder the diffusion of Mn(II),
- interesting information regarding the nature of Mn in lake Brêt. Indeed, since voltammetry measures only the mobile Mn species with sizes of a few nanometers, whereas ICP techniques measure the total metal concentration in the different samples, the similar Mn concentrations obtained with both techniques indicate that Mn in lake Brêt is present predominantly in the mobile form, i.e. Mn^{2+} and probably small inorganic complexes, at this period of the year.

These field tests have allowed us to demonstrate:

- the reliability of the VIP System using gel integrated microsensors for real-time in-situ measurements in natural water,
- the validity of the equation, determined in the laboratory, for the correction of temperature effect,
- the independence of voltammetric signal as a function of pressure variation,
- the efficiency and necessity of the protective agarose gel layer to eliminate fouling problems.



In-situ trace metal monitoring in oxygen saturated sea water.

Continuous monitoring of trace metals for quality control is becoming of prime importance in many estuaries and coastal zones. The potentiality of the VIP System for such purpose was tested in the Venice Lagoon (Venice-Italy) and in the Gullmar Fjord (Sweden).

Venice Lagoon: Transept in-situ measurements were performed in three different stations: 1) Breda, which is located in the middle of the industrial area and represents one of the most polluted part of the Lagoon, 2) Fusina, which is at the limit of the southern part of the industrial area in a wide artificial navigation canal and finally 3) Bocca di Porto, which is located at the main entrance to the Lagoon. Samples were also drawn to allow laboratory total metal concentration measurements performed by voltammetry in UV irradiated, acidified samples.

Trace metal measurements in Venice Lagoon (Venice, March 12-13 1997)

Stations	Cd(II) [nM]		Pb(II) [nM]		Cu(II) [nM]	
	C _v (VIP)	C _t (labo)	C _v (VIP)	C _t (labo)	C _v (VIP)	C _t (labo)
Breda	0.18 ± 0.04	1.33 ± 0.03	1.64 ± 0.11	3.05 ± 0.17	3.93 ± 0.86	10.57 ± 1.08
Fusina	0.25 ± 0.04	1.20 ± 0.01	0.42 ± 0.05	3.10 ± 0.10	1.56 ± 0.39	23.33 ± 2.60
Bocca di Porto	0.02 ± 0.005	0.23 ± 0.03	0.06 ± 0.01	1.0 ± 0.10		5.97 ± 0.81

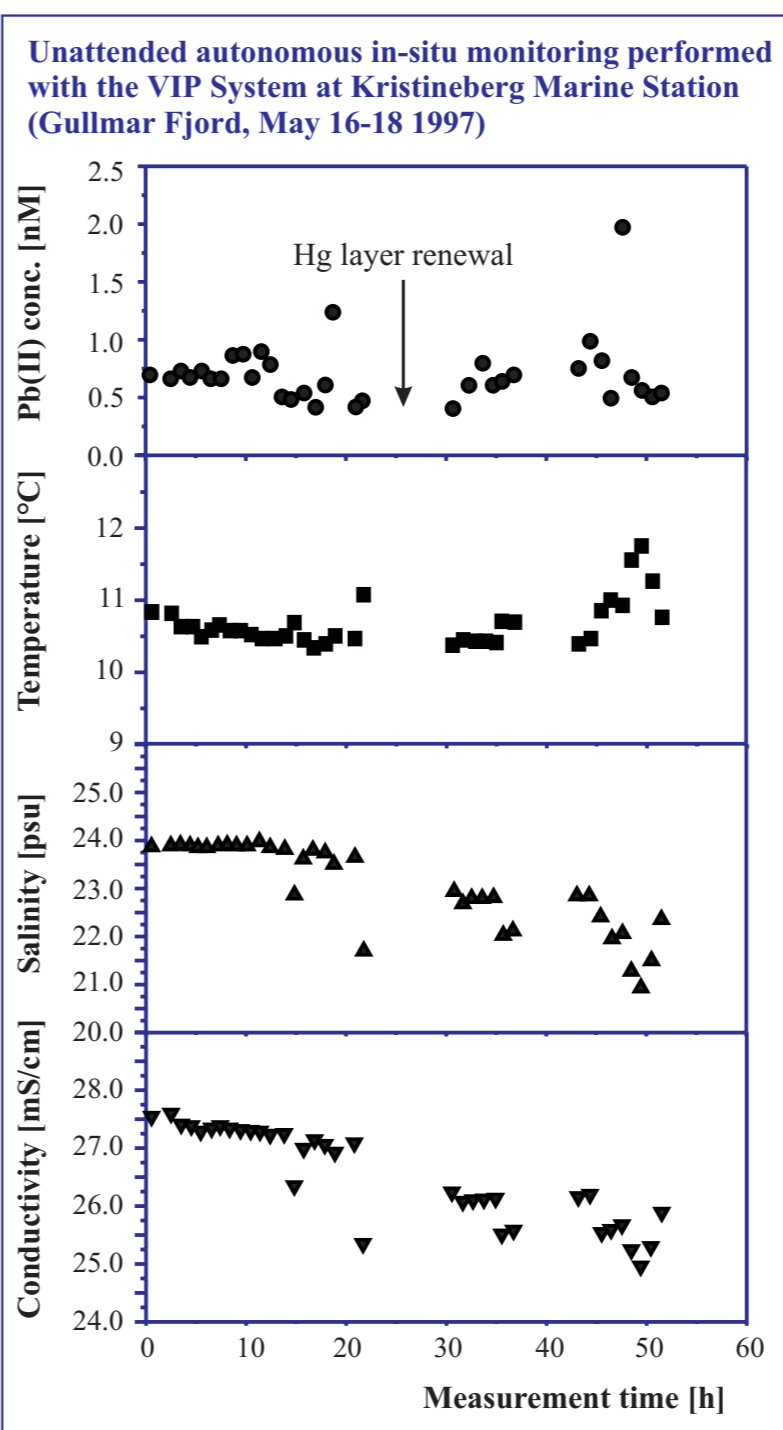
In-situ measurements with the VIP System (μ -AMMIE)
 C_v (VIP) = concentration of the mobile fraction of trace metals
 Voltammetric laboratory measurements in UV irradiated, acidified samples
 C_t (labo) = total metal concentration

The results showed that:

- the mobile fraction of trace metals (VIP in-situ measurements) represent in general only 10 to 20% of the total metal concentrations (laboratory measurements),
- concentrations as well as variation in concentrations in the ppt level of the mobile fraction (i.e. the fraction which is easily assimilated by the organisms and plants and thus generally considered as the most toxic fraction) can be measured directly in-situ, i.e. without any perturbation of the sample, with a good reproducibility using the VIP System.



Gullmar Fjord: the reliability of the VIP System for real-time monitoring and profiling of trace metal in oxygen saturated sea water were confirmed during field trials performed aboard R/V Arne Tiselius vessel. In addition, the first tests of unattended autonomous in-situ monitoring using the VIP System were performed at Kristineberg Marine Station. Measurements were automatically performed every hour for 52 hours with a renewal of the Hg layer over the μ -AMMIE sensor after 22 hours.



The temperature, salinity and conductivity data, measured simultaneously with in-situ VIP Pb(II) concentration using the Ocean Seven 301 multiparameter probe, showed that fresh, warmer water was advected into the measurement site during the experiment. At each of such event, significant variation of in-situ Pb(II) concentration were also observed. Even if more extensive studies are required for rigorous interpretation, these results show the potentiality of the VIP System as a tool to identify and study specific changes. In addition, the possibility to identify any variation of concentration in real-time is particularly important for quality control as it is the only way to detect, punctually, any toxic release and take remedial action in time.

CONCLUSIONS

The combination of voltammetric principles with recent breakthrough in electronic and micromechanic has allowed the development of a sophisticated, compact, reliable, in-situ analytical device for trace element measurements in natural aquatic systems thanks to the use of reproducible and well characterised gel-integrated microsensors. In particular ppt level of the mobile fraction, which is the most difficult fraction to measure without analytical artefacts, can be determined by direct in-situ measurements, i.e. without perturbing the samples. In addition punctual changes can be identified and studied. Further development are under way:

- coupling flow injection system to the flow-through voltammetric cell to allow in-situ total metal concentration measurements in addition to the mobile fractions,
- adapting the VIP System to a Radio Buoy Profile to allow continuous, autonomous, automatic in-situ monitoring over extended period of time respectively.

Both points are important for efficient environmental monitoring and more rigorous interpretation of trace element cycles in natural aquatic systems.

ACKNOWLEDGEMENTS

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