

***In Situ* Monitoring of Electroactive Species by Using Voltammetry at Microelectrodes**

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Usou-se microeletrodos de platina recobertos de mercúrio, em solo e águas sedimentares, para a determinação *in situ* de espécies “redox”, de importância ambiental. Amostras de areia foram consideradas como o modelo para solos, na detecção *in situ* de oxigênio. Medidas diretas de sulfeto foram realizadas em sedimentos anóxidos coletados nos lagos de Veneza. Uma investigação da interação entre metais pesados, sulfeto e partículas sólidas em água corrente, extraídas dos sedimentos, também foi feita. A quantificação das várias espécies eletroativas examinadas, foi feita por procedimentos sem necessidade de calibração.

Mercury coated platinum microelectrodes were employed for the *in situ* determination, in soils and porewater of sediments, of redox key species of environmental interest. Sand samples were considered as soil model for the *in situ* detection of oxygen. Direct measurements of sulphide were performed in anoxic sediments collected in the Lagoon of Venice. An investigation on the interaction among heavy metals, sulphide and solid particles in pore-water extracted from the sediments was also performed. For the quantification of the various electroactive species examined, calibrantless procedures were employed.

Keywords: mercury microelectrodes, soils, sediments, oxygen, sulphide, heavy metals

Introduction

In recent years, there has been considerable interest in the development of probes and analytical methods for *in situ* analysis.¹⁻⁵ *In situ* analysis is attractive because it allows, for instance, elimination of many artefacts due to sample handling and real time analysis for the rapid detection of pollutant inputs in environmental samples.

In general, microsensors and microanalytical systems are key steps in the development of *in situ* analytical procedures. To this purpose voltammetric methods are competitive,⁶ with respect to other instrumental analytical techniques, and offer several advantages as, for instance, simple and compact low cost apparatus, reliable automatic measurements, high sensitivity and speciation capabilities.¹ Moreover, with the advent of microelectrodes,^{7,8} the analytical applications have been extended to resistive media,⁹ not accessible to conventional voltammetry with macroelectrodes (*i.e.*, electrodes with radii > 0.1 mm). Moreover, the use of microelectrodes reduces the requirement of well defined cell geometry, thus leading to the simplification of the electrochemical apparatus. A two-

terminal system is needed,^{7,8} in place of the classical three electrode cell, while the rapid achievement of steady-state conditions provides a means to avoid forced convection when preconcentration steps are needed to increase the sensitivity for trace analysis measurements.^{10,11}

The purpose of this paper is to show the performance of mercury microelectrodes for the *in situ* detection of some key electroactive species in samples of environmental interest. Here, *in situ* is synonymous with measurements taken directly in the sample with no or minimum pretreatment. Either homogeneous or “semisolid samples”, as soils and sediments, and the electroactive species oxygen, sulphide and heavy metal ions are investigated.

Experimental

Apparatus

Voltammetric experiments were carried out by using an EG&G Mod. 283 potentiostat/galvanostat (PAR, Princeton, N.J., USA), controlled with a personal computer *via* the EG&G PAR 270 electrochemical software.

All measurements were carried out in a two-electrode cell, located inside a Faraday cage made of sheets of aluminium. The cell apparatus employed for measurements

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in the sediment samples was an air-tight vessel made of glass, which contained a small Teflon cup 1.5 mL volume, into which the solid sample was placed. A micromanipulator was used to hold the microelectrode in place. The reference electrode was either an Ag/AgCl saturated with KCl or a pseudo reference silver wire of 0.5 mm radius.

The platinum microdisk electrode, which served as substrate for mercury deposition, was prepared by sealing a 25 μm diameter platinum wire (Goodfellow Metals, Cambridge, UK) into glass. Before use, the disk surface was polished mechanically with aqueous suspensions of graded alumina powder of different sizes (1, 0.3 and 0.05 μm) supported on a polishing microcloth (Buehler, Lake Bluff, IL, USA). Sphere-cap¹² mercury microelectrodes were prepared by *ex situ* deposition of mercury, under potentiostatic control, onto the platinum microdisk, as reported elsewhere.^{10,13,14} The height, h , of the sphere cap was calculated on the basis of the plating charge spent during the electrodeposition step.^{10,13,14}

The steady-state diffusion limiting current I_d at the platinum disk or at the sphere-cap mercury microelectrodes can be predicted by:¹⁰⁻¹⁵

$$I_d = k n F D C^b r \quad (1)$$

where k is a parameter that depends on the electrode geometry (for the disk $k = 4$,¹⁵ while for the sphere cap, it depends on the h/r ratio^{10,12-14}), C^b is the bulk concentration of the electroactive species and r is the radius of the microdisk. This equation was employed for the determination either of the effective radius of the microdisk or the k values of the various sphere cap mercury microelectrodes. The steady-state limiting current was obtained from a 1 mmol L⁻¹ Ru(NH₃)Cl₃ in Milli-Q water containing 0.1 mol L⁻¹ NaClO₄. In this way, each sphere cap microelectrode employed for the calibrationless quantification (see later) was well characterised. Calculated k values for the various mercury microelectrodes employed here varied over the range 6.18 - 6.45.

Unless otherwise stated, the experiments were carried out at room temperature that varied between 15 and 36 °C (spring and summer periods).

Reagents and samples

All the chemicals employed were of analytical-reagent grade. Unless otherwise stated, the solutions were prepared with water purified with a Milli-Q purification system (Millipore, USA), and deaerated with nitrogen (99.99%) supplied by SIAD (Bergamo, Italy).

Sulphide stock solutions, approximately 1x10⁻² mol L⁻¹,

were prepared by dissolving large sodium sulphide crystals, which were previously washed with Milli-Q water and dried with acetone to remove any oxidised surface layer,¹⁶ in a 1 mol L⁻¹ NaOH well deaerated solution. The stock solution was kept, under nitrogen atmosphere, in a tightly closed flask, and was standardised by potentiometric measurements with a sulphide ion-selective electrode, adopting the standard addition method.

For the measurements in sand samples, typically, 10 g of sand were mixed with 3.5 mL of water solutions and the mixture was allowed to equilibrate for 24 h. The sampling of the sediment cores were performed in the Lagoon of Venice and taken with Plexiglass core tubes approximately 30 cm long and 6 cm wide. Stoppers were placed in the bottoms of the tubes and then taped immediately after the samples were taken, to minimise the sample exposure to air. Samples were then brought to the laboratory and the analysis performed on sections taken at different depth and put in the small Teflon cup of the voltammetric cell (see above). The measurements in soil samples were made with the mercury microelectrode immersed directly into them.

Pore-water was extracted from the sediments by squeezing of core sections and the analyses were performed in the unfiltered samples. The sediment samples were squeezed with a Reeburgh-type¹⁷ squeezer in air atmosphere. The natural pH of the pore-water was, on average, equal to 8.5 \pm 2.

Results and Discussion

Detection of oxygen in the soil liquids

The soil liquids (the water phase) are held by the pores of the soil system, in the vadose and the saturated zone.¹⁸ In the former, they are partly filled with water and partly with air. The oxygen content in the water phase is important parameter telling on the extent to which oxidation processes may occur at the water-solid interface.^{19,20} For instance, the major changes that occur in redox conditions between oxic waters and anoxic sediments can have profound influences on the speciation and bioavailability of many trace metals.²¹

In order to ascertain the performance of the mercury microelectrode for the direct determination of the oxygen concentration by voltammetry in the water phase of soils, a series of measurements was performed in sand samples that were equilibrated with water.

Figure 1 shows typical voltammograms recorded with a mercury microelectrode, at 10 mV s⁻¹, on a sand sample equilibrated with air-saturated (curve a) or purged with a

stream of pure nitrogen (curve b) aqueous solutions, containing 0.5 mol L^{-1} NaCl. In the presence of oxygen, the voltammogram displays two well defined waves that follow the expected sigmoidal shape, typical for voltammetry with microelectrodes under steady-state conditions.^{7,8} These waves are due to the irreversible reduction of oxygen to hydrogen peroxide and water (first and second waves, respectively).²² The involvement of oxygen in the reduction process is confirmed by the lack of waves in the voltammogram recorded in the samples equilibrated with purged aqueous solutions (curve b). To investigate on the reproducibility of the current responses, the oxygen reduction voltammogram was cycled with the same mercury microelectrode immersed in the soil over a period of about 90 min. It was found that the steady-state limiting current of the first wave was constant within 3%, thus indicating good electrode stability under the experimental conditions employed here.

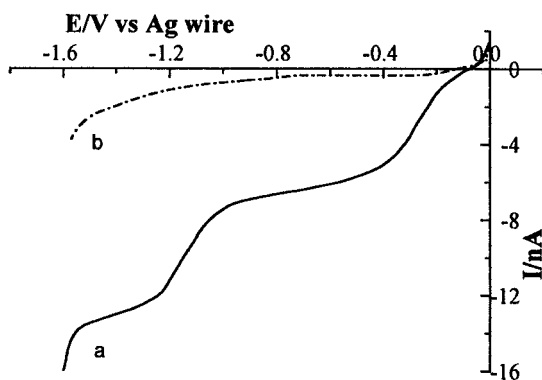


Figure 1. Linear sweep voltammograms recorded at a Hg microelectrode $h/r = 6.20$ in a sand sample equilibrated with a) air-saturated and b) purged aqueous solutions containing 0.5 mol L^{-1} NaCl. Scan rate 10 mVs^{-1} .

In real samples, the distribution of air and water in the vadose depends on the climate (temperature, rainfall and evaporation).¹⁸ To simulate these different conditions, voltammograms were recorded in sand samples equilibrated with water kept at different temperatures over the range $15 - 35 \text{ }^\circ\text{C}$. Moreover, the current signal of the first plateau was monitored for an entire working day (about 8 h) at $31 \text{ }^\circ\text{C}$, room temperature in a summer day. For the determination of the oxygen concentration in soil, the height of the first wave of curve a in Figure 1 along with equation (1) was employed. In the calculation, the following parameters were used: $n=2$, the diffusion coefficient of O_2 at $25 \text{ }^\circ\text{C}$, $D = 2.12 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$,²³ was corrected for temperature effect by taking into account the Stokes-Einstein equation;²⁴ k values were those evaluated

for the specific mercury microelectrode, as described in the experimental section. Figure 2 shows the experimental data thus obtained. The oxygen concentration decreases with temperature, while it is almost constant with time although some water evaporation from the soil-water mixtures occurred. The trends observed clearly reflect the solubility of oxygen in water. In fact, the experimental data fall within the theoretical values of oxygen solubility from air saturated aqueous solutions,²⁵ that are also included in Figure 2. These results indicate that the oxygen content in soils can be determined by a simple linear sweep voltammetry and exploiting the steady-state limiting current equation that holds for sphere-cap mercury microelectrodes.

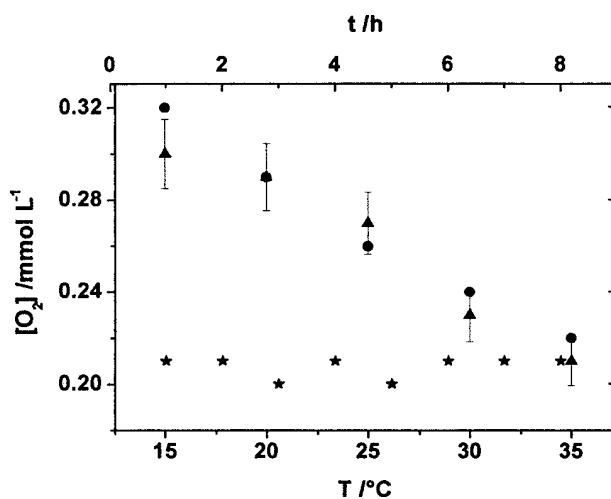


Figure 2. Oxygen concentration as determined with a mercury microelectrode in sand samples at different temperatures (\bullet , \blacktriangle) and time (\star). Experimental (\blacktriangle) and theoretical (\bullet) values.

Detection of sulphide ions

Inorganic sulphur compounds have been the subject of great laboratory and field interest in the environmental literature.²⁶⁻³³ Characterisation and monitoring of such species are in fact critical for understanding of sulphur and metal cycling in suboxic sedimentary environments. For the detection of sulphide ions in aqueous solution, the following electrode process occurring at a mercury electrode is usually exploited:^{26,34}

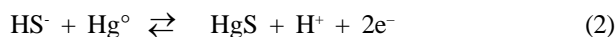


Figure 3 shows typical cyclic voltammograms recorded at 50 mV s^{-1} in a $0.02 \text{ mmol L}^{-1} \text{ Na}_2\text{S} + 0.5 \text{ NaCl}$ solution, adjusted to $\text{pH}=12$ by addition of a proper amount of a $1 \text{ mmol L}^{-1} \text{ NaOH}$ solution. Starting from -0.8 V , where no

process occurred, the potential was reversed at -0.4 V. The small anodic process is due to the formation of mercury sulphide onto the electrode surface.³⁴⁻³⁸ The cathodic wave is due to the reduction of the HgS present onto the electrode surface, according to the inverse of reaction 2. Both position and height of this wave depended on the sulphide concentration in the solution as well as on the amount of HgS accumulated onto the electrode surface. In particular, it was found that the peak potential shifted towards less negative values by 30 mV for a tenfold decrease of the sulphide concentration, while the peak shifted towards a more negative potential as the amount of HgS accumulated on the mercury surface increased.

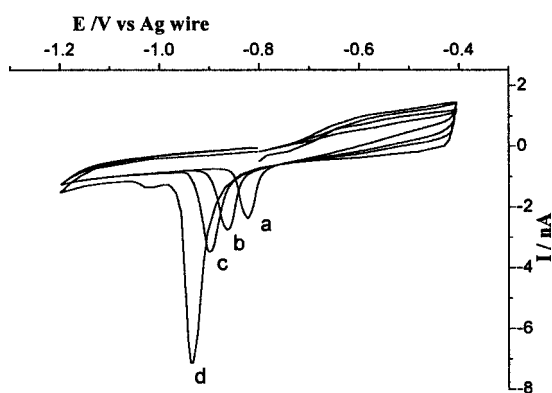


Figure 3. Cyclic voltammograms recorded at 50 mV s^{-1} with a mercury microelectrode in a $0.02 \text{ mmol L}^{-1} \text{ Na}_2\text{S} + 0.1 \text{ mol L}^{-1} \text{ NaCl}$ aqueous solution, $\text{pH}=12$; Starting potential $E=-0.8 \text{ V}$. Cathodic stripping peak recorded at different preconcentration times starting from $E = -0.4 \text{ V}$ vs Ag wire. Preconcentration time: a) 0, b) 10, c) 20, d) 60 s.

It must be noticed that cathodic peaks were in any case observed, even in very dilute aqueous solutions, provided that a HgS film was allowed to form on the electrode surface at a potential $\geq -0.4 \text{ V}$. The effect of preconcentration time on the cathodic stripping peak is also shown in Figure 3, and as expected, it becomes larger and shifts towards more negative values upon increasing the preconcentration time.^{37,38}

The possibility to monitor reduced sulphur directly in the pore water of anoxic sediments with mercury microelectrodes was investigated. To this purpose a series of cathodic stripping voltammograms was recorded directly on sections of sediment taken at 11 cm depth. The deposition potential was set at -0.4 V vs Ag wire, and accumulation times over the range 0-60 s were employed. In all experiments cathodic stripping peaks, conceivably due to the reduction of HgS accumulated onto the electrode surface, were observed. This was confirmed by the fact that both position and height of the cathodic peak changed

as a function of the preconcentration times in the same manner seen above in the synthetic aqueous solutions (see Figure 3).

Since the process involving sulphide is a surface process, a conditioning step was necessary to restore the electrode surface between measurements, and to avoid signal degradation during measurements. This was achieved by maintaining the potential at -1.6 V vs Ag wire, for 20-30 s. At this potential both reduction of HgS and hydrogen evolution occur, which allowed to restore the electrode surface. In fact, 10 replicates performed with the same mercury microelectrode, each measurement ensuing the latter procedure, provided peak current and charge reproducible within 5%.

For the quantification of sulphide in the sediment samples a calibrationless procedure was employed. In fact, in such matrices classical standardisation procedures such as single or multiple standard addition are not applicable. The calibrationless approach is based on the following equation:³⁸

$$Q_c = nFC^b [1.13A (D t_{d,eff})^{1/2} + krD t_{d,eff}] \quad (3)$$

where Q_c is the charge associated to the cathodic stripping peak, $n=2$ (according to reaction (2)), $A = \pi (r^2 + h^2)$ ^{13,14} is the electrode surface, D is the diffusion coefficient of the sulphide ion, $t_{d,eff}$ is the effective deposition time,³⁸ and the other symbols have their usual meaning. The use of equation (3) for the determination of concentration requires the knowledge of the diffusion coefficient of sulphide in the medium investigated or in a similar medium, as D depends on the ionic strength and viscosity.²⁴ Therefore, the diffusion coefficient of sulphide ion was evaluated in surface sea water in the following manner. First, the absence of sulphide in the water sample was ascertained. Second, the water sample was spiked with known concentrations of sulphide over the range $1 - 5 \mu\text{mol L}^{-1}$, and cathodic stripping voltammograms were recorded with the mercury microelectrode. The preconcentration time employed was as long as to make the first term in equation (3) negligible (that is, to achieve steady-state conditions). The charge Q_c of the stripping peak was plotted against concentration and, as expected, a straight line with a correlation coefficient of 0.999 was obtained. From the slope of the straight line, $D = 1.39 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was calculated, the other parameters being known.

Various sediment samples were examined and it was found that both position and height of the cathodic stripping peak, at a given preconcentration time and mercury microelectrode, depended on the different collecting sites and depth. As expected, anoxic sediments gave in general relatively large cathodic stripping peaks

due to the HgS reduction. Moreover, the samples investigated soon after they were brought to the laboratory showed intense stripping peaks due to sulphide, whereas sediment samples that were exposed to air atmosphere or examined after they were stored for several days at 4 °C, revealed smaller cathodic stripping peaks due to sulphide. The effects of keeping the sediment in contact with air is shown in Figure 4 where sulphur is monitored for about 8 hours. The HgS reduction peak decreases with time, probably because of oxidation of sulphide by oxygen from air.

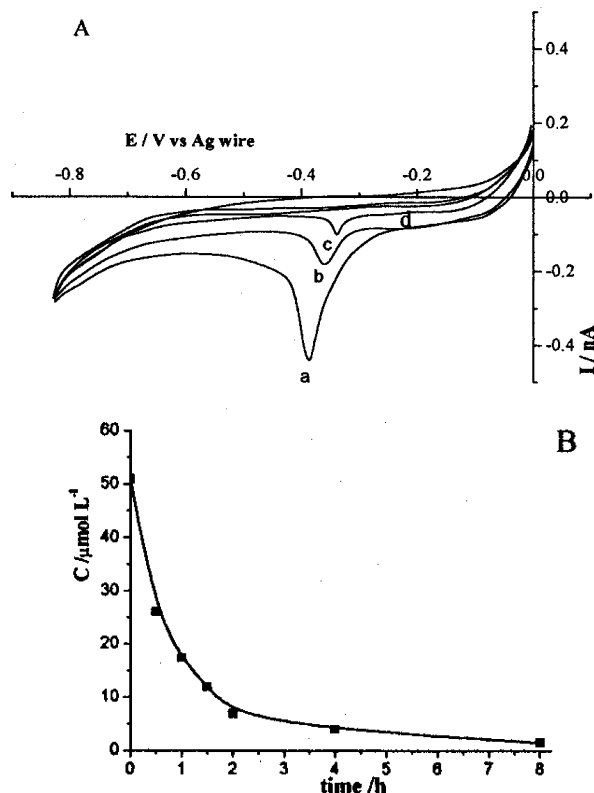


Figure 4. A) Cathodic stripping voltammograms recorded by linear sweep voltammetry at 50 mV s⁻¹ with a mercury microelectrode in a sediment sample at different times after collection: a) 1, b) 2, c) 4, d) 8 h. Deposition potential E = 0.0 V vs Ag wire, preconcentration time 30 s. B) Sulphide concentration against time plot.

Data shown in Figure 4B were calculated by equation 3 from the full set of voltammograms relevant to the experiments described in Figure 4A.

The calibrationless approach was also employed for the evaluation of sulphide depth profile. To this purpose a series of cathodic stripping measurements was carried out on sediment sections taken at different depth, and Figure 5 shows a typical set of data obtained. This profile is similar to others reported in the literature in similar environments.^{19, 30,31,39} In fact the concentration of sulphide in sediments increases with depth, as a result of sulphate reduction during the decomposition of organic matter.^{30,31}

These data confirm also that all sediment cores examined were anoxic. This view was also confirmed by the fact that no detectable oxygen wave was ever recorded in the sediments at all depths investigated, in agreement with the fact that oxygen is depleted quickly below the sediment-water interface.^{19, 30,31,39}

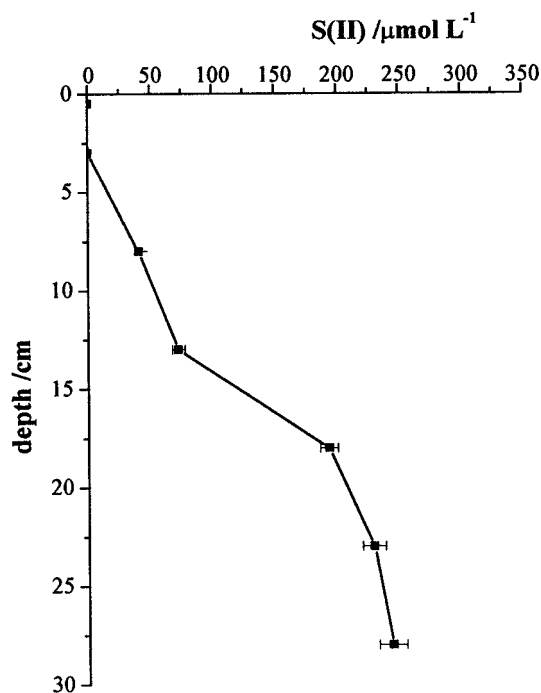


Figure 5. Depth profile of sulphide in a sediment sample collected in the Lagoon of Venice.

Investigation of trace metal in pore-water of sediments

Pore-water composition is considered as a useful indicator of the types and the extent of reactions that take place between pollutant-loaded sediment particles and the aqueous phase that contacts them.⁴⁰ The biogeochemical cycle of many trace elements depends on the partitioning of the total concentration among several forms.^{21,41,42} At natural pH, a large fraction of trace metals is usually associated to particulate matter either inorganic or organic in nature.^{40,42} Moreover, because sulphide reacts with many divalent transition metal ions to form very insoluble precipitate, the metal ion concentration in pore-water may also depend on the free sulphide concentration.

In order to investigate on these interactions, a series of measurements was performed on the heavy metals Cd, Pb and Cu, that have gained great significance in chemical and toxicological studies of environment.⁴⁰ The measurements were carried out in pore-water samples extracted at 14 cm depth and the analysis performed in the

water samples without filtration. Residual sulphide and the heavy metal ions were determined in pore-water samples that were: just extracted and at their natural pH; after they were exposed to air for 2, 24 and 48 h at their natural pH; after acidification down to pH = 2. In this way both labile, under various conditions, and total metal concentration were evaluated. Sulphide analysis was performed as described above, while trace metal analysis was performed by anodic stripping voltammetry.⁴³ The metal ions were deposited simultaneously at -1.0 V, and linear sweep voltammetry was applied in the stripping step. Figure 6 shows a typical anodic stripping voltammogram recorded with the mercury microelectrode in a quiescent pore-water sample acidified with HCl down to pH = 2. Under these conditions three anodic peaks corresponding to Cd (-0.58 V), Pb (-0.42 V) and Cu (-0.16 V) were observed. The identification of these ions was made by spiking the sample with known amounts of each element.

Depending on the particular conditions under which the anodic stripping tests were performed, no or some of

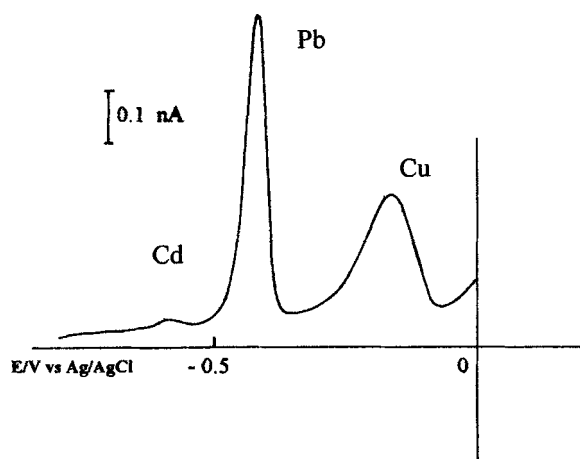


Figure 6. Anodic stripping voltammogram recorded at a mercury microelectrode in a pore-water sample acidified at pH = 2. Scan rate 50 mV s⁻¹.

the stripping peaks shown in Figure 6 were observed (see later).

For the quantification of the heavy metal ions either a calibrationless approach based on equation 3 (specialised for the investigated ions) or the multiple standard addition method was employed. However, with the latter procedure linear calibration plots for all ions were obtained only in the acidified samples. In the samples examined at their natural pH, no linear trend was observed, probably because of the interaction of the spiked metal ions with particulate matter or residual sulphide. In acidified samples, instead, data obtained with the calibrationless and standard procedures agreed within 7%.

In the determination of heavy metals with the calibrationless approach, the diffusion coefficients employed for the various metal ions were, respectively, $6.3 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, $8.7 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ and $6.2 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ for Cd²⁺, Pb²⁺ and Cu²⁺. They were obtained in sea water samples spiked with relatively large amounts of each metal ion and from the steady-state limiting current recorded with a mercury microelectrode, as described in detail elsewhere.^{10,44}

Table 1 summarises the data obtained for the various species examined. From this table it is evident that no detectable amount of trace metals was obtained in the pore-water sample at its natural pH and still containing a relatively large amount of sulphide, even if a deposition time as long as 30 min was employed in the preconcentration step. Higher heavy metal ion concentrations are found either decreasing sulphide concentration or at lower pH values. This trend agrees with expectation on the basis of lability criteria as a function of pH.^{45,46} In fact, as also mentioned above, in neutral or basic aqueous solutions most of the metal ions are bound to particulate matter, while they are released in acidic media. Also, the data reported in Table 1 agree with the fact that sulphide controls metal concentration in pore-water. The decrease of the free sulphide with time can be due to its oxidation with air.

Table 1. Analysis of sulphide and heavy metals under different conditions in a pore water sample extracted from a sediment section at 14 cm depth

Conditions of the samples	S(II)/ $\mu\text{mol L}^{-1}$	Cd/nmol L ⁻¹	Pb/nmol L ⁻¹	Cu/nmol L ⁻¹
Just extracted pH=8.5	6.9	*	*	*
Examined after 2 h pH=8.5	0.31	*	7.9	12.4
Examined after 24 h pH=8.4	0.002	1.9	27.4	40.8
Examined after 48 h pH=8.4	*	9.4	41.5	46.3
pH=2	*	69.4	1330	750

*Undetectable, deposition time 30 min.

All values were averaged from three replicates. The relative standard deviation is within 4%.

This in turn leads to the release of the metal ions in the solution, from their insoluble precipitates.

Conclusions

In this paper it has been shown that mercury coated platinum microelectrodes can be employed for the measurement of the key redox species oxygen and sulphide directly in soils and sediments. In fact, the mercury microelectrodes were stable enough to withstand penetration into the soils, and no loss of the mercury deposit was observed even for measurements performed for relatively long times. This, for instance, has allowed the monitoring of the oxygen solubility in the water phase of soils and the depth profile of sulphide in the sediment. The mercury microelectrodes have displayed good performance in the investigation of chemical interaction between heavy metal ions and sulphide or particulate matter in pore-water. Moreover, thanks to the microelectrode properties, calibrationless procedures for the quantification of the electroactive species have been employed.

Acknowledgements

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