

Voltammetric In situ Profiling System

Introducing the only existing submersible voltammetric probe for *in situ* trace element monitoring and profiling.



Check out these features !

- simultaneous multi-element analysis
- possible extension to other compounds
- original, long-term reliable gel protected micro-sensor
- wide dynamic range (ng/l to mg/l)
- chemical speciation capability
- easy combination with CTD, oxygen, pH, redox sensors,
- flexibility of operation: spot or long-term monitoring,
- autonomous data analysis and transmission to land,
- profiling capability between 0 and 500 metres
- advanced computer controlled analysis

ENVIRONMENTAL MONITORING



Rivers



Lakes

Groundwaters



Estuaries
Fjords



Oceans

POLLUTION CONTROL MONITORING



Industrial channels



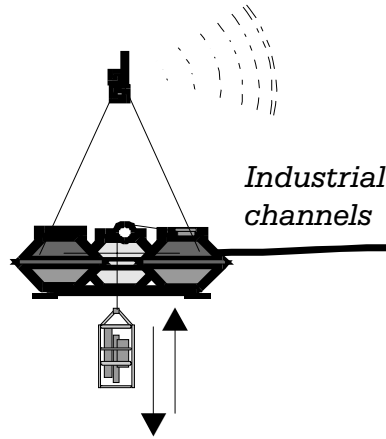
Water reservoirs



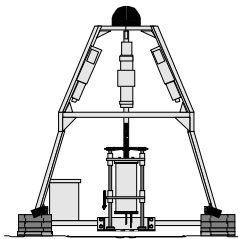
Harbour monitoring



Coastal zones



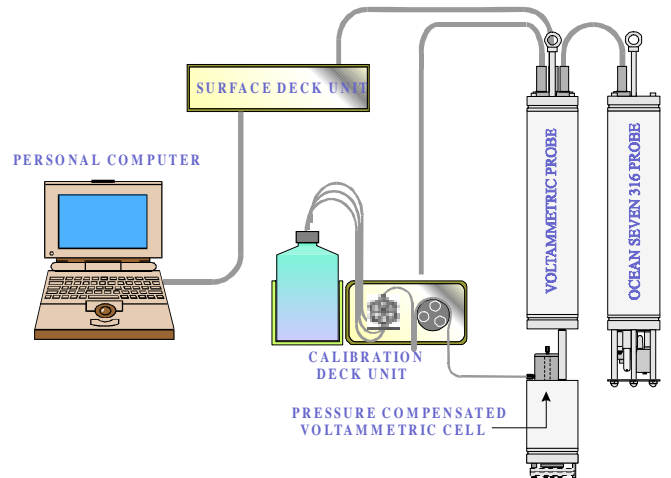
TELEPHONE LINK (GSM)



The Italian company IDRONAUT, in collaboration with the CABE Group of the University of Geneva – Switzerland, has developed a **submersible voltammetric probe** with which reproducible and reliable *in situ*, continuous monitoring/profiling of trace elements in natural aquatic ecosystems can be performed.

The whole VIP system consists of several units: the submersible voltammetric probe based on a unique micro-sensor, a submersible on-line O₂ removal module, a submersible Ocean Seven 316 multiparameter probe, a calibration deck unit, a surface deck unit and a management software running on WINDOWS PCs.

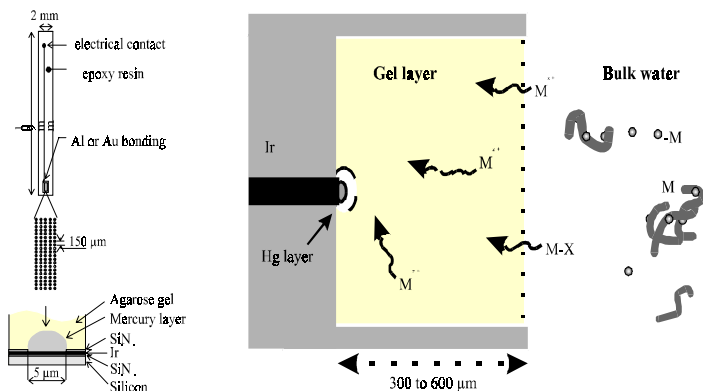
It allows simultaneous measurements of Cu(II), Pb(II), Cd(II) and Zn(II) with a sensitivity at the ppt level, as well as Mn(II) and Fe(II) with a sensitivity at the ppb level (extension to other elements and organic compounds are foreseen). It is usable in sea and fresh water down to 500 m. It is controlled either by an operator from the surface or in autonomous mode, under pre-set sequences. When interfaced with an automatic Buoy Profiler, the VIP System allows the whole water column to be automatically monitored for at least one week, at prefixed periods.



The VIP System is a no-compromise, state-of-the-art analytical system to address the requirements of every environmental laboratory interested by real-time monitoring of aquatic ecosystems.

Unique micro-sensor

The heart of a VIP is its sensor. It measures a signal intensity, produced by the chemical reaction at its surface, which is proportional to the concentration of the analytes. However, to perform automatic measurements over extended periods in complex media such as natural waters, most of the currently available sensors are not reliable nor sensitive enough for monitoring very low concentration of chemical compounds.

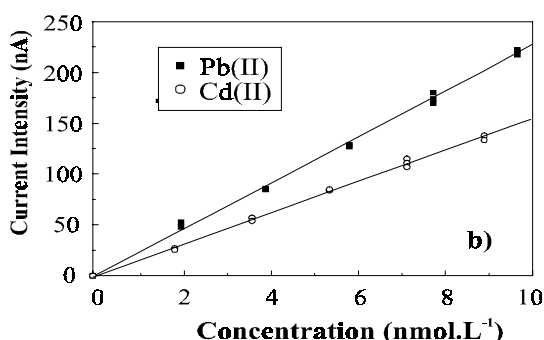
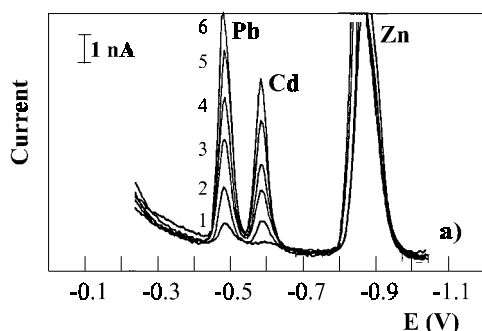


In addition, fouling problem, due to the adsorption of organic and inorganic matters at the sensor surface, is an important limitation of direct voltammetric measurements in complex matrices. The VIP sensor is a unique micro-sensor which has been developed by CABB and IMT (University of Neuchâtel-Switzerland) to solve all the above problems. It is produced by thin film technology on chips and photolithographic technique. It consists of an array of 5 x 20 interconnected Iridium microdiscs, having a diameter of 5 μm and a centre to centre spacing of 150 μm, coated by Hg layers and covered by an hydrophilic protective gel membrane. Measurements with this gel-integrated micro-sensor are performed in two successive steps:

- equilibration of the gel with the sample (typically 5 minutes for a membrane thickness of 300 μm);
- voltammetric analysis inside the gel.

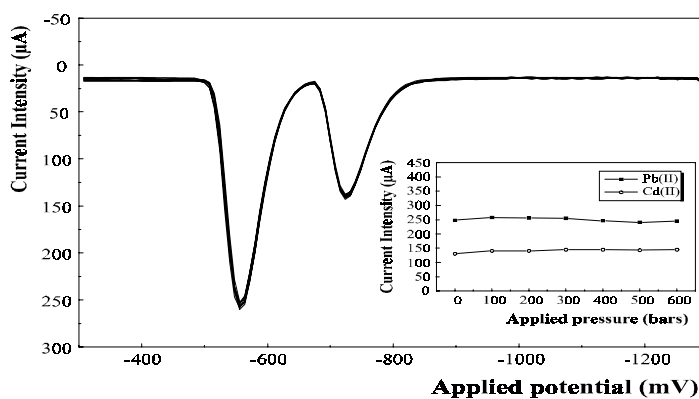
The main key features of the VIP micro-sensors for *in situ* measurements are:

- 1) high sensitivity and reliability;



- 2) organic and inorganic colloidal and particulate material, which might adsorb on the surface sensor (fouling problem), are efficiently excluded from the gel and do not interfere with voltammetric measurement;
- 3) the protective gel membrane prevents irreproducibility of the measured signal due to external ill-controlled convection;
- 4) external medium is not modified by the voltammetric measurements (i.e. the voltammetric diffusion layer is small compared with the gel membrane thickness (see figure gel principle));
- 5) effects of temperature variation on the current intensity measured can be readily corrected (note that peak current variations of 3 to 8% °C⁻¹, depending on the analyte, were observed which are of significant concern for concentration profiling in water columns where temperature may vary from typically 4 to 25°C);

SWASV peak currents = f (pressure)



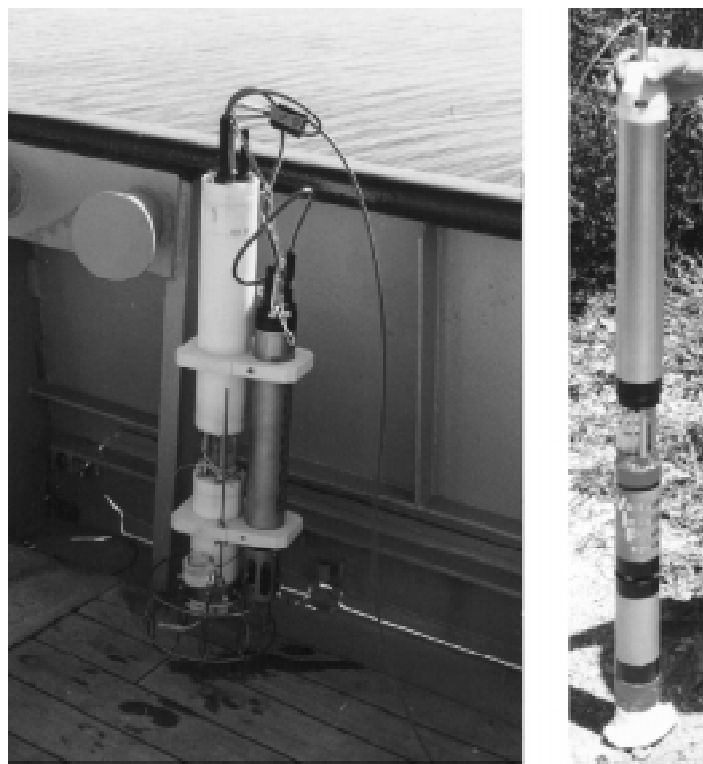
9.65 μM Pb(II) and 8.89 μM Cd(II) in N₂ degassed 0.1 M NaNO₃ sol.
(Two electrode system; E_{dep} = -1.3 V vs Pt, t_{dep} = 5 s)

- 6) signals are independent of the pressure in the range 1 to 600 bars;
- 7) micro-sized-electrodes allow direct measurements in low ionic strength fresh waters without the addition of an electrolyte;
- 8) current intensity measured at micro-sized electrodes is controlled by a spherical diffusion and reaches a non-zero steady-state value at constant potential, i.e. stirring is not required during the preconcentration step of stripping techniques (Note: this is absolutely required to allow anodic stripping voltammetric measurements inside the protective gel membrane);
- 9) signals measured at micro-sized electrodes are proportional to the diffusion coefficient values of the target compounds and negligible for species larger than a few nm.

Points 1) to 6) are unique key features of the VIP gel-integrated micro-sensors. They are required to enable rigorous interpretation of voltammetric data obtained from direct measurements in complex media as well as reliable operation of chemical sensors in complex media for a long period of time (typically standard deviations of max. 10% were observed for continuous trace metal measurements, at the nanomolar level, over two weeks using the same Hg layers).

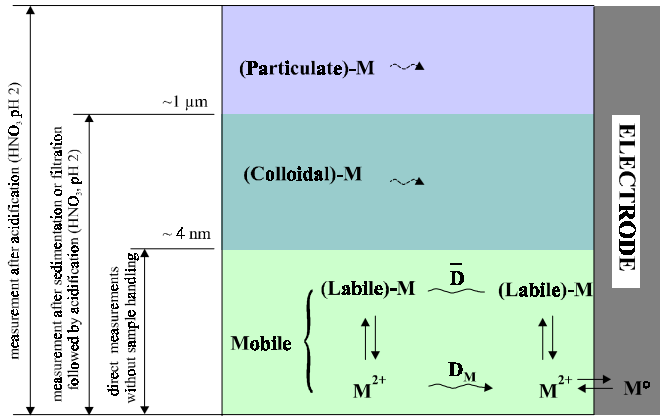
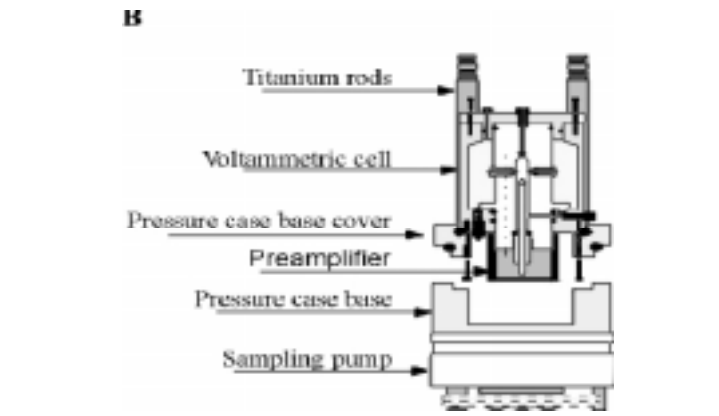
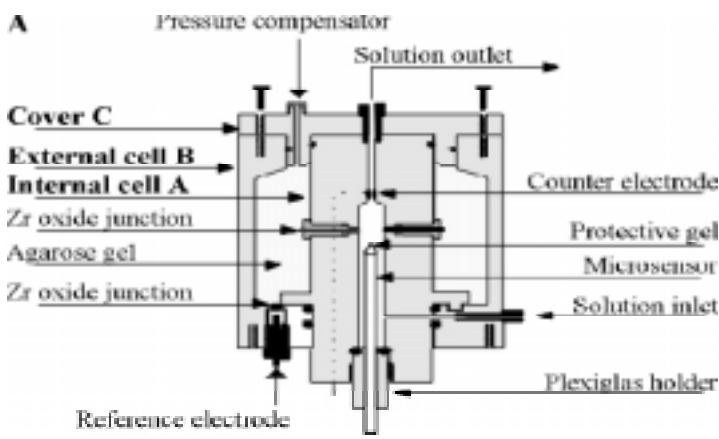
Points 7) to 9) are features of voltammetric techniques coupled to micro-electrodes. Point 9) is a key feature for trace metal speciation studies, i.e. the VIP voltammetric probe measures *in situ* specifically the dissolved

fraction of trace metals (i.e. free metal ions and small labile complexes with size of few nanometers) without any sample pre-treatment. Additional determination of the total metal concentrations in acidified, filtered and raw samples permits calculation of colloidal and particulate metal species by difference.



The flow-through voltammetric cell is based on a three-electrode system. It has been specifically designed for *in situ* measurements based on the following criteria:

- optimum positioning of the three electrodes in order to: i) prevent the products formed at the auxiliary electrode to interfere at the working micro-electrode, ii) minimize the attachment on the working micro-sensor tip of gas microbubbles formed by temperature changes, iii) minimize electrical resistance thanks to very short distances between the different electrodes;
- robustness;
- possibility of maintenance and/or replacement of the working and reference electrodes in field conditions;
- pressure compensation.



The distinction between these three different fractions is important to understand the role and the fate of vital or harmful trace elements. In particular, the dissolved fraction is the most important one for bioavailability and ecotoxicity interpretation. The fraction is also the most difficult to measure without analytical artifact (due to sample degradation and risk of contamination) and thus it requires direct *in situ* measurements. The mobile and the particulate forms play different important roles in metal circulation and residence time, e.g. fast sedimentation followed by accumulation in sediments of the particulate species and slow coagulation/sedimentation of the colloidal species.

Submersible voltammetric probe

The submersible voltammetric probe has been designed in two different models: model 1 with POM housing (dimensions: 86 cm length, 10 cm diameter; weight: 8 kg in air, 4 kg in water) for *in situ* measurements in surface water; model 2 with Titanium housing (dimensions: 100 cm length, 7 cm diameter; weight: 6 kg in air, 6 kg in water) for *in situ* measurements of trace elements in ground-water and mining boreholes. It comprises distinct, specific, modules: an electronic probe housing (upper part), a pressure compensated flow-through plexiglas voltammetric cell, a pressure case base incorporating the preamplifier for the voltammetric micro-sensor and the sampling submersible peristaltic pump (lower part). This design allows direct access for the user to the key parts of the probe so as to simplify the maintenance of the system as much as possible.

The electronic housing contains all the hardware and firmware necessary to manage: i) the voltammetric measurements, ii) the interfacing of the Itronaut Ocean 316 multiparameter probe via an RS232C interface, the calibration deck unit and the submersible peristaltic pump, and finally iii) the data acquisition and data transfer by telemetry to the surface deck unit or to a surface Buoy Profiler. Data files are stored in an internal non volatile memory having its own battery which guarantees high data retention and protection.

It consists of two specific parts: an internal flow-through cell A and an external cell B held together by means of the plexiglas cover C. The working micro-sensor and the counter electrode are located in the internal cell A. The latter consists of a built-in platinum ring (2 mm internal diameter) while the former is a novel either single or array micro-sensor (see below) held in the cell by means of a plexiglas holder and an o-ring. The compartment between the internal cell A and the external cell B is completely filled with a 1.5% LGL agarose/1M NaNO₃ gel. This gel plays several important roles: i) it acts as a double bridge, via two zirconium oxide porous junctions that are in contact with the working solution, for the home-made manufactured Ag/AgCl/KCl saturated gel reference electrode that has a zirconium oxide junction located at the bottom of the cell B; ii) it shields both the micro-sensor and the counter electrode; and most important iii) it acts as a pressure equalizer through the rubber pressure compensator. Pressure compensation of the cell allows *in situ* measurements at high depth and also solves the problem of liquid junction of the reference electrode. The cell is screwed to the cover of the pressure case base with o-ring seals.

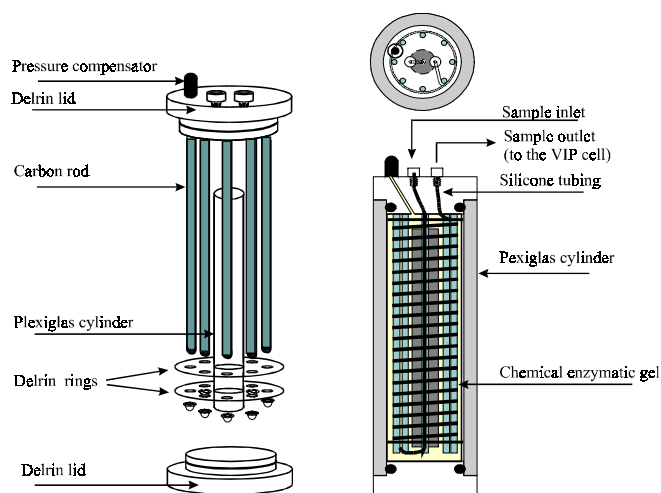
The pressure case base incorporates the preamplifier of the working micro-sensor and the motor of the submersible peristaltic pump. It is mechanically assembled to the electronic housing via two titanium rod connectors, through which the electrical connections of the three electrodes, the micro-sensor preamplifier and the submersible pump are performed.

The advantages of this configuration are :

- the flow-through voltammetric cell is protected against shocks;
- maintenance and replacement of the working reference electrodes are easy since they are simply screwed with o-ring seals;
- watertightness of all the electrical connections is possibly made by using normal connectors;
- the preamplifier is isolated from the main electronic part which minimizes an important source of noise.

Submersible on-line oxygen removal module

This module is required only for *in situ* trace element monitoring in oxygen containing freshwater. It consists of a silicone tubing surrounded by a chemical reducing gel agent. It is connected between the sampling pump and the inlet of the flow-through voltammetric cell. When the water is pumped through the silicone tubing, the oxygen diffuses through its wall and is consumed on the other side by the reducing gel agent.



The submersible pump is a specially built peristaltic pump. It has been carefully manufactured to ensure watertightness and proper functioning down to 500 m without the requirement of an oil immersion system. The fittings used for sampling are standard 1/4" 28 thread fittings made of inert, metal free Teflon materials. The tubing used for the fluidic system are in Teflon or Tygon.



Submersible Ocean Seven 316 multiparameter probe

This probe allows to control the exact position of the VIP voltammetric probe at depth and to simultaneously measure the following parameters: temperature, conductivity, salinity, dissolved oxygen, pH and Redox potential. Temperature measurements are absolutely required to correct the effect of temperature variation (typically in the range 25° to 4°C) on the voltammetric signal. The other parameters are important for trace element data interpretation. In the case of the probe model 2, developed for application in groundwater, a temperature and a depth sensor are incorporated to the submersible voltammetric probe to minimize the size of the submersible unit.

Calibration deck unit

This unit enables to perform in laboratory, on shore or on board i) the renewal of the micro-sensor Hg layer (see below), ii) the calibration of the probe, and iii) the measurements of standards or collected chemically modified natural samples (e.g. acidified raw or filtered samples for measurements of the colloidal and particulate forms (see: Features and selectivity of gel-integrated micro-sensors). When the voltammetric probe is ready for deployment, this unit is disconnected.

Surface deck unit

The surface deck unit powers and interfaces, by telemetry, the measuring system with a Personal Computer. This unit allows an autonomy of about 35 hours and can be recharged either in continuous mode using solar captor or after use. The communication between the Personal Computer and the voltammetric probe is carried out by using the Terminal Emulator under Windows and a management software.

Management software

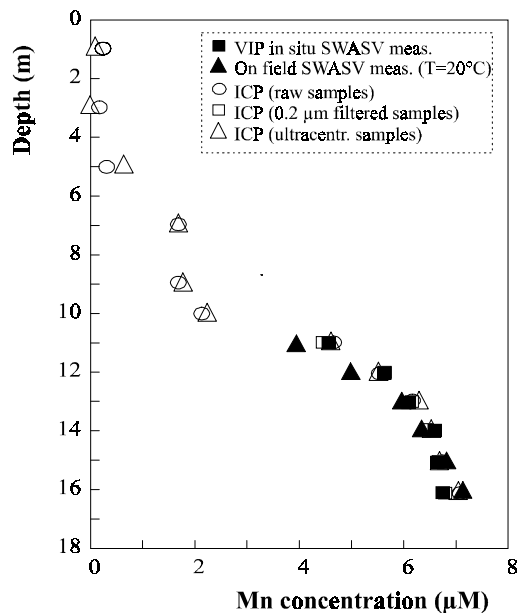
A user friendly management software allows the user to manage all the functions required by the VIP System during each working activity. They are in particular: voltammetric probe calibration and maintenance, measurements and profiling, automatic data retrieving, data processing and the support of the operator during each phase of the working activities.

Technical and analytical improvements

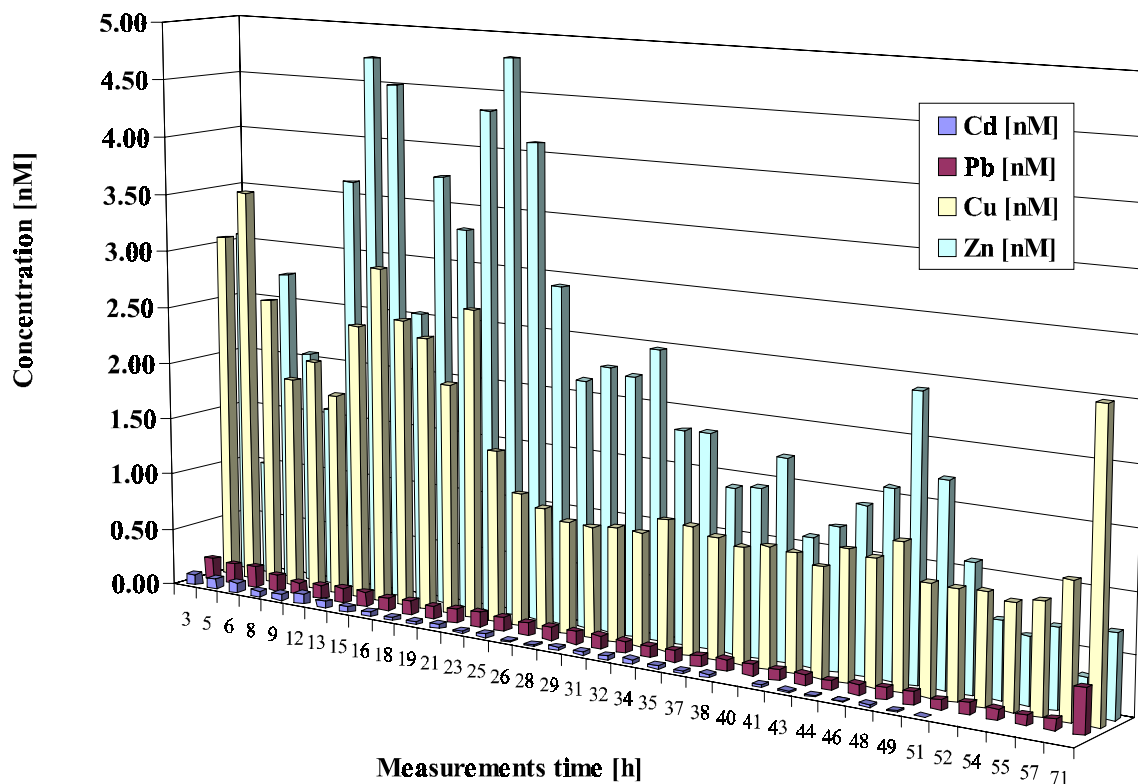
Further technical and analytical developments are underway to extend the features of the VIP System. In particular:

- development of a submersible mini-flow injection system, coupled to the multichannel voltammetric flow-through cell, to allow in situ measurements of other trace metal species in addition to the mobile fractions, i.e. *in situ speciation*;
- development and/or optimisation of new voltammetric sensors and/or analytical procedures for *measurements of other relevant elements*;
- coupling of other submersible probes for *simultaneous in situ measurements* of other important parameters for the interpretation / understanding of trace metal cycling, e.g. *nutrients and chlorophyll*.

Typical example of Mn(II) concentration profiles determined from voltammetric VIP in situ and on field measurements and comparison with laboratory ICP measurements. (Lake Bret-Switzerland - 20.8.97)

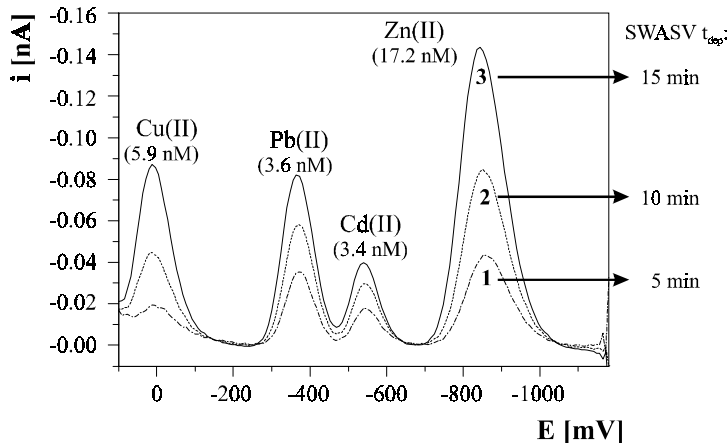


VIP in situ, autonomous measurements of trace metals. (Lake Lucerne-Switzerland, June 27-30, 2000)



Reliability of trace metal measurements and calibration using the VIP probe

Typical trace metal SWASV voltammograms as a function of the deposition time measured in synthetic freshwater.



Other SWASV cond.: $E_{dep} = -1200$ mV; $E_r = +100$ mV; pulse ampl. = 25 mV; step ampl. = 8 mV; frequency = 200 Hz; $E_{preleas.} = +100$ mV; $t_{preleas.} = 60$ s.

Averaged values of calibration slopes for trace metals obtained in $NaNO_3$ and synthetic sea and fresh waters

Trace metals	Slopes [nA/nM min]	N	Detection limit* [pM]
Cu(II)	0.82 +/- 0.025	4	200
Pb(II)	1.07 +/- 0.025	8	50
Cd(II)	0.68 +/- 0.05	5	50
Zn(II)	0.37 +/- 0.05	4	300

N = number of individual calibration slope
* for a deposition time of 15 min

In situ trace element measurements in borehole using a specially designed Titanium VIP submersible voltammetric probe. (Rio Tinto Mining Area, Spain May 1998)



a)		Tot. depth [m]	Pb(II) [nM]	Cd(II) [nM]	Zn(II) [nM]	Mn(II) [mM]
		75.0	0.5	1.5	48.1	no meas.
		81.0	0.3	0.6	25.3	no meas.
		85.0	0.4	0.6	7.3	19.8
		91.0	0.4	0.5	4.6	18.5
		96.0	0.3	0.5	5.8	16.2
b)		Tot. depth [m]	Pb _{tot} [nM]	Cd _{tot} [nM]	Zn _{tot} [nM]	Mn _{tot} [mM]
		85	4.8	4.5	140.0	20.0

a): in situ measurements with the VIP System
b): ICP-MS laboratory measurements in acidified

Concentration of the mobile fraction (C_m) of trace metals measured in situ in three location of Venice Lagoon using the VIP System and total concentration of these metals (C_{tot}) measured in laboratory by voltammetry after UV irradiation of acidified samples. (Venice, March 12-13, 1997)

Stations	Cd(II) [nM]		Pb(II) [nM]		Cu(II) [nM]	
	C_m (VIP)	C_{tot} (lab)	C_m (VIP)	C_{tot} (lab)	C_m (VIP)	C_{tot} (lab)
Breda	0.18 ± 0.04	1.33 ± 0.03	1.64 ± 0.11	3.03 ± 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

Breda: industrial area; Fusina: artificial boat channel; Bocca di Porto: main entrance of the lagoon

Voltammetric In-line Analyzer for on-Field monitoring

The technical and analytical advances of the VIP submersible voltammetric probe have been used to develop a compact portable Voltammetric In-line Analyzer (VIA-Field). ***It provides on-site reliable concentration measurements of various fractions of trace elements at the ppt level in minutes***, eliminating problems associated with conventional sampling, storing and laboratory analyzing and thus significantly reducing the cost, time and difficulties of testing.

Battery-powered, lightweight and weatherproof, the VIA-Field is ideal for stationary source testing and hazardous-waste site investigation,

Engineered for the field, the VIA-Field is designed to withstand harsh testing environment. It consists of a voltammetric analyzer module, a mini-flow injection module, an optional multiparameter probe and reagent/waste containers integrated in a unbreakable, corrosion proof and airtight protective case. The electronic stainless steel housing of the different modules were designed under given similar specific format, to facilitate their integration and minimize at maximum the size of the whole system.

Voltammetric analyzer module

The voltammetric analyzer module consists of the VIP flow-through plexiglas cell (incorporating the unique VIP microsensors), a cell holder and an electronic housing. The ***electronic housing*** is based on mechanical modification and adaptation of the VIP voltammetric probe housing and electronic boards. The hardware and firmware, similar to

those of the VIP probe, allow to manage : i) the voltammetric measurements, ii) the interfacing of the optional field-portable multiparameter probe via an RS232C interface, the mini-flow injection module and finally iii) the data acquisition and data transfer, via RS 232C interface to a portable PC or via cellular phone to a control station. Data files are stored in an internal non volatile memory having its own battery which guaranty high data retention and protection.

The ***flow-through voltammetric cell*** is screwed on the cover of the cell holder. The ***cell holder*** incorporates a preamplifier for the microsensor. It is made of a POM cover, on which is screwed the flow-through cell, and shielded housing.

Mini-flow injection module

The mini-flow injection system consists of a peristaltic pump, a multi-way rotary valve and filters. It enables to perform in laboratory or on-field:

- ◆ the renewal of the microsensor Hg layers.
- ◆ the calibration of the system.
- ◆ the sampling of the natural waters.
- ◆ the direct measurements of unmodified natural water samples, i.e. specific ***measurements of the mobile fraction of trace metals*** defined as free metal ions and small labile complexes with size of few nanometers.
- ◆ the measurements of in-line chemically modified natural samples, e.g. acidified raw or filtered samples for the determination of colloidal and particulate forms of the trace elements.



VIP PROBE SPECIFICATIONS

Analytical specifications:

Measurable elements or compounds:	Cu(II), Pb(II), Cd(II), Zn(II), Mn(II), Fe(II) extension to other elements or compounds is possible, metal speciation (see text)
Lowest detection limits:	50 pM (10 ppt) (15 minutes deposition time)
Measurement range:	0.2 nM to 500 nM (5 minutes deposition time) 40 ppt to 1000 ppt (5 minutes deposition time)

Measurement techniques:

Chronoamperometry	
potential range:	± 2048 mV
Cyclic Voltammetry (CV)	
Linear Sweep Voltammetry (LSV)	
Anodic Stripping Voltammetry (ASV)	
potential range:	± 2048 mV
scan rate:	1 mV/s to 1 V/s
Square Wave Voltammetry (SWV)	
Square Wave Anodic Stripping Voltammetry (SWASV)	
potential range:	± 2048 mV
pulse amplitude:	1 to 250 mV
step amplitude:	1 to 250 mV
pulse frequency:	1 to 1000 Hz (period: 1 ms to 1 s)

CALIBRATION DECK UNIT SPECIFICATIONS

Allows laboratory and on-site conditioning and calibration operations. It incorporates the computer controlled six position rotary valve and the peristaltic pump. The unit is provided with a holder containing (up to four) solution bottles; each bottle is equipped with cap, micro-filter and vent hole. The Calibration Unit is complete with a wall-cube power supply able to power, in laboratory, the Voltammetric Probe.

Dimensions: 130 x 270 x 86 mm. Weight: 1 kg.

SURFACE DECK UNIT SPECIFICATIONS

The function of the PORTABLE DECK UNIT is to power and interface, by telemetry, the Voltammetric Probe with a portable Personal Computer. This unit contains a rechargeable lead battery (12V - 6.5 A/h) which allows about 35 hours of continuous operation even without external power (100, 110 or 220V AC, 50/60 Hz).

The PORTABLE DECK UNIT is provided with an adjustable power supply to power the Probe, an internal power supply to recharge the 12 V internal battery and a transceiver able to transform commands coming from the PC and data coming from the probe into an RS232C asynchronous transmission format, HALF-DUPLEX mode.

Dimensions: 275 x 250 x 75 mm. Weight: 4.5 kg.

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University of Geneva-Switzerland
Web page: <http://www.unige.ch/cabe>
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