

Feature Article

Solid Microelectrodes for In Situ Voltammetric Measurements

Ivanka Pižeta,^{a*} Gabriel Billon,^b Jean-Claude Fischer,^b Michel Wartel^b^a Center for Marine and Environmental Research, Ruđer Bošković Institute, P. O. Box 180, 10002 Zagreb, Croatia

* e-mail: pizeta@rudjer.irb.hr

^b Université des Sciences et Technologies de Lille 1, Laboratoire de Chimie Analytique et Marine, Bât C8, 59655 Villeneuve d'Ascq Cedex, France – UMR CNRS 8013

Received: June 3, 2002

Final version: September 26, 2002

Abstract

Solid Au and Ag microelectrodes for both, model, and in situ voltammetric measurements, have been designed and tested. Amalgamation procedure and the parameters of measurement procedure are discussed. Differences between gold and silver electrodes were studied. Silver electrodes showed more stable behavior and were used prevalently for calibration and in situ measurements. Calibration of a 30- μm diameter Ag electrode for Mn(II), Fe(II), I(–I) and S(–II) showed good linearity with reasonable confidence intervals, necessary for quantification of the signals obtained in situ, with average sensitivity of 0.05, 0.01, 0.16 and 1.10 nA/($\mu\text{mol L}^{-1}$) and minimal detection limit of 3.5, 28, 0.3 and 0.05 $\mu\text{mol L}^{-1}$, respectively. Additional checking of the electrode sensitivity with the reduction peaks of oxygen is proposed.

Keywords: Microelectrode, In situ, Voltammetry, Mn(II), Fe(II), I(–I), S(–II)

1. Introduction

For an analytical chemist who uses voltammetric techniques it makes a great change to substitute a renewable mercury electrode for a solid one, as well as to work without standard addition and to rely upon a calibration line when determining the concentration of an analyte. However, to gain better understanding of the behavior, speciation and spatial and/or time distribution of elements such as sulfur, iron and manganese in natural waters and sediments, where the parameters such as oxygen abundance and redox potential vary considerably with time and depth and are difficult to preserve in samples, an in situ approach is a worthwhile challenge.

Theoretical and experimental approval for analytical utility of microelectrodes of different materials has been given [1–12]. They seem to meet our needs for in situ application. An important property and advantage of microelectrodes when compared to the electrodes of larger surfaces is their better signal/noise ratio. The reason is that the capacity of the double layer and the capacitive current decrease exponentially with the surface, while the faradaic current decreases linearly [1]. Microelectrodes are not greatly affected by stirring the solution since the concentration gradient exists only a few diameters from the electrode, which is very convenient in the case of in situ measurements, where no stirring is possible. Measurements in low conductivity media, which can be the case in the environment, are facilitated with the use of microelectrodes because the effect of uncompensated resistance between a working and a reference electrode is negligible due to low currents. Under these conditions it is not necessary to position the reference electrode near the working electrode,

there being no danger of polarizing the reference electrode by passing the cell current through it [13, p. 218]. A method for preparation of silver-based mercury film electrode was given in 1975 by Stojek and Kublik [4]. They took care about resolving the problems of mercury layer renewal and finding the optimal working conditions. Wikiel and Osteryoung [5] gave the dependence of peak height, position and half-width on mercury film thickness, frequency and diffusion coefficient of the reactant in direct square-wave voltammetry (DSWV) as well as in square-wave anodic stripping voltammetry (SWASV) for silver electrodes covered with mercury layer. They also gave the theoretical propositions for the conditions when peak current is proportional to the bulk concentration in the solution.

Liquid mercury is toxic and its use should be limited or completely avoided. Mikkelsen and Schröder report on the usefulness of alloy electrodes, the most interesting and promising being dental amalgam, i.e., silver amalgam [14, 15], but also silver contaminated with 4% of bismuth and PbO, or just silver electrodes [16]. They claim the property of high hydrogen overpotential of such alloys, and apply them for in situ monitoring of heavy metals. Their electrodes are a few millimeters in diameter and are not considered as microsensors. Silver and copper solid amalgam electrodes with mercury meniscus were shown appropriate for analytical purposes [17], while bismuth plated on a glassy carbon [18] has some advantages over mercury. Such electrodes, modified accordingly, could also be checked for application as in situ sensors.

In the literature there have lately been discerned two groups of authors dealing with voltammetric in situ measurements with solid microelectrodes. One group with G. W. Luther uses gold amalgamated microelectrode [19–29]

while the other group with J. Buffle uses iridium-based microelectrode array covered with antifouling gel membrane, through which, before measurement, mercury film is plated too [30–36]. If the electrode is not covered with protective gel, it could be cleaned from unwanted fouling by applying rather negative pulses, which in turn produce hydrogen that cleans the electrode. Both groups claim successful use of calibration plots and of a “pilot ion method” which relies upon the fact that the sensitivity ratios for all calibration plots of different reactants remain constant, thus making it necessary to determine only one plot before and after field measurement and recalculate the others.

It has now been well-established that the first biogeochemical transformations, which control early diagenetic processes in estuarine environments, begin to take place just at the water – sediment interface [37–39]. It is also necessary to focus the investigations on the first millimeters of the sedimentary column. The development of microelectrodes to be used in situ will allow better characterization of some diagenetic processes at a very fine vertical scale (for instance the reduction of O_2 , iron and manganese hydroxides, and sulphate species). Such a tool permits also scanning of a relatively fine interface area to point out the heterogeneity of a sediment (bound for instance to bio-irrigation). Moreover, a determination of concentration profiles of metal pollutants such as cadmium and lead is very useful for estimates of diffusive fluxes between the sediment and the aquatic system [40, 41], permitting a semiquantitative estimation of possible water contamination by the sediment.

In the frame of this work, Ag and Au microelectrodes appropriate for both, calibration and in situ measurements, have been constructed and critically compared. Also, the combination of previously published procedures has been modified for our specific needs, and the complete experimental set-up is described and optimized in order to obtain a good stability of the electrode response during experiments and to realize semiquantitative multielement analyses. With regard of the latter point, the difference between the complexity of sediment environment (in which organic compounds can interact with microelectrodes) and the standard calibration plots realized in laboratory prepared solution, combined with the “pilot ion method” and the propagation of errors that should be taken into account, justifies the term of semiquantitative analyses.

2. Experimental

2.1. Chemicals

The following chemicals were used during the experiments: HCl (30%), HNO_3 (65%) – Merck *s.p.*; $HClO_4$ (70%) – Prolabo *p.a.*; NaCl; NaOH · H_2O – Merck *s.p.*; $Hg(NO_3)_2 \cdot H_2O$ – Merck *p.a.*; $MnCl_2$ standard – Merck Titrisol; $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ Merck *p.a.*; KI Panreac *p.a.*; $Na_2S \cdot 9H_2O$ – Sigma, *p.a.*; NH_4CH_3COO , Na_2CO_3 , $NaHCO_3$ – Merck *p.a.*

Ultrapure water was generated using Milli-(Q) Plusfilter apparatus (Millipore); seawater of the salinity $S = 31\text{‰}$ was filtered through a $0.45 \mu m$ filter and kept at $4^\circ C$.

2.2. Instrumental Set-Up

A μ Autolab 2, multimode polarograph with the software package GPES 4.8 (Ecochemie, Utrecht) was used. Its small dimensions and high sensitivity make it usable for in situ measurements. A Methrom Stand 663 was used for amalgamation and calibration steps where a facility for proper purging with nitrogen was needed. Reference electrodes were all Ag/AgCl, and counter electrodes were a Pt wire or a glassy carbon rod. Measuring method was in most of cases square-wave voltammetry (SWV). All the potentials were measured versus Ag/AgCl.

2.3. Working Electrode Construction and Preparation

Working electrode was designed so as to enable its easy and skilful handling through all the phases of its preparation and measurement, both, in voltammetric cell and in situ. It is a pencil-shaped 12 cm long, 4 mm-diameter glass capillary. At its pointed end of 1 mm in diameter, a gold or a silver disk of $40 \mu m$ or $30 \mu m$ -diameter wire, respectively, which is sealed in glass, is facing the solution. At the other end, a stainless steel contact 2 mm in diameter is placed. In order to fit a standard electrochemical cell, an adapter has been designed, which holds the electrode and enables its fix positioning in the cell and subsequent tight sealing and degassing of the cell in the phases of mercury plating and performing model and calibration measurements.

A microscope of 100 fold magnification or larger is necessary for visual inspection of the electrode surface in every phase of its preparation.

The electrode was treated according to the suggestions of Stojek and Kublik [4], Wikiel and Osteryoung [5], Ciszowska et al. [42] and Brendel and Luther [19]. The surface of the electrode was polished when necessary with sand paper, finishing with $0.3 \mu m$ Al_2O_3 wet powder on appropriate tissue. Amalgamation and mercury plating of the electrode is accomplished in a voltammetric cell containing 0.05 mol L^{-1} [$Hg(NO_3)_2 + HNO_3$], which was preliminarily deaerated. The electrode was put at -0.4 V (vs. Ag/AgCl) until approximately 0.3 mC of charge has passed. Microscopic observation should show a single glittering droplet, almost a hemisphere. According to Stojek and Kublik [4] it is recommended to force some amalgam to enter the body of the electrode. It is accomplished by applying -9 V between the plated working electrode and a platinum one, during 120 s in a cell containing 1 mol L^{-1} NaOH, which is accompanied with evolution of hydrogen gas bubbles. During this period it is recommended to move the electrode and to put it in as horizontal position as possible (a narrow cell that can be inclined is appreciated). In order to get rid of sodium species, which were attracted to the electrode by

negative potential, it is necessary to dip the electrode for a few seconds in a beaker containing acid solution ($0.01 \text{ mol L}^{-1} \text{ HClO}_4$).

The last step before using the electrode is its stabilization, accomplished by cycling the potential in the range of interest, i.e., from -0.1 V to -1.8 V . We established the procedure of 10 scans with the scan rate of 1 Vs^{-1} , and step potential of 0.002 V . This should be done in the same cell where the calibration procedure will be performed.

After accomplishing the calibration procedure, which is based on a pilot-ion method, as given by Brendel and Luther [19], the electrode is ready for in situ measurement. However, after in situ measurement, it is useful to check the stability of the electrode by remeasuring the last point of the calibration line (the solution in the cell should be kept waiting). To facilitate the whole procedure and to avoid accidental pollution, we used and recommend the use of different cells and counter and reference electrodes assemblies throughout the different phases of preparation. In this case it is only necessary to rinse the working electrode with distilled water when transferred from one assembly to another. During the measurements, however, we modified the procedure in a way that we did not observe so closely the surface of the electrode, but the main criteria were the stability of the signals and high enough hydrogen overpotential to distinguish our reactants of interest, i.e., Fe(II) and especially Mn(II) . When inspecting the electrode we could observe sometimes that its surface was solid and not uniform, probably mostly of silver amalgam, thus, somewhat approaching the work of Mikkelsen and Schröder [14, 15]. Silver electrodes were much more stable than the gold ones, which will be shown on examples.

According to the theory of microelectrodes, the noise and generally the interferences with the electrodes, both in the cell and in the sediment, were not an obstacle to our investigation. This can be seen from the figures, where all the curves are original, if not stated otherwise. More noise is found when measuring in sediments, and in that case some attention should be paid on the positioning of the cable between the instrument and the electrodes. The working electrodes were kept in distilled water overnight and, once well amalgamated, they worked well for many days. However, sometimes, they needed more often renewal of the surface. We suppose that this comes from the rather macroscopic recipe for preparation of the surface, while the properties of the electrode depend on microscopic interactions of the metal of the electrode, the amalgam and the mercury layer.

3. Results and Discussion

3.1. Model Solutions

In order to get to know the behavior of the electrode, to choose the optimal parameters of the voltammetric techniques as well as to be able to detect early evidence of the degradation of its optimal performances, a set of measurements in model solutions was performed.

The basic electrolyte for model and calibration measurements was in most of cases filtered seawater or NaCl solutions.

Square-wave (SW) voltammetry was chosen as a fast method, which should have its advantages for measuring in situ [43]. The frequency of 50 Hz was chosen according to the highest signal for the reaction of Fe(II) reduction (Fig. 1) because the electrode is the least sensitive to that reaction among those of interest [19, 20]. When measuring with the frequency of 50 Hz , for diffusion coefficient D_0 in the range from 0.5 to $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [44], the diffusion layer thickness defined as $2(D_0 t)^{1/2}$ is still smaller than the diameter of the electrode, so the steady state has not been reached [13, p. 163]. For analytical purposes, the priority is to have the detection and determination limits as low as possible. The amplitude of the pulses was adjusted to two electron processes [45], i.e., 25 mV , step increment was 2 mV . The sequence of potentials to stabilize and clean the electrode was taken as suggested by Brendel and Luther [19], distinguishing the absence and the presence of sulfur species in solution. However, it was found the most useful for the electrode stability to control its potential all the time. It was accomplished by the mode "cell on after measurement" with

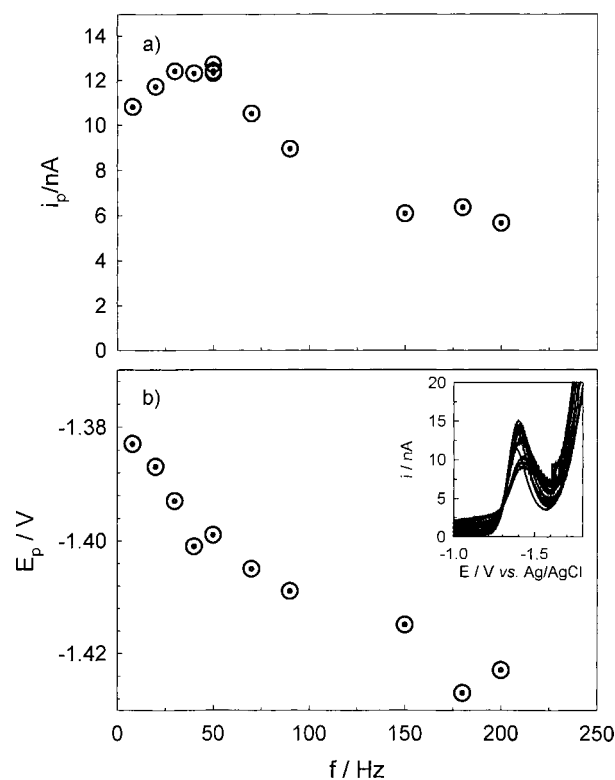


Fig. 1. Dependence of peak height of reduction of Fe(II) on SW frequency. Solution: seawater, salinity = 31‰, pH 5.47, $[\text{Fe(II)}] = 1 \times 10^{-3} \text{ mol L}^{-1}$. a) peak heights, b) peak positions. Measuring conditions: SWV, step increment 2 mV , amplitude 25 mV , conditioning potential -1 V , conditioning time 120 s , deposition potential -0.1 V , deposition time 3 s , initial potential -0.1 V , final potential -1.8 V , cell on after measurement, standby potential -0.8 V . Inset: original signals of the reduction of Fe(II) .

a standby potential from -0.8 V to -1 V. In such a way longer pauses between the measurements did not affect the behavior of the electrode. Initial and final potentials in most of the measurements read -0.1 V and -1.8 V, respectively. We also noticed that the electrode was destabilized by changing its running mode from cathodic to anodic one. The whole set of measurements should be done in one direction. We can also prove the experience of others [4, 42] that the electrode with an old amalgam covered with a fresh layer of mercury, or even an electrode with nonuniform surface showed the best behavior.

For analytical purposes of in situ measurements, model solutions for obtaining reliable calibration plots are necessary. The results for the calibration lines are presented with confidence intervals for 95% confidence level, minimum detection limits (MDL) were calculated according to Miller and Miller [46, p. 115].

3.2 Calibration Plots

3.2.1. Calibration of Mn(II)

Manganese is considered the easiest to make a reliable calibration plot, which then can be used by the principle of a "pilot ion method" to recalculate calibration plots for the other elements of interest.

Two calibration plots were constructed from the measurements using silver electrode and shown in Figure 2. The points represent reduction current peak heights of subsequently added Mn(II) ions into the filtered seawater of the salinity of 31‰ in the concentration range from 23.8 to $1550 \mu\text{mol L}^{-1}$ (1), and of the salinity of 15.5‰ in the range from 50 to $405 \mu\text{mol L}^{-1}$ (2). The first plot was constructed from 67 points. It covers almost two orders of magnitude of Mn(II) concentration and shows very good linearity ($(0.0331 \pm 0.0003) \text{ nA}/(\mu\text{mol L}^{-1})$, $r = 0.9994$, $n = 67$ points). The second is obtained with the electrode that was immediately afterwards put into a sediment. This plot shows the sensitivity of the electrode for the respective day and the given salinity ($(0.048 \pm 0.001) \text{ nA}/(\mu\text{mol L}^{-1})$, $r = 0.9996$, $n = 14$ points). Such a plot should be produced every day before in situ measurement. After 5 hours of measurement in the sediment, the electrode was put again in the calibration cell, showing satisfactory behavior (\blacktriangledown in Figure 2). In Figure 2b, dependence of peak potential on Mn(II) concentration is shown as well. This parameter should be monitored as an evidence of the stability of the electrode. MDL was $3.5 \mu\text{mol L}^{-1}$.

The dependence of manganese(II) peak height on the salinity was measured as well. The salinity varied from 0.9 to 30‰. A good linear correlation is found between the peak height and the logarithm of the salinity S $i(\text{nA}) = (-4.35 \pm 0.05)\log(S) + (12.73 \pm 0.05)$, with standard deviation of regression line $s_{y/x} = 0.085$, $r = -0.9988$, $n = 66$ points. By these two calibration lines and the corrections for temperature and pH values, an estimate of the concentration in situ can be made.

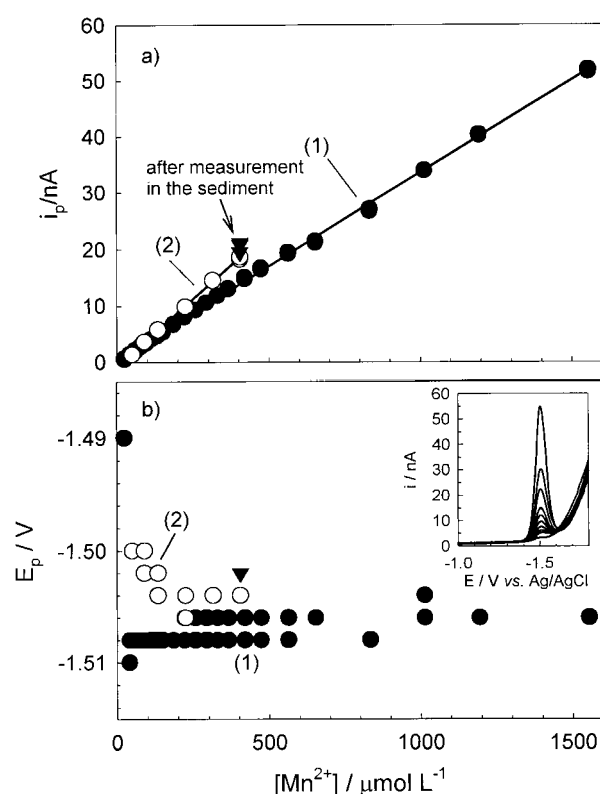


Fig. 2. a) Calibration lines constructed from measurements of reduction current peak heights of Mn(II) in filtered seawater of pH 7.8–8.2: 1) in the concentration range from 23.8 to $1550 \mu\text{mol L}^{-1}$, salinity = 31‰ and 2) in the concentration range from 50 to $405 \mu\text{mol L}^{-1}$, salinity = 15.5‰; \blacktriangledown) measurements in the cell for the case (2) after measurement in the sediment. Sensitivity for (1) is $(0.0331 \pm 0.0003) \text{ nA}/(\mu\text{mol L}^{-1})$, $r = 0.9994$, $n = 67$ points, sensitivity for (2) is $(0.048 \pm 0.001) \text{ nA}/(\mu\text{mol L}^{-1})$, $r = 0.9996$, $n = 14$ points. b) Corresponding peak potentials of the reduction current. Electrode: Ag, $30 \mu\text{m}$ in diameter. The frequency was 50 Hz, other measuring conditions as in Figure 1. Inset: some of the original signals of the reduction of Mn(II), used for constructing of the line (1).

3.2.2. Calibration of Fe(II)

We find it indicative and instructive to show the behavior of a gold and a silver electrode of $40 \mu\text{m}$ and $30 \mu\text{m}$ in diameter, respectively, as an example of the calibration procedure of iron(II). Both of the electrodes were amalgamated in the same way, the procedure, the solution and standard additions of Fe(II) were the same. The heights and the potentials of the peaks of Fe(II) ions reduction measured by the two electrodes are shown in Figures 3a and 3b, 1) corresponding to the silver electrode and 2) to the gold one. In contrast to the silver electrode, by which a straight calibration line was obtained (sensitivity $(0.0130 \pm 0.0003) \text{ nA}/(\mu\text{mol L}^{-1})$, $r = 0.9976$, $n = 51$ points, MDL = $28 \mu\text{mol L}^{-1}$), the gold electrode showed irregular behavior. After measurement in the solution with $1500 \mu\text{mol L}^{-1}$ Fe(II), an inspection of the electrode was provided, which proved that the electrode had changed. After a new

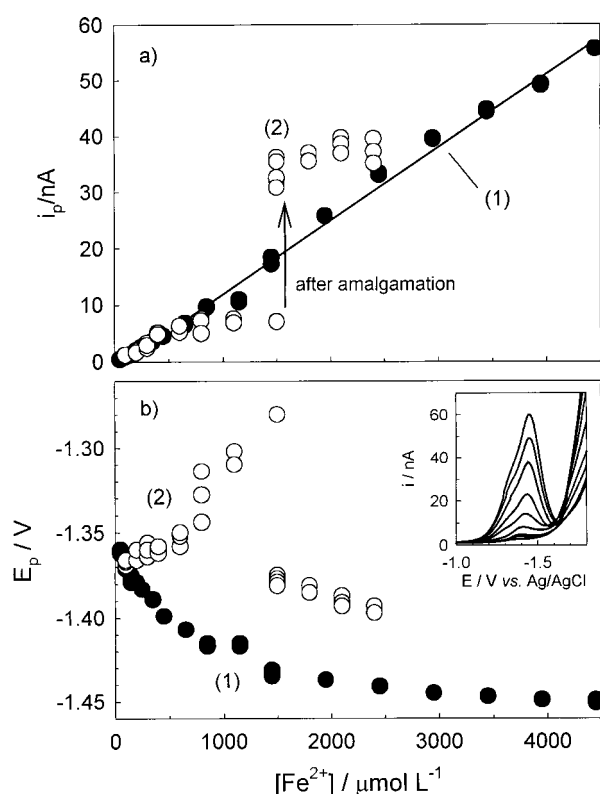


Fig. 3. a) 1) Calibration line constructed from measurements of height of reduction peak of Fe(II) in filtered seawater of pH 5.5–3.2 in the range from 50 to 4450 $\mu mol L^{-1}$, salinity = 31‰, measured by the silver electrode, 30 μm in diameter, sensitivity $(0.0130 \pm 0.0003) nA/(\mu mol L^{-1})$, $r = 0.9976$, $n = 51$ points. 2) Peak heights of reduction of Fe(II) in filtered seawater of pH 5.6–3.4 in the range from 100 to 2400 $\mu mol L^{-1}$, salinity 31‰, Au electrode, 40 μm in diameter. b) Corresponding peak potentials of the reduction peak currents in (a). Measuring conditions: same as in Figure 2. Inset: some of the original signals of the reduction of Fe(II), used for constructing of the line (1).

amalgamation procedure the measurement with the same solution was repeated and the calibration procedure continued. However, the electrode was not stable yet, as can be seen from the peak heights and peak potentials in Figure 3.

This and other similar experiments confirmed the opinion of Ciszowska et al. [42] that silver electrodes are more appropriate for the amalgamation procedure which is necessary in such types of measurements, owing to the lower solubility of silver in mercury compared to gold. Since, in contrast, the group of Luther [19–29] report very reliable analytical results with gold electrode, we came to the conclusion that the behavior of our electrodes might come from our modification of the electrode surface preparation towards solid amalgam, where the metal substrate plays a bigger role than in the case of mercury meniscus.

3.2.3. Calibration of I(–I) and S(–II)

Species of sulfur can be found in sediment porewaters. Because of the large affinity between sulfur and other

metals (Fe, Cd, Cu, Pb...) its determination is of great interest for environmental studies [47–51] and for better understanding of its cycle in sediments (see for example Luther et al. [52], Morse et al. [53], Hurtgen et al. [54], Billon et al. [55]). On the other hand, the study of iodine permits pointing out a problem bound to the interpretation of voltammograms since there are other components that are reduced at the same potential as Hg_2I_2 (especially O_2 and Fe(III) species (Luther et al. [23], Taillefert et al. [27])). To be able to estimate their presence and quantities, model measurements and calibration lines were obtained. The peak of reduction of Hg_2I_2 appears from -0.25 to -0.3 V (vs. Ag/AgCl), with a halfwidth of about 0.130 V. Calibration of I(–I) was performed in a solution containing 0.05 mol L^{-1} NaCl and 0.025 mol L^{-1} CH_3COO/NH_4 , at pH 6.65. In the concentration range from 0.5 to 5 $\mu mol L^{-1}$ of I(–I), the sensitivity of the electrode was found to be $(0.162 \pm 0.006) nA/(\mu mol L^{-1})$, with $r = 0.9975$, $n = 18$ points, MDL was 0.3 $\mu mol L^{-1}$. The procedure was as described previously, with the conditioning period of 60 s at -1 V; 5 s deposition at -0.1 V, which was enough for deposition of Hg_2I_2 at the electrode. Higher deposition times or higher concentrations in the solution would cause less pronounced, broader peaks.

For calibration of S(–II) a solution containing 0.05 mol L^{-1} NaCl and 0.025 mol L^{-1} HCO_3^-/CO_3^{2-} at pH ca. 10 was prepared. In the concentration range from 98.4 to 984 nmol L^{-1} of S(–II), the sensitivity of the electrode was found to be $(1.10 \pm 0.03) nA/(\mu mol L^{-1})$, with $r = 0.9987$, $n = 20$ points, MDL = 0.05 $\mu mol L^{-1}$. The procedure was as described previously, but deposition time at -0.1 V was 30 s, which was necessary to obtain high enough peaks at the concentration range of interest. The measurements performed at pH ca. 7 showed the same sensitivity but were not stable.

3.2.4. Calibration with Oxygen Peaks

As we started every calibration measurement with the registration of a blank (filtered seawater of different pH and salinity), before and after purging, we always obtained similar signals with two oxygen peaks, which disappeared after purging (Fig. 4). According to the before mentioned pilot ion principle we found the dependence of the sensitivity of the electrode for Mn(II) for the respective day on those peak heights. The correlation for the first peak height at about -0.25 V was not statistically significant, but that of the second one at about -1.19 V was significant, with $r = 0.936$ for $n = 7$ points, and with the slope of $(0.007 \pm 0.003) (nA/(\mu mol L^{-1})) / nA$. The poor correlation of the first wave is probably caused by the fact that it is at the edge of the potential window, and it is not easy to determine a real baseline and consequently the peak height. This correlation might be used for additional checking of the sensitivity of the electrode under the assumption of constant starting concentration of oxygen in seawater, which we might call a saturation concentration.

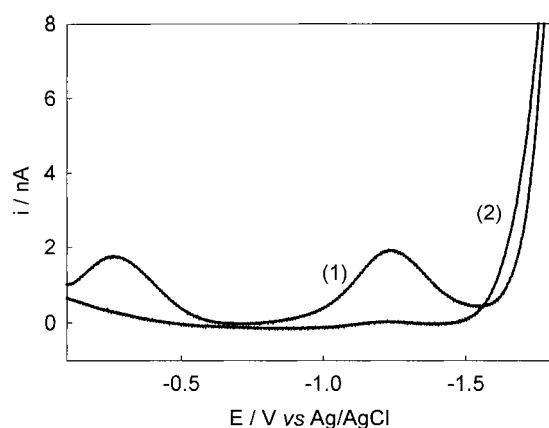


Fig. 4. SW voltammograms of seawater, salinity = 3.1‰, pH 7.8 before purging (1), and after 1 min. of purging (2). Measuring conditions: same as in Figure 2.

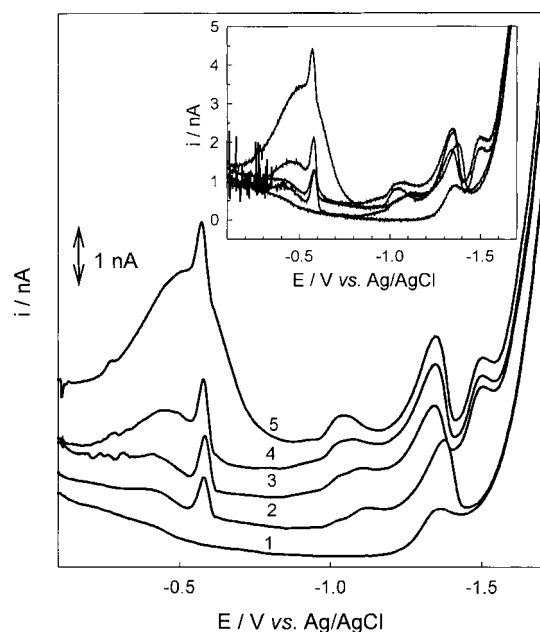


Fig. 5. SW voltammograms of seawater (smoothed and shifted), salinity 31‰, pH 6.9. 1) after addition of $122 \mu\text{mol L}^{-1}$ Fe(II); 2) after further addition of $2.65 \mu\text{mol L}^{-1}$ of S(-II); 3 to 5) after further addition of $91 \mu\text{mol L}^{-1}$ of Mn(II). Deposition time at -0.1 V for plots 1 to 3 was 2 s and that for plots 4 and 5 was 7 and 22 s, respectively. Other measuring conditions same as in Figure 2. Inset: original signals before smoothing and shifting.

3.2.5. Interaction of S(-II) with Fe(II) and Mn(II)

In order to approach the expected in situ situation, we performed some model measurements for studying the interaction of S(-II) with Fe(II) and Mn(II). The results are shown in Figure 5. They confirm the investigation of Theberge and Luther [21], Xu et al. [22] and Taillefert et al. [27]. Curve 1 is recorded in seawater of the salinity of 31‰ (pH of 6.9 was adjusted by addition of HCl), to which a $122 \mu\text{mol L}^{-1}$ of Fe(II) was added. Curve 2 was recorded

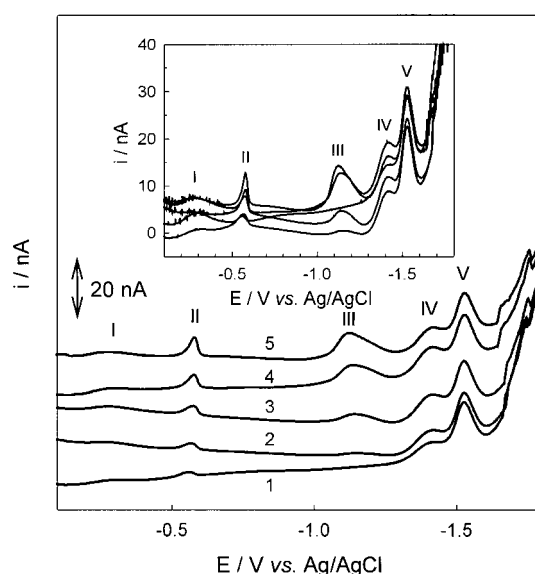


Fig. 6. SW voltammograms of a boxcore (smoothed and shifted), salinity = 10‰, pH 7.0, $E \approx -200$ mV. Curves 1 to 5: repetitions at one depth in intervals of 60 s. The sensitivity of the electrode for Mn(II) was $(0.023 \pm 0.001) \text{ nA}/(\mu\text{mol L}^{-1})$, for salinity of 3.1‰; deposition potential: -0.1 V, deposition time: 20 s. Other measuring conditions: same as in Figure 2. Inset: original signals before smoothing and shifting.

after the addition of $2.65 \mu\text{mol L}^{-1}$ of S(-II). Curves 3 to 5 were recorded after further addition of $91 \mu\text{mol L}^{-1}$ of Mn(II). Deposition time at -0.1 V for plots 1 to 3 was 2 s, and that for plots 4 and 5 was 7 and 22 s, respectively. The reaction of S(-II) with Fe(II) can be observed in appearance of "FeS" peak at about -1.1 V. At the same time the peak of reduction of Fe(II) has changed its height. With increasing the deposition time, a peak that corresponds to the reaction of Fe(III) to Fe(II) reduction at about -0.5 V increases as well. Fe(III) originates from oxidation of Fe(II) although the solution was freshly prepared. In the literature this peak has been attributed to Fe(III) colloidal and/or organic complexes, which adsorb at the electrode [19, 22, 27]. However, the same can be expected in the sediments. The peak of manganese remained unaffected by the reactions with sulfur species, at least at the observation time.

3.3 In Situ Measurements

An example of measuring in a boxcore is given. Salinity, pH and potential E were as follows: salinity = 10‰, pH 7.0, $E \approx -200$ mV. For this measurement the electrode was dipped about 2 centimeters into the sediment, the reference and the counter electrode were put a few centimeters apart. Curves obtained by 5 repetitions at one depth are presented in Figure 6 (the sensitivity of the electrode for Mn(II) was $0.023 \pm 0.001 \text{ nA}/(\mu\text{mol L}^{-1})$). We ascribe the peaks I to V to the following reactants: I(-I), S(-II), FeS, Fe(II), and Mn(II), respectively. The estimated concentration for Mn(II), the reduction peak of which was at -1.526 V (vs.

Ag/AgCl), is $750 \pm 50 \mu\text{mol L}^{-1}$ (calculated from the mean value of five peak heights (13.7 ± 0.7), and by the correction for salinity and sensitivity of the electrode as given before, taking into account the propagation of errors [46, p. 46].

The peak at -1.133 V , which is ascribed to FeS, shows evolution in time. Ideas and explanations can be found in literature [21, 56–58]. It is interesting to note matching of its double nature to that in Fig. 1a of Theberge and Luther [21], where a more positive peak is higher, opposite to the situation with laboratory prepared solution (Fig. 1b of the same article), which can be compared to the peak at -1.1 V in Figure 5 of this article. Of course, definite explanation and quantification of a process “seen” by the electrode is difficult to propose. A more detailed study along with well designed model measurements and more in a core and in situ measurements should be done before. Important fact is that the inspection of the electrode when taken out of mud showed no visible differences and that remeasuring of the last calibration point in the cell showed no significant differences either.

4. Conclusions

The Au and Ag microelectrodes were designed and constructed for easy operation, both in a voltammetric cell and in situ. They were tested in model solutions and in boxcore sediments. The effort was put to the preparation and the maintenance of the amalgam and the mercury layer in the sense of their reproducibility. We were faced with the problem that the recipe of the preparation of the electrode is rather macroscopic and not ideally reflected in the later behavior of the electrode, i.e., we did not control the thickness and the mutual interactions of the metal of the electrode, the amalgam and the mercury layer, which presumably play the role, so we applied the method of trial and error by reamalgamating the electrodes. Silver electrodes showed to be much more stable, so for practical reason, we focused on them in our measurements. The problem of not having enough control over electrode surface properties, expressed in its variable sensitivity, was successfully overcome with frequent calibrations. An important improvement in the stability of the electrode was achieved by permanent control of its potential even in the periods between measurements. Two operational parameters for judging satisfactory performance of the electrode were established: the repeatability of peak heights and negative enough hydrogen overpotential that enables distinguishing the reduction peaks of Fe(II) and Mn(II). Calibration plots for Mn(II), Fe(II), I(–I) and S(–II) were obtained successfully, with average sensitivity of 0.05, 0.01, 0.16 and $1.10 \text{ nA}/(\mu\text{mol L}^{-1})$ and the minimal detection limit of 3.5, 28, 0.3 and $0.05 \mu\text{mol L}^{-1}$, respectively, which were comparable with the reports in the literature [19], especially when comparing the surfaces of the electrodes used in these two cases. A good correlation was found between the electrode sensitivity for Mn(II) and the oxygen peak height, which might be used for checking or even instead of the calibration

procedure. The whole procedure, however, should strictly be named as semiquantitative. Namely, with the “pilot ion method” and propagation of errors taken into account, confidence limits of the concentrations of measured analytes might easily surpass 50% of the value. The most important information from in situ measurements is expected from the relative changes of the depth profiles, and/or changes in time in a single spot.

Further experiments will be oriented toward precise monitoring of the sediment profiles while improving our knowledge on controlling the sensitivity and the stability of the electrode.

5. Acknowledgements

We thank Dr. Sylvia Sander, Eco Chemie, Utrecht, The Netherlands for helpful information and Dr. Mikolaj Donten, University of Warsaw, Department of Chemistry, Poland for the production and helpful suggestions in the preparation of the electrodes. This research was supported by PNETOX and INTERREG (Franco-Flamand Programs). I. P. has benefited from the CNRS grant.

6. References

- [1] R. M. Wightman, *Anal. Chem.* **1981**, 53, 1125A.
- [2] K. R. Wehmeyer, R. M. Wightman, *Anal. Chem.* **1985**, 57, 1989.
- [3] R. M. Wightman, *Science* **1988**, 240, 415.
- [4] Z. Stojek, Z. Kublik, *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, 60, 349.
- [5] K. Wikel, J. Osteryoung, *Anal. Chem.* **1989**, 61, 2086.
- [6] J. Wang, D. Larson, N. Foster, S. Armalis, J. Lu, X. Rongrong, K. Olsen, A. Zirino, *Anal. Chem.* **1995**, 67, 1481.
- [7] M. Penczek, Z. Stojek, *J. Electroanal. Chem.* **1985**, 191, 91.
- [8] M. Ciszowska, Z. Stojek, *J. Electroanal. Chem.* **1985**, 191, 101.
- [9] Š. Komorsky-Lovrić, M. Lovrić, A. M. Bond, *Electroanalysis* **1993**, 5, 29.
- [10] S. P. Kounaves, W. Deng, *Anal. Chem.* **1993**, 65, 375.
- [11] S. P. Kounaves, J. J. O'Dea, P. Chandrasekhar, J. Osteryoung, *Anal. Chem.* **1987**, 59, 386.
- [12] J. Golas, Z. Galus, J. Osteryoung, *Anal. Chem.* **1987**, 59, 389.
- [13] A. J. Bard, Z. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, **2001**.
- [14] Ø. Mikkelsen, K. H. Schrøder, *Analyst* **2000**, 125, 2163.
- [15] Ø. Mikkelsen, K. Schrøder, *Anal. Lett.* **2000**, 33, 3253.
- [16] Ø. Mikkelsen, K. H. Schrøder, *Electroanalysis* **2001**, 13, 687.
- [17] B. Yosypchuk, L. Novotný, *Talanta* **2002**, 56, 971.
- [18] J. Wang, J. Lu, *Electrochem. Commun.* **2000**, 2, 390.
- [19] P. J. Brendel, G. W. Luther III, *Environ. Sci. Technol.* **1995**, 29, 751.
- [20] G. W. Luther III, C. E. Reimers, D. B. Nuzzio, D. Lovalvo, *Environ. Sci. Technol.* **1999**, 33, 4352.
- [21] S. M. Theberge, G. W. Luther III, *Aquat. Geochem.* **1997**, 3, 191.
- [22] K. Xu, S. C. Dexter, G. W. Luther III, *Corrosion* **1998**, 54, 814.
- [23] G. W. Luther III, P. J. Brendel, B. L. Lewis, B. Sundby, L. Lefrançois, N. Silverberg, D. B. Nuzzio, *Limnol. Oceanogr.* **1998**, 43, 325.

- [24] M. Huettel, W. Ziebis, S. Forster, G. W. Luther III, *Geochim. Cosmochim. Acta* **1998**, 62, 613.
- [25] M. E. Dollhopf, K. H. Nealson, D. M. Simon, G. W. Luther III, *Mar. Chem.* **2000**, 70, 171.
- [26] M. Taillefert, G. W. Luther III, D. B. Nuzzio, *Electroanalysis* **2000**, 12, 401.
- [27] M. Taillefert, A. B. Bono, G. W. Luther III, *Environ. Sci. Technol.* **2000**, 34, 2169.
- [28] G. W. Luther III, T. F. Rozan, M. Taillefert, D. B. Nuzzio, C. DiMeo, T. M. Shank, R. A. Lutz, S. C. Cary, *Nature* **2001**, 410, 813.
- [29] P. Anschütz, B. Sundby, L. Lefrançois, G. W. Luther III, A. Mucci, *Geochim. Cosmochim. Acta* **2000**, 64, 2751.
- [30] M.-L. Tercier, J. Buffle, F. Graziottin, *Electroanalysis* **1998**, 10, 355.
- [31] C. Belmont-Hébert, M. L. Tercier, J. Buffle, G. C. Fiaccabrino, N. F. deRoos, M. Koudelka-Hep, *Anal. Chem.* **1998**, 70, 2949.
- [32] M.-L. Tercier, J. Buffle, *Anal. Chem.* **1996**, 68, 3670.
- [33] R. R. DeVitre, M.-L. Tercier, M. Tsacopoulos, J. Buffle, *Anal. Chim. Acta* **1991**, 249, 419.
- [34] M.-L. Tercier, N. Parthasarathy, J. Buffle, *Electroanalysis* **1995**, 7, 55.
- [35] C. Belmont, M.-L. Tercier, J. Buffle, G. C. Fiaccabrino, M. Koudelka-Hep, *Anal. Chim. Acta* **1996**, 329, 203.
- [36] M.-L. Tercier, J. Buffle, *Electroanalysis* **1993**, 5, 187.
- [37] Y. Song, G. Müller, *Sediment-Water Interactions Inanoxic Freshwater Sediments*, Springer, Heidelberg **1999**.
- [38] P. Santschi, P. Hohener, G. Benoit, M. Buchholtz-TenBrink, *Mar. Chem.* **1990**, 30, 269.
- [39] W. J. Cai, C. E. Reimers, *Limnol. Oceanogr.* **1993**, 38, 1776.
- [40] B. P. Boudreau, *Diagenetic Models and Their Implementation*, Springer, Heidelberg **1997**.
- [41] L. Denis, *Dynamique des flux d'oxygène et des sels nutritifs à l'interface eau-sédiment sur la marge continentale du Golf du Lion*, Thesis, Université de la Méditerranée, Marseille, **1999**.
- [42] M. Ciszowska, M. Donten, Z. Stojek, *Anal. Chem.* **1994**, 66, 4112.
- [43] M. Lovrić, in *Electroanalytical Methods, Guide to Experiments and Application* (Ed: F. Scholz), Springer-Verlag, Berlin Heidelberg, **2002**, pp 111.
- [44] R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworths, London **1959**.
- [45] J. Osteryoung, J. J. O'Dea, in *Electroanalytical Chemistry*, Vol. 14 (Ed: A. J. Bard), Marcel Dekker, New York **1986**, pp. 222.
- [46] J. C. Miller, J. N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood, Chichester, UK **1989**.
- [47] G. T. Ankley, *Environ. Tox. Chem.* **1996**, 15, 2138.
- [48] *The Utility of AVS/eqP in Hazardous Waste Site Evaluations*, Proceedings of a workshop sponsored by the Coastal Resource Coordination Branch, Hazardous Materials Response and Assessment division, NOAA, Seattle, Washington **1995**, p. 101.
- [49] B. G. Lee, J. S. Lee, S. N. Luoma, H. J. Choi, C. H. Koh, *Environ. Sci. Technol.* **2000**, 34, 4517.
- [50] G. Billon, B. Ouddane, J. Laureyns, A. Boughriet, *Phys. Chem. Chem. Phys.* **2001**, 3, 3586.
- [51] H. F. Passier, J. J. Middelburg, B. J. H. van Os, G. J. de-Lange, *Geochim. Cosmochim. Acta* **1996**, 60, 751.
- [52] G. W. Luther III, A. E. Giblin, R. Varsolona, *Limnol. Ocean.* **1985**, 30, 727.
- [53] J. Morse, F. Millero, J. Cornwell, D. Rickard, *Earth Sci. Rev.* **1987**, 24, 1.
- [54] M. T. Hurtgen, T. W. Lyons, E. D. Ingall, A. M. Cruse, *Am. J. Sci.* **1999**, 299, 556.
- [55] G. Billon, B. Ouddane, A. Boughriet, *Talanta* **2001**, 53, 971.
- [56] J. Buffle, R. R. DeVitre, D. Perret, G. G. Leppard, in *Metal Speciation, Theory, Analysis and Application* (Eds: J. R. Kramer, H. E. Allen), Lewis, **1988**, pp. 107.
- [57] T. F. Rozan, S. M. Theberge, G. W. Luther III, *Anal. Chim. Acta* **2000**, 415, 175.
- [58] W. Davison, J. Buffle, R. DeVitre, *Pure Appl. Chem.* **1988**, 60, 1535.