

COMPLEXING GEL INTEGRATED MICROELECTRODE ARRAY FOR DIRECT DETECTION OF FREE METAL ION CONCENTRATIONS IN NATURAL WATERS.

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Abstract. A novel Complexing Gel Integrated Microelectrode (CGIME) for direct measurements of free metal ion concentrations in natural waters has been developed. It is prepared by successive deposition of a chelating resin, an antifouling agarose gel and Hg layers on an 100-interconnected Ir-based microelectrode array. Reliability of trace metal accumulation on the chelating resin, their release in acidic media and detection using Square Wave Anodic Stripping Voltammetry has been demonstrated by a series of replicate laboratory tests. Finally, the CGIME sensor has been applied to the Cu and Pb free metal concentration measurements in sea water samples. The CGIME results were comparable with those of free metal ion concentration measurements performed using Hollow Fiber Permeation Liquid Membrane (HF -PLM). Similar concentration values were found for both metals with both techniques which validate CGIME measurements.

1. INTRODUCTION

Measurements of relevant fractions of trace metals in natural waters are essential to improve our understanding of their behavior and long-term impact [1]. Free metal ions is of particular interest since these species are related to biological uptake. There is however actually no direct analytical technique which allows their detection in complex media.

Therefore, a novel Complexing Gel Integrated Microelectrode (CGIME) for specific monitoring of free metal ions in natural waters was developed. It is based on the Gel Integrated Microelectrode (GIME) [2] and the Diffusion Gradients in Thin-film (DGT) principles [3]. It consists of an 100-interconnected Hg plated Ir-based microelectrode array covered by a thin 3.5 • m layer of complexing resin, itself covered by a thick 300 • m antifouling agarose gel layer. During equilibration with the test water, metals accumulate on the resin proportional to free metal ion concentrations. After equilibration, the fixed metals are released by acid and immediately measured by the voltammetric electrode. A major advantage of this approach over the classical preconcentration by a resin placed in the flow of a test solution, is that the colloids do not contaminate the resin as they do not penetrate the agarose gel. The key features of this development are i) the choice of appropriate complexing gel layers based on the complexing capacity and stability and acid-base constants of the corresponding polymer or nano-particles; ii) the optimisation of a procedure allowing reliable and uniform covering of the microelectrode array surface with a few tens • m thick complexing layer and iii) the CGIME calibration as a function SW pre-concentration time as well as accumulation time and trace metal concentration in the test solution. In this paper, these features as well as an example of CGIME application for direct free metal ion concentration measurements in real sea water samples are presented.

2. EXPERIMENTAL SECTION

2.1 Complexing gel layers

Preliminary screening of possible complexing resins for the development of the CGIME sensor was made on the basis of the literature survey and the following criteria:

- It should have a complexing capacity in the range 2.5 to 3.5 meq/g and stability constant in the range 5.7 to 10.6 for the trace metals of interest (i.e. Cu, Pb, Cd and Zn),
- It should be selective to Cu, Pb, Cd, Zn (as well as Ni, Co and Mn) at similar pH and in a pH range 6 to 9,
- It should desorb trace metal without using too drastic chemical conditions (i.e. $\text{pH} \geq 1$).

Another important criteria which must be considered is the bead size of the resin. Indeed, the thickness of the CGIME complexing layer should be in few tens of micrometer range to insure accumulation of trace metals proportional to free metal ions. Based on these criteria, the Microchelex resin (polystyrene immobilized iminodiacetate, Cetac Technologies-USA), in the bead form having size of $0.2 \mu\text{m}$ was selected as trace metal complexing resin to prepare the novel CGIME sensor.

2.2 Microchelex based CGIME preparation

The preparation of the CGIME involves the successive deposition of the complexing resin, the agarose gel and the Hg layers. The deposition of the Microchelex resin on the interconnected 5×20 Ir-based microelectrode array (chip size: 1.8×4 mm; [2]) was performed as follows: $1 \mu\text{L}$ of a 2.5% (p/V) Microchelex aqueous suspension solution was deposited in the containment ring surrounding the sensor chip by means of a micro-pipette. The sensor was gently rotated in the four directions until a white deposit, covering the whole sensor surface, was observed. Then, it was stored in a horizontal position, in a plastic box at least 12 hours to insure complete evaporation of water. The theoretical thickness, calculated by assuming an uniform deposit, is $3.5 \mu\text{m}$. The agarose gel antifouling membrane was then deposited on the chelating resin by filling the containment ring with 1.5% LGL agarose gel at 80°C by means of a pipette. Using a computer controlled Amel 433A potentiostat, Hg deposition was performed at a constant E of -400 mV in a N_2 degassed $5 \text{ mM Hg}(\text{CH}_3\text{COO})_2$, 10^{-1} M HClO_4 solution using a deposition time of 7 min. Hg reoxidation was performed by scanning the potential from -300 mV to $+300$ mV in a N_2 degassed 1 M KSCN solution.

2.3 Microchelex based CGIME characterization

The Microchelex based CGIME was first characterized by performing voltammetric measurements of trace metal desorption kinetics using a computer controlled Amel 433A potentiostat. The procedure used was as follows. SWASV voltammetric measurements were first performed in 0.1 M NaNO_3 , 0.1 M HNO_3 blank solution to release trace metal impurities fixed on the resin. When a flat base line was observed, the solution was replaced by a N_2 degassed 0.1 M NaNO_3 solution spiked with known concentrations of Cu(II), Pb(II) and Cd(II). The CGIME was left to equilibrate in this solution for various time in the range 10 to 180 min. The solution was quickly replaced by a N_2 degassed acidified (HNO_3 pH 1 or 2) 0.1 M NaNO_3 blank solution and automatic replicate SWASV measurements were performed over a period of 2 to 12 hours. At pH 2, the decomplexation times of Pb(II) and Cd(II) were found to be ≥ 2 hours and < 40 min respectively. No signal was obtained for copper, suggesting that a pH 2 is insufficient to release strongly complexed metal despite at this pH, theoretically, the complexing sites of the resin should be totally protonated. This is due to the slow decomplexation kinetics and is supported by the fact that at pH 1 the decomplexation is much faster and similar for the three target metals, i.e. typically 30 min.

SWASV metal concentrations measured using CGIME sensors depend on three different parameters: i) the free metal ion concentrations in the test samples; ii) the accumulation time and iii) the SWASV pre-concentration time. Systematic tests have been performed to study the influence of these parameters. SWASV measurements using pre-concentration time in a range 1 to 30 min were performed after CGIME accumulation steps performed in constant conditions of Me concentrations and using an accumulation time of 3 hours. For the three metals and both tests, a linear increase in peak current intensities was observed up to $t_{\text{dep}} \leq 5$ min, then the peak current intensities tend to level off (Fig. 1).

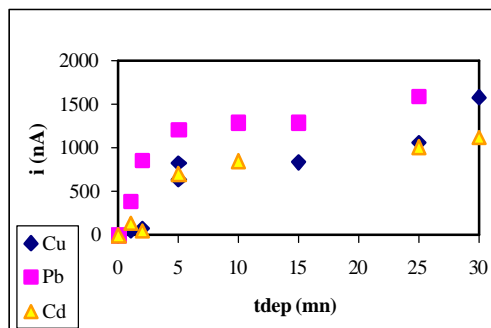


Figure 1: Typical example of CGIME metal peak current intensities as a function of the SWASV pre-concentration time. Accumulation step performed under constant conditions.

A SWASV $t_{\text{dep}} = 5$ min was used to test the influence of the two other parameters. For point i), the CGIME was left to equilibrate for a constant time in 0.1M NaNO₃ solution spiked with various concentrations of Cu(II), Pb(II) and/or Cd(II). For point ii), the CGIME was left equilibrated in times in the range 1 to 15 hours in freshly prepared 0.1M NaNO₃ solutions spiked and concentrations of each metal were kept constant. Typical example of voltammograms obtained at different accumulation times are reported in Fig. 2. A linear relationship was obtained from the graphs $i_p = f(\text{Me concentration in solution})$ and $i_p = f(t_{\text{accumulation}})$ for the three target elements and the normalized slopes, expressed in nA/nM \times h_{accu}, were found to be similar (Table 1).

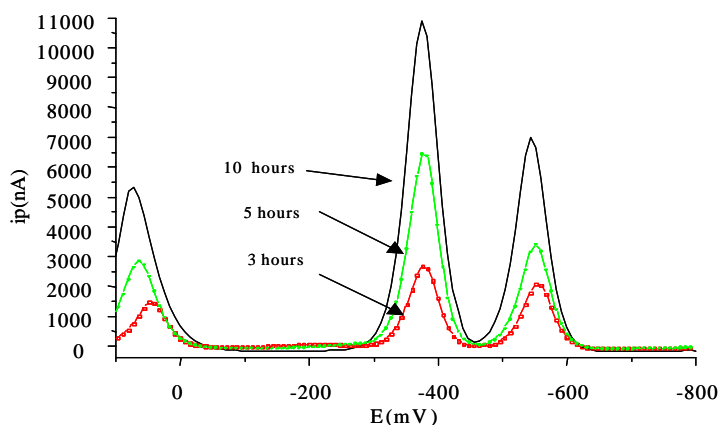


Figure 2: Example of CGIME SWASV voltammograms measured in pH 1 desorption solution after various accumulation times in 10 nM Cu(II), Pb(II) and Cd(II), 0.1 M NaNO₃ solution.

Table 1: CGIME normalized calibration slopes obtained from the curves $i = f(\text{metal conc.})$ and $i = f(\text{accumulation t.})$.

Metal of interest	Normalised slopes (nA / (nM _{sol} \times h _{accu}))		
	Pb	Cd	Cu
$i = f(C_{\text{sol}}) \{t_{\text{accu}} = 1\text{h}\}$	106.0	8.5	45.6
$i = f(C_{\text{sol}}) \{t_{\text{accu}} = 2\text{h}\}$	76.0	7.0	48.0
$i = f(t_{\text{accu}}) \{C_{\text{sol}}: \text{Pb} = 10 \text{ nM}; \text{Cd} = 10 \text{ nM}; \text{Cu} = 80 \text{ nM}\}$	68.9	5.1	31.3
$i = f(t_{\text{accu}}) \{C_{\text{sol}}: \text{Pb} = 5 \text{ nM}; \text{Cd} = 20 \text{ nM}; \text{Cu} = 40 \text{ nM}\}$	57.5	16.5	59.2
Average	77.1	10.7	46.0
Standard deviation	17.9	4.2	8.9
Average + SD	77.1 \pm 17.9	10.7 \pm 4.2	46.0 \pm 8.9

2.3 Preliminary on-field tests of the Microchelex-based CGIME.

Preliminary tests of the application of the Microchelex-based CGIME for direct free metal ion concentration measurements in real natural samples were performed at the Kristineberg Marine station (Sweden, August 18-26 2002). Average calibration curves reported in Table 1 were used to determine CGIME trace metal concentrations. For comparison purpose, hollow fiber PLM (HF-PLM) devices were used for laboratory separation and pre-concentration of free metal ions [4] in parallel to CGIME measurements. Laboratory CGIME and PLM measurements were performed in filtered and raw, non-acidified samples collected, using Go-Flos bottles, at different stations and depths in Gullmar fjord.

Samples were stored at 4°C directly after sampling and measured as soon as possible (i.e. max 24 h later). Results obtained for Cu and Pb with both techniques are reported in Fig. 3. Cd concentrations were found

to be below detection limit for both techniques. Despite some contamination problem, Cu and Pb concentrations measured using CGIME sensors and HF-PLM/ICP-MS were found to be relatively similar in most of the samples analysed.

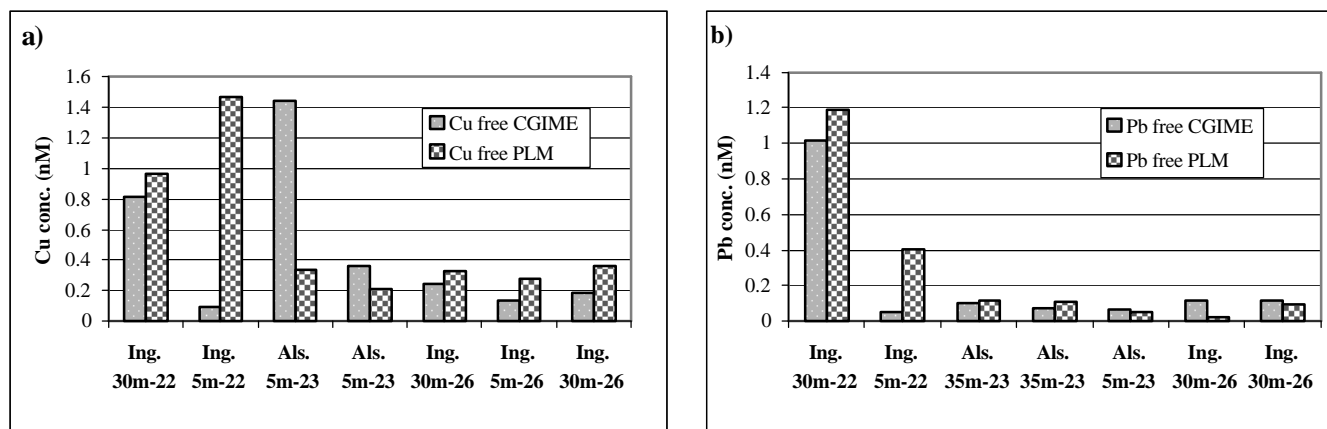


Figure 3: Comparison of a) Cu and b) Pb concentrations measured in samples of Gullmar fjord using CGIME and HF-PLM.

3. CONCLUSION AND DISCUSSION

The tests carried out with the CGIME developed in this work show that a thin complexing resin can be inserted between the surface of the sensor and the agarose gel without impairing the Hg layer deposition and the trace metal SWASV measurements. Systematic laboratory analytical tests have allowed to characterize and calibrate the Microchelex-based CGIME sensor. Results obtained for preliminary application studies of this CGIME sensor for direct measurements in real sea water are very promising. In particular, comparison with results obtained using HF-PLM/ICP-MS has demonstrated the potentiality of the CGIME sensor developed for direct detection of free metal ions in natural aquatic systems.

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