

## Full Paper

# Remote Stripping Analysis of Lead and Copper by a Mercury-Coated Platinum Microelectrode

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## Abstract

The performance of a remote stripping sensor based on mercury microelectrodes (MM-RS) for the in situ detection of trace metals in aquatic systems, was investigated. The submersible device employed here consists of a single mercury-coated platinum disk microelectrode assembled in a two-electrode cell configuration, and connected remotely by a 30 m long shielded cable. First, the MM-RS device is characterized in  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Pb}^{2+}$  synthetic aqueous solutions by applying cyclic voltammetry and anodic stripping voltammetry (ASV), respectively. The results obtained show that the small electrode dimensions and the related low currents involved, the long remote connection cable or the use of a two-electrode system do not cause noise effects or uncompensated resistance problems in the measurements. Using square-wave voltammetry in the stripping step, linear calibration graphs for  $\text{Pb}^{2+}$  ions over the concentration range  $1 \times 10^{-9} - 5 \times 10^{-7}$  M were obtained, and a detection limit, DL, of 0.15 nM was found. The relative standard deviation (RSD), at  $5 \times 10^{-8}$  M  $\text{Pb}^{2+}$  level, was within 5%. The effect of humic acid and of sodium dodecylsulfate surfactants on the stripping responses was also investigated. The performance of the submersible MM-RS system was tested for the in situ monitoring of the labile fraction of lead and copper on a site of the Lagoon of Venice. In situ  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  concentrations were monitored for about 8 hours, by leaving the sensor immersed in the lagoon waters (2 m depth) and recording the response every hour. Under these field conditions, reliable in situ data for the labile fraction of these metal ions with a satisfactory precision, the RSD being within 7 and 9 % for lead and copper, respectively, were obtained.

**Keywords:** Remote stripping sensor, Mercury microelectrode, Lead and copper, In situ analysis

## 1. Introduction

The growing demand for reliable and real-time monitoring of trace metal contaminants in natural waters has prompted the development of new methods and appropriate sensors to perform in situ measurements with little perturbation of the aquatic system [1–3]. Voltammetric stripping analysis has been employed widely for trace element analysis and a few submersible stripping systems, based either on gold or mercury-coated metal microelectrodes, have been developed for performing in situ monitoring of trace metals [2–7]. In particular a 100- $\mu\text{m}$  gold fiber electrode, inserted in a three-electrode system, has been successfully used for the remote in situ detection of the bioavailable fraction of heavy metals present in natural waters [2, 4, 8–10]. This type of mercury-free submersible device may suffer, however, from intermetallic interference when, for instance, the simultaneous detection of copper and lead is required.

Mercury-coated iridium microelectrodes covered with an agarose gel membrane [6], and microlithographically fabricated iridium microelectrode arrays [7] have also been developed and applied for in situ monitoring of trace metals in natural aquatic systems. Although these mercury-coated systems have displayed good results, they are somewhat laborious to construct.

The objective of this paper was to verify the performance of a remote mercury microelectrode system with a simpler design, for the in situ detection of lead and copper in natural aquatic systems. In fact, single mercury microelectrodes, fabricated onto platinum disk microelectrodes, have been applied successfully for laboratory-based stripping measurements of trace metals in real samples such as wine, rain and sea waters, pore-waters of sediments [1, 11–16]. Hg-coated platinum microelectrodes can be prepared easily, possess a good stability and, moreover, their size can be determined accurately [11, 13, 18]. In the remote submersible device described here, a single mercury-coated platinum microelectrode is assembled in a two-electrode cell configuration and connected remotely by a long shielded cable. Since, with this configuration, currents of about two orders of magnitude lower than those typically recorded with microfibers, or microelectrode arrays, are involved, preliminarily the effects of the long connecting cable on the voltammetric responses were assessed on synthetic solutions containing  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Pb}^{2+}$  ions. An application concerning in situ measurements of the labile fraction of lead and copper in the Lagoon of Venice was also addressed.

## 2. Experimental

### 2.1. Reagents and Samples

Titrisol lead and copper standards (Merck, Darmstadt, Germany) were used to prepare stock solutions ( $1000 \text{ mg L}^{-1}$ ) of these metal ions. The supporting electrolytes (NaCl or KCl) for trace determinations in synthetic samples, and the hydrochloric acid used to acidify the natural samples for the determination of the total metal concentration, were of Suprapur grade (Merck, Darmstadt, Germany). The other chemicals employed were of analytical-reagent grade.  $\text{Ru}(\text{NH}_3)_3\text{Cl}_3$  was purchased from Alfa Aesar (Johnson Matthey GmbH, Karlsruhe, Germany). All synthetic solutions were prepared with water purified with a Milli-Q purification system (Millipore, Bedford, USA). When necessary, pure nitrogen (99.99%) supplied by SIAD (Bergamo, Italy) was used to remove oxygen from the test solutions.

In situ measurements were performed at a site of the Lagoon of Venice located in the Canale della Giudecca, in the center of Venice. Laboratory and instant lagoon measurements were made in the sample without any chemical or physical pre-treatment. In particular, no filtration for solid particles and colloidal compounds elimination was employed prior to analysis. The samples collected for laboratory experiments, were stored at  $4^\circ\text{C}$  until their use.

### 2.2. Apparatus and Procedures

Chronoamperometric, cyclic, linear sweep and square-wave anodic stripping voltammetric experiments were carried out using a PAR Mod. 283A potentiostat/galvanostat (EG&G

Princeton Applied Research, Princeton, N.J. USA), together with the PAR 270 electrochemical software (EG&G).

The schematic diagram of the submersible stripping sensor employed, which comes from a modification of the earlier configurations containing the gold fiber [2, 4, 8–10], is shown in Figure 1. It consists of a two-electrode assembly, which contains an ex situ constructed mercury-coated platinum microelectrode, and a homemade Ag/AgCl/KCl reference electrode. This assembly is mounted in a PVC housing tube of the remote tool and connected through an environmentally sealed rubber connector to the shielded cable, about 30 m long. To protect the working electrode from water movements and other disturbances during the field experiments, a cylindrical PVC tube, about 5 cm long, was mounted to the threaded end of the housing unit of the sensor.

The platinum microdisk electrode, which served as the substrate for mercury deposition, was prepared by sealing a  $25 \mu\text{m}$  diameter platinum wire (Goodfellow Metals, Cambridge, UK) into bicomponent epoxy resin. The final tips were typically 1.5 cm long and 2 mm circular base diameter. A male screw was sealed to one end of the electrode body, for mounting it to the PVC housing tube.

Prior to mercury deposition, the Pt disk surface was polished mechanically with aqueous suspensions of graded alumina powder of different sizes (1, 0.3 and  $0.05 \mu\text{m}$ ) supported on a polishing microcloth (Buehler, Lake Bluff, IL, USA). A range of mercury sphere-caps of different sizes were prepared ex situ, by cathodic deposition of mercury under potentiostatic control, onto the platinum microdisk, as reported elsewhere [13]. The height,  $h$ , of the sphere-caps was calculated on the basis of the plating charge spent during the electrodeposition step [13, 17–19]. Under the different experimental conditions employed here, the plating charge

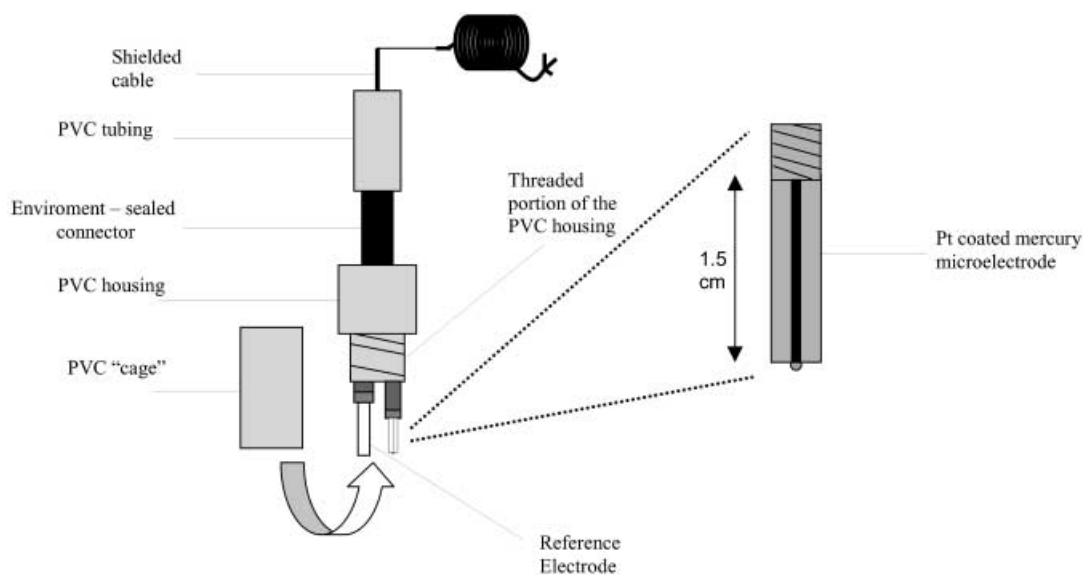


Fig. 1. Schematic diagram of the Pt-coated mercury microelectrode stripping sensor.

ranged from 12.0 to 76.1  $\mu\text{C}$ , and the heights of the mercury deposits varied from 6.9 to 22.8  $\mu\text{m}$ , respectively. In what follows, the sizes of the mercury microelectrodes will be referred to as  $h/r$ , that is the sphere-cap height to the electrode's basal radius,  $r$ , ratio.

The steady-state diffusion limiting current  $I_d$  at the platinum disk or at the sphere-cap mercury microelectrodes can be predicted by [13, 15, 17–20]:

$$I_d = knFDC^b r \quad (1)$$

where  $k$  is a parameter that depends on the geometry of the microelectrode (for the disk  $k = 4$  [20], while for the sphere-caps, it depends on the  $h/r$  ratio [13, 17–20]),  $C^b$  is the bulk concentration of the electroactive species and the other symbols have their usual meanings. The effective radius of the Pt microdisk substrate, or the experimental values of the geometric coefficient  $k$  for the Hg sphere-caps were determined by recording the steady-state diffusion limiting current from a 1 mM  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  in Milli-Q water solution containing 0.1 M  $\text{NaClO}_4$ , and using Equation 1. The sphere-caps employed here were characterized by  $k$  values ranging from 4.9 to 10.2.

For comparison, voltammetric experiments were carried out with the mercury microelectrode either connected (MM-RS) or not (MM) to the remote device.

In the laboratory experiments, the electrochemical cell was located inside a Faraday cage made of sheets of aluminium. The cell was made either of glass or PTFE for stripping analysis. In the latter case, it was cleaned before the experiments using recommended procedures for trace element analysis [21].

Stripping measurements were carried out in quiescent synthetic solutions or natural samples, both unpurged and purged with a nitrogen flux. Unless otherwise stated, the following conditions were employed for square-wave anodic stripping measurements (SWASV): pulse height of 50 mV, step height of 2 mV and a frequency,  $f$ , of 100 Hz.

A Metrohm 605 pH-meter (Herisau, Switzerland) was employed for pH measurements, and a Wild Heerbrugg microscope (Germany) was used for examining the microelectrode surface.

### 3. Results and Discussions

#### 3.1. Cyclic Voltammetric Characterization of the MM-RS Device

Figure 2 shows typical cyclic voltammograms (CV) recorded at  $10 \text{ mV s}^{-1}$  in a 1 mM  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3 + 0.1 \text{ M KCl}$  solution, with a mercury microelectrode ( $h/r$  ratio = 0.97) in the MM-RS (full line), and MM configuration (dotted line). Both voltammograms display the sigmoidal shape expected for a microelectrode working under steady-state conditions. In the MM-RS configuration, however, the voltammogram displays a larger degree of hysteresis which is probably due to a slightly larger contribution of capacitive current. The

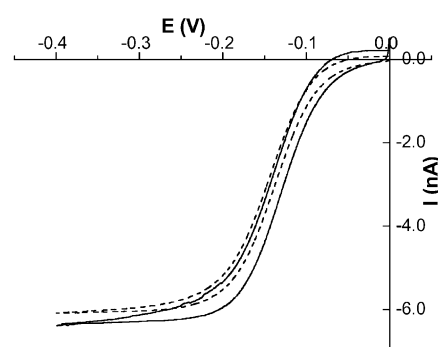


Fig. 2. Cyclic voltammograms recorded in 1 mM  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3 + 0.1 \text{ M KCl}$  aqueous solution with a mercury microelectrode,  $h/r = 0.97$ , in the (—) MM-RS, and (---) MM configurations. Scan rate,  $10 \text{ mV s}^{-1}$ .

analysis of the Tomes difference ( $E_{1/4} - E_{3/4}$ ), i.e., the difference between the potentials recorded at 1/4 and 3/4 of the steady-state limiting current, of the forward waves gave  $58 \pm 2$  and  $56 \pm 1 \text{ mV}$  values for the MM-RS and MM systems, respectively; these agree well with 56.5 mV expected theoretically for a one-electron reversible process at  $25^\circ\text{C}$  [22]. Also the half-wave potential,  $E_{1/2}$ , and the diffusion limiting currents,  $I_d$ , values obtained at the same mercury microelectrode assembled in the two different configurations were very close to each others ( $E_{1/2} = -135 \pm 4 \text{ mV}$ ,  $I_d = 6.18 \pm 0.12 \text{ nA}$ , the differences being within 3%).

Replicate measurements performed with the MM-RS configuration, yielded voltammograms whose  $E_{1/2}$  and  $I_d$  values were reproducible within 2% ( $n = 5$ ) with that shown in Figure 2. CV and results similar to those shown above were also obtained with a range of sphere-caps of different sizes, assembled in both MM-RS and MM configurations. The mercury-coated platinum microelectrodes employed here displayed also a good stability and resistance against fall of the mercury deposit, even if used for several hours. In fact, a number of repeated sets of three replicate measurements performed with the MM-RS system over a working day (8 hours) displayed current values reproducible within 3%.

#### 3.2. ASV Measurements

In order to verify the performance of the MM-RS device under ASV conditions, a series of measurements were carried out on synthetic solutions containing  $\text{Pb}^{2+}$  as test ion. Figure 3 shows typical anodic stripping voltammograms recorded in a  $5.0 \times 10^{-8} \text{ M Pb}^{2+} + 0.5 \text{ M NaCl}$  solution, both with the MM-RS (full line) and MM (dotted line) system, setting the deposition potential,  $E_d = -1.1 \text{ V}$  and a deposition time,  $t_d = 2 \text{ min}$ . Both square-wave voltammetry in unpurged solution, (SWW, Fig. 3a), and linear sweep voltammetry in purged solution, (LSV, Fig. 3b), were employed during the stripping step. Table 1 summarizes relevant stripping voltammetric parameters, i.e., peak

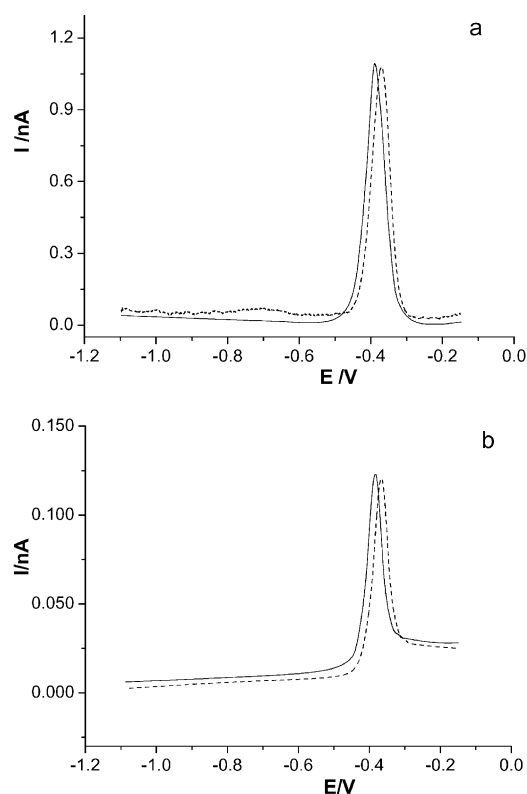


Fig. 3. ASV responses recorded in a  $5.0 \times 10^{-8}$  M  $\text{Pb}^{2+}$  + 0.5 M NaCl aqueous solution with a mercury microelectrode,  $h/r = 0.99$ , in the (—) MM-RS, and (---) MM configurations, employing as stripping mode: a) SWV, unpurged solution,  $E_d = -1.1$  V,  $t_d = 2$  min,  $f = 100$  Hz; b) LSV, purged solution,  $E_d = -1.1$  V,  $t_d = 2$  min; scan rate,  $20 \text{ mV s}^{-1}$ .

current,  $I_p$ , peak potential,  $E_p$ , and peak width at half height,  $w_{1/2}$ , obtained for both configurations and stripping modes. It can be observed that also in ASV experiments, the signals are very similar regardless of the fact that the mercury microelectrode is connected or not to the remote system, being the differences in the ASV parameters within 3%. In particular, it is worth noticing that  $w_{1/2}$  values obtained here compare quite well with the theoretical value of 49.6 mV for SWV, and the experimental value of 45 mV reported in the literature for LSV for thin mercury film electrodes [23, 24]. Moreover, the agreement between  $w_{1/2}$  data obtained with the MM-RS and MM systems indicates that, in the anodic stripping mode, the contribution of the capacitive current on the voltammetric response is negligible even in connection

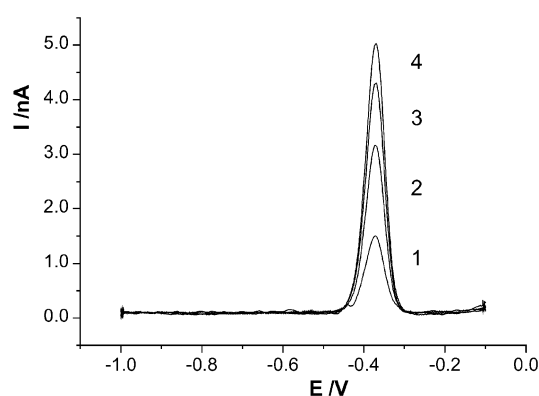


Fig. 4. Effect of the deposition time. SWASV responses recorded with the MM-RS system in  $0.1 \mu\text{M Pb}^{2+}$  + 0.5 M NaCl aerated aqueous solution,  $t_d = 0$  (1), 120 (2), 180 (3), 300 s (4).  $E_d = -1.0$  V,  $f = 100$  Hz.

to LSV technique. Because in situ measurements in natural waters must be performed in the presence of oxygen, and due to the higher sensitivity, only SWV was further considered here.

The influence of deposition time and frequency on the stripping responses was investigated. Figure 4 shows a series of SWASV responses recorded with the MM-RS system in a  $0.1 \mu\text{M Pb}^{2+}$  aerated aqueous solution, varying the deposition time  $t_d$  over the range 0–300 s (in connection to a deposition potential of  $-1.0$  V). Similar measurements were also carried out in aqueous solutions containing lower  $\text{Pb}^{2+}$  ions concentrations (down to 5 nM), but over the deposition time range of 10–30 min. In any case, both the anodic peak current,  $I_p$ , and stripping charge,  $Q_a$ , values were linearly dependent on time, and the linear regression analysis for  $I_p$  vs.  $t_d$  and  $Q_a$  vs.  $t_d$  plots, yielded correlation coefficients,  $R^2$ , larger than 0.999.

The peak current, as expected, depended also linearly on frequency, and over the range 20–200 Hz, the linear fit  $I_p$  vs.  $f$  gave a correlation coefficient of 0.9992.

The effect of metal ion concentration on the anodic stripping peak was examined, using  $f = 150$  Hz. Typical SWASV responses obtained for  $\text{Pb}^{2+}$  aerated aqueous solutions are shown in Figure 5. Over the wide concentration range of  $1 \times 10^{-9}$ – $5 \times 10^{-7}$  M, peak current and/or stripping charge against metal ion concentration yielded straight lines with correlation coefficients higher than 0.999. In particular, the linear fit of  $I_p$  vs.  $C_{\text{Pb}}$  plot gave a  $R^2$  value of

Table 1. SWV and LSV stripping parameters obtained for a  $5.0 \times 10^{-8}$  M  $\text{Pb}^{2+}$  solution.  $E_d = -1.1$  V;  $t_d = 2$  min. SWV conditions: pulse height 50 mV, frequency 100 Hz, step height 2 mV. LSV conditions: scan rate  $20 \text{ mV s}^{-1}$ . MM-RS: measurements conducted with a Hg microelectrode connected to the remote sensor; MM: measurements conducted with a Hg microelectrode in the classical two-cell configuration; in parenthesis: standard deviations calculated for five replicates.

	$I_p$ (nA)		$E_p$ (mV)		$w_{1/2}$ (mV)	
	SWV	LSV	SWV	LSV	SWV	LSV
MM-RS	1.06(0.04)	0.109(0.03)	−388(3)	−385(3)	60(2)	46(2)
MM	1.04(0.03)	0.106(0.02)	−370(3)	−368(3)	59(2)	45(2)

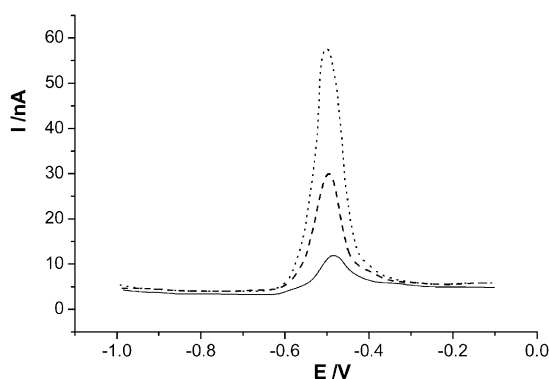


Fig. 5. SWASV responses recorded with the MM-RS system in 0.5 M NaCl aerated aqueous solutions containing:  $\text{Pb}^{2+}$  0.1 (—), 0.3 (---), 0.5  $\mu\text{M}$  (⋯⋯).  $t_d = 600$  s,  $E_d = -1.0$  V,  $f = 100$  Hz.

0.9996, a slope,  $m$ , of  $61.8 \text{ nA } \mu\text{M}^{-1}$  and an intercept of  $0.018 \text{ nA}$ . From the slope and the standard deviation of mean value of the blank response,  $s_B$ , ( $0.0217 \pm 0.003 \text{ nA}$ ) obtained under the experimental conditions employed, a detection limit, calculated as  $DL = 3 s_B/m$  [25], of  $0.15 \text{ nM}$  was evaluated.

The reproducibility of the anodic stripping peak of  $\text{Pb}^{2+}$  in aerated solutions at  $5 \times 10^{-8} \text{ M}$   $\text{Pb}^{2+}$  level, provided a relative standard deviation (RSD) for both peak current and charge within 5% (from six replicates).

The ASV signals recorded with a mercury electrode in natural waters, may be affected by the presence of organic and/or inorganic materials, dissolved or present in the medium in colloidal forms [3, 6]. In order to investigate on this aspect, humic acid (HA) and sodium dodecylsulfate (SDS) were taken as test complexing and surfactant matters. Their influence on the  $\text{Pb}^{2+}$  stripping peaks recorded with the MM-RS system was investigated, in both aerated and purged solutions using either SWASV or LSASV techniques, respectively. In particular, tests were done in 0.5 M NaCl solutions containing  $\text{Pb}^{2+}$  ions over the  $5 \times 10^{-8} - 5 \times 10^{-7} \text{ M}$  range, in connection to increasing concentrations of HA (from 10 to  $60 \text{ mg L}^{-1}$ ) or SDS (from 1.0 to  $5 \text{ g L}^{-1}$ ). Under such conditions, the major effect observed was a stripping peak current decrease, while a negligible variation on shape or peak potential was observed with both techniques. In particular, peak currents decreased, as compared to those obtained in the absence of HA or SDS, of about 10% in the unnaturally high amounts of  $60 \text{ mg L}^{-1}$  HA and  $5 \text{ g L}^{-1}$  SDS solutions. Nevertheless, in any case both  $I_p$  vs.  $t_d$  and  $I_p$  vs.  $C$  plots were found to be linear, and the regression analysis gave again correlation coefficients higher than 0.999.

### 3.3. In Situ Monitoring of Trace Metals in Natural Aquatic Systems

The real-life performance of the submersible MM-RS system was tested for the in situ monitoring of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  on a site of the Lagoon of Venice. A typical SWASV

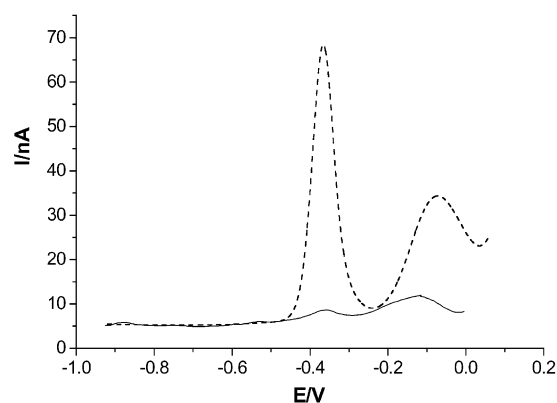


Fig. 6. SWASV responses recorded with the MM-RS system in the Giudecca Channel of the Lagoon of Venice, obtained: (—) in situ by immersion of the remote sensor (2 m depth) in the Channel waters; (---) in laboratory in the water sample acidified to pH 1 with HCl.  $E_d = -1.0$  V,  $t_d = 30$  min,  $f = 100$  Hz.

response obtained in the natural sample is shown in Figure 6 (full line). Two anodic peaks located at about  $-0.370$  and  $-0.120$  V, are observed. They were assigned to  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ , respectively, by a series of laboratory measurements performed on the untreated water samples, collected in the same site and depth in the lagoon, and spiked with different concentrations of the two ions. In fact both peak heights and/or areas increased upon spiking with increasing amounts of the two ions. The plots of the peak current (or stripping charge) against metal ion concentration, obtained using the same experimental SWASV parameters as in Figure 6, were linear up to  $1 \mu\text{g L}^{-1}$ , and the linear regression analysis gave correlation coefficients larger than 0.995. The plots thus recorded were used as external calibration plots for the quantification of the labile fraction of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions from the in situ measurements performed with the remote sensor in the lagoon.

The concentration of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  was monitored for about 8 hours, by leaving the sensor immersed in the same place and recording the response every hour. Figure 7 shows the results obtained, by averaging each datum from three replicates. The reproducibility found was satisfactory, the RSD being within 7 and 9% for lead and copper, respectively. As can be seen from these results, during this relatively short monitoring period, some variations of the in situ  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  concentrations (of 33 and 46%, as maximum, respectively) are observed. These variations could be attributed to relevant local concentration changes in the Lagoon water system due to tide or wave movements, or other parameters (temperature, oxygen content, etc.) occurring during the experiments [26]. It must be noted that relatively small changes of water fluxes that may occur during the deposition step should not affect the ASV signals, due to the relatively low sensitivity to solution flow rates that characterizes the microelectrodes employed here [27, 28]. Moreover, the experimental set-up of the MM-RS device, which includes a PVC cage to protect the working electrode (see Sec. 2. and Fig. 1), allows one to make the

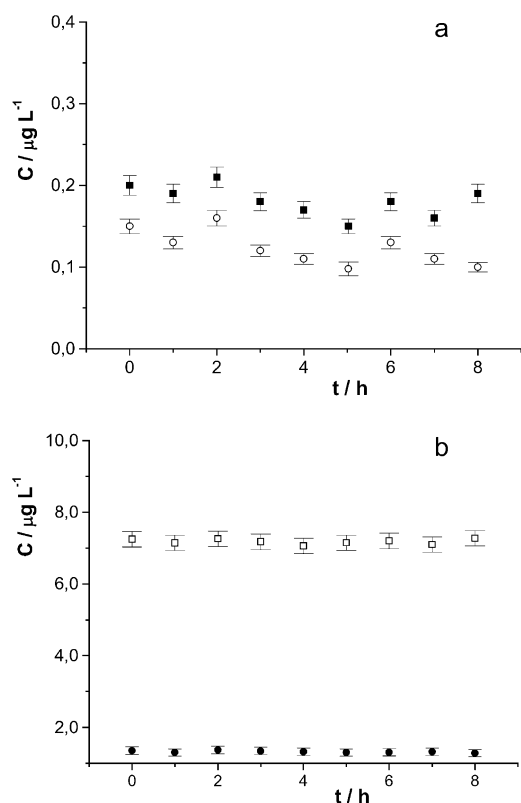


Fig. 7. Metal ions monitoring with the MM-RS system in the Giudecca Channel of the Lagoon of Venice: a) in situ by immersion of the remote sensor (2 m depth) in the Channel waters, for (■) Pb and (●) Cu at natural pH (8.3); b) in laboratory in the water samples acidified to pH 1 with HCl, for (□) Pb and (●) Cu. SWASV conditions:  $E_d = -1.0$  V,  $t_d = 30$  min,  $f = 100$  Hz.

close surrounding of the microelectrode almost quiescent. However, in order to establish the effect of eventually small changes of water fluxes during the preconcentration step, some laboratory experiments with variable low stirring were carried out. In particular ASV responses were recorded with the MM-RS device in a  $0.1 \mu\text{M}$   $\text{Pb}^{2+}$  level solution while stirring at slow rates (300–600 rpm), to address the effect of seawater's natural convection [4, 8]. It was found that both current and charge of the  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  stripping peaks enhanced to a maximum extent of 15–20% with respect to the quiescent solution. This variability is however lower than that shown in Figure 7 over the whole period in which the two metal ions were monitored.

Some information on metal speciation were also acquired by performing laboratory measurements in the instant seawater samples acidified with hydrochloric acid to pH 1 and left to equilibrate overnight. Figure 6 (dotted line) includes the stripping response obtained under these conditions (see Fig. 6, full line). As expected, under acidified conditions larger SWASV stripping peaks are recorded, in agreement with the fact that in acidified sea-water samples, most of metal ions is released from their inert complexes, solid particles or colloids [29]. The metal ions content at pH 1 monitored in the sampled water is shown in Figure 7b. In this

case, the concentration levels during the monitoring period are substantially invariable.

It can be finally noted that the concentration levels measured here for these trace elements are in the same range of those available in the literature dealing with the in situ determination of the mobile fraction of these metal ions in the Lagoon of Venice [6, 10, 26].

#### 4. Conclusions

The results reported here indicate that in spite of the small electrode dimensions, the relatively low currents involved, the long remote connection cable, the electrical connections of the MM-RS system, or the use of two-electrode system, no problems, noise effects or uncompensated resistance in the measurements, were observed. The mercury microelectrodes here employed are therefore very compatible with the remote connection of the probe without leading to sensitivity problems of the system. They are also characterized by a very good stability and resistance against fall of the mercury deposit. Moreover, the design of the MM-RS system is simple and does not require a particular skilfulness for its construction.

From the results shown here, it can be also concluded that this submersible device is compatible with field operations, and it can be useful for in situ monitoring of the labile fraction of metallic species in the sea-water column, and for providing information on the spatial-temporal distribution of contaminants. Because of the good performance displayed by mercury microelectrodes for ASV measurements in low-ionic strength waters [24], the MM-RS system may favourably be employed for monitoring heavy-metal ions concentrations also in well waters.

#### 5. Acknowledgement

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