

The Application of a VIP (Voltammetric In-situ Profiling) System in Estuaries for the Quantification and Speciation of Cu, Pb, and Cd Trace Metals



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Introduction

Recent literature has reported the use of a submersible, compact, fully automated, *in-situ* VIP (voltammetric *in-situ* profiling) system¹. The VIP system was developed by the University of Geneva, in collaboration with Idronaut, Milan. The VIP system allows the quantification of truly dissolved trace metals in aquatic systems through, rapid, continuous, automated profiling of trace metals (Cd(II), Cu(II), Pb(II)) in both sea and fresh water. The applications of the VIP system to dynamic estuarine waters are currently being explored. The VIP system has been deployed in the Tamar and Fal estuaries, U.K., in order to obtain valuable information on trace metal speciation which will lead to a better understanding of the bio-geochemistry within aquatic systems. This poster presents laboratory characterisation and estuarine deployment of the VIP system.

Instrumentation

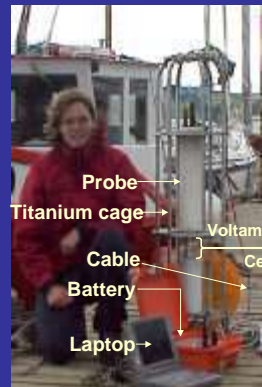


Figure 1 The VIP system on Quay side following a deployment

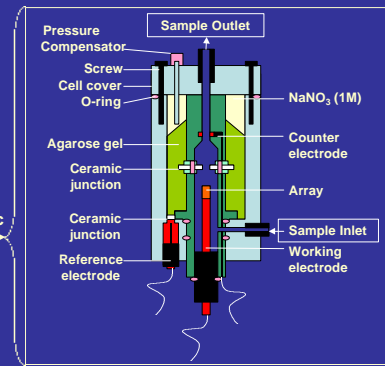


Figure 2 The VIP voltammetric flow-through cell

The VIP system (Figure 1) consists of a voltammetric probe with internal hardware that also houses a voltammetric cell through which sample is passed using a peristaltic pump. The voltammetric probe is remotely operated from the surface via a laptop by means of a coaxial cable that enables data transmission. The heart of the VIP system consists of a flow through cell which houses a Hg plated, iridium based working microelectrode (WE) (Figure 2). The WE is coated with a layer of agarose gel that prevents irreparable fouling of the iridium surface by organic species. The porosity of the gel is such that it allows penetration of metal ions to the WE, whilst acting as a barrier to larger organic species, that would cause bio-fouling. An equilibration period is required during analysis whilst sample equilibrates with the gel.

Voltammetric Scan

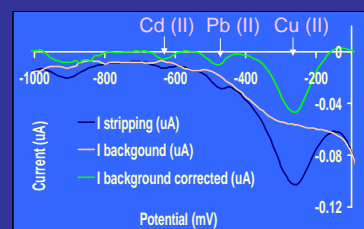


Figure 3 Anodic stripping curve, showing metals in, Tamar estuary sample, Plymouth, England.

Sample is pumped through the cell and trace metals are reduced and 'pre-concentrated' or 'deposited' in the Hg film. After deposition, (usually between 5 to 30 min) the metals are re-oxidised at their specific reduction potential producing an anodic current directly proportional to the concentration of trace metal in the sample (Figure 3).

References

1. Tercier, M. L., Buffle, J., *Analytical Chemistry*, 1996, 68, 3670-78
2. VIP Owners Manual, 2002, www.idronaut.it

Laboratory Optimisation

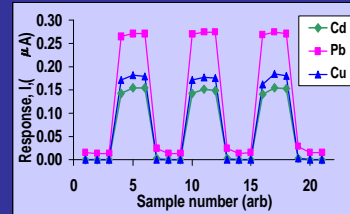


Figure 4 At manufacturers recommended Conditions

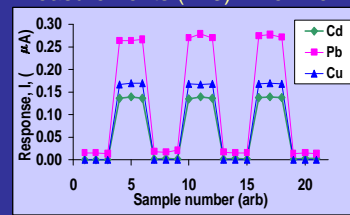


Figure 5 At optimised conditions

The instrument was set to the manufacturers recommended settings, for gel equilibration period and for sample flushing through the system between samples². Standards (n=3), containing 20 nM of each of Cu, Cd, and Pb, followed by blanks (n=3) were measured at these settings (Figure 4). A memory effect was observed for all metals. In addition there was an underestimation of the first measurement of the standard in a series of measurements (n=3). The memory effect was found to be due to insufficient flushing of the system with fresh sample. The underestimation of the first measurement due to insufficient gel equilibration period. By increasing both the sample flushing and gel equilibration period these problems were eliminated (Figure 5).

Analytical Figures of Merit

At 20 Minutes deposition:

At 40 Minutes deposition:

Metal	LOD (nM)	Precision (at 0.25 nM) (%)	Linear Range (nM)	Correlation (R ²)	Metal	CRM Total Dissolved (nM)	Stated Value (nM)	VIP Determined Value (nM)
Cd	0.200	2.10	0.200 to 20.0	0.9984	Cd	River water (SLRS-3)	0.116 ± 17	0.128 ± 12
Pb	0.100	3.81	0.100 to 17.5	0.9999	Pb	River water (SLRS-3)	0.415 ± 34	0.434 ± 10
Cu	1.500	4.29	1.500 to 21.0	0.9961				

Effect of Estuarine Variables

An estuarine environment is highly dynamic and physico-chemical variables within it lead to changes in the speciation of trace metals. This section shows the results of subjecting the system, in the laboratory, to the various variable estuarine conditions.

2. Temperature

Temperature effects the diffusion kinetics to, and charge transfer at, the WE leading to changes in current response. For totally reversible reactions, temperature follows Arrhenius behaviour shown by Figure 6.

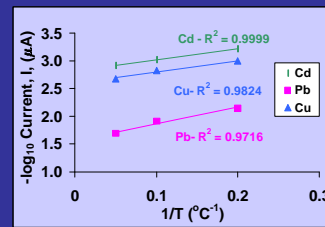


Figure 7 Arrhenius behaviour of WE

The gradient of Figure 7, gives the value of $-\Delta G$ for reduction. Current response (μA) of the instrument changes between 1-4 % per degree of the response @ 20°C and correction must be made.

$$i = i_0 \exp\left(\frac{-\Delta G^*}{RT}\right)$$

Figure 6 Arrhenius equation

3. pH

The effect of pH between pH 2 to pH 7.8 on current response was investigated using a sample containing 10nM of Pb and Cd, at 15 mins deposition (Figure 8).

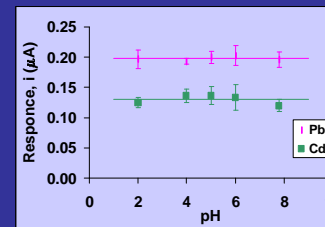


Figure 8 The effect of pH on current response.

No significant change in current response was observed in the pH range 2 to 7.8, so no pH correction is needed.

1. Salinity

The conductivity of estuarine water in the salinity range 0.5 to 35 ‰ shows a linear relationship *cf.* to NaNO₃ (0.05 to 0.6 M). NaNO₃ was used as an analogue for estuarine waters.

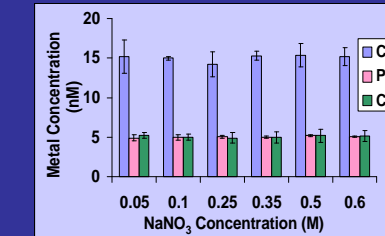


Figure 9 The effect of salinity analogue on Cu, Pb and Cd

Standards containing Cu (15 nM), Pb and Cd (5 nM) were made up at increasing NaNO₃ concentrations. No change in response of the instrument was found. It was therefore concluded that salinity does not affect the response (Figure 9).

2. Dissolved Oxygen

Calibrations using oxygen saturated and de-oxygenated standard were carried out at pH 2 and there was found to be no effect on the sensitivity of the instrument (Figures 10-12).

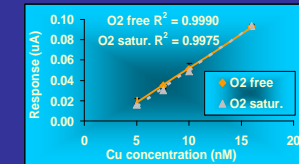


Figure 10 The effect of dissolved oxygen on Cu

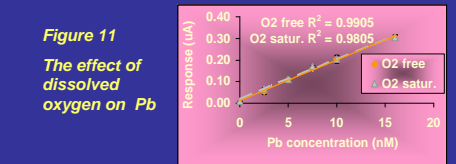


Figure 11 The effect of dissolved oxygen on Pb

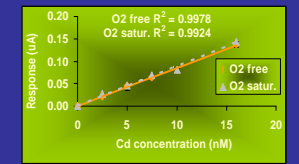


Figure 12 The effect of dissolved oxygen on Cd

In situ Deployments

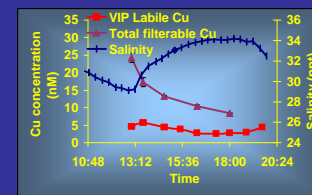


Figure 14 Tidal cycle showing speciation of Cu in the Tamar estuary

A tidal cycle was undertaken in the Tamar estuary (a macro-tidal estuary) (Figure 13) on 15/11/01 and results for Cu shown in (Figure 14). The concentration of the VIP



Figure 13 The Tamar Estuary, Devon, UK

labile Cu is much lower than the total filterable (0.45 μM , polycarbonate filter). The VIP measures only truly dissolved Cu ions. The total filterable concentration includes metal ions bound to organic/ inorganic ligands and to colloids. The largest difference between the two measurements was observed at lowest salinity (highest riverine input) suggesting that a large proportion of Cu is strongly bound, in low salinity waters, compared to seawater. Maximum concentrations for both VIP labile and total filterable Cu were observed at lowest salinity (ebb tide).

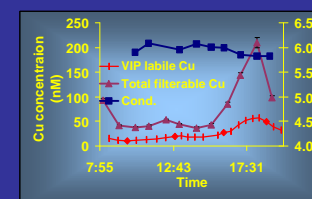


Figure 16 Tidal cycle showing Cu speciation in the Fal estuary

The Carnon river receives a large amount of acid mine drainage, and historically, the estuary receives large concentrations of trace metals. A Cu tidal cycle in the Carnon estuary on 02/08/02 is shown (Figure 16). A large difference between the two metal fractions (VIP labile and total filterable) was observed at lowest salinity, as in the Tamar survey, showing Cu is bound. Maximum concentrations for both VIP labile and total filterable Cu were observed at lowest salinity values. The concentrations also show much higher VIP labile Cu concentrations than in the Tamar.

Acknowledgements

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