

Pseudopolarography of lead (II) in sediment and in interstitial water measured with a solid microelectrode

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Abstract

Pseudopolarograms of lead (II) constructed from the voltammograms measured in situ in the sediment and in the interstitial water by using an Ir solid microelectrode with a thin mercury film have shown as a kind of fingerprints of the sample. Despite shortcomings when compared to measurements with the mercury drop electrode and in model solutions, the measurement procedure was adapted for enough signal repeatability, avoiding to a reasonable extent the memory effect and electrode surface blocking. To make the best use of the information available, besides the classical pseudopolarograms, i.e. besides the dependence of the peak-height on the deposition potential, it is necessary to analyze the peak-area, the peak-position and the half-peak width versus deposition potential, and combine them with the knowledge from various theoretical and model situations. They have shown to contain interesting information about speciation. This information is not always unambiguous, it is often semi-quantitative, and cannot be reached by other methods, however, in combination with other methods it could be useful for the characterization of the sample solution. Pseudopolarograms of lead (II) in different liquid fractions of the sediment were measured and compared, the electrode sensitivity varying from 4 to 20 nA/μmol L⁻¹ of lead (II). The differences in half-wave potentials recorded were ranging up to 0.6 V and those in the slopes of pseudopolarograms were three-fold, having interesting relationships with the peak potentials of single voltammetric curves.

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1. Introduction

Pseudopolarography is a method appropriate for distinguishing the labile from the inert complexes of dissolved trace metals with ligands in their natural concentrations [1–29]. It can be particularly applied for the speciation of trace metals that form amalgams, being based on anodic stripping voltammetry or lately on stripping chronopotentiometry as

well [30–33]. A pseudopolarogram, which is similar in shape to the classical polarogram, is the dependence of peak-heights of a redox reaction on the deposition potential, which changes in subsequent voltammetric measurement cycles [1,3,4,7,8], and which reflects thermodynamic and kinetic properties of metal ions as well as geometric and hydrodynamic characteristics of the working electrode. The main parameters used for the speciation of trace metals using pseudopolarographic data are the half-wave potential and the limiting current. However, we can benefit from the entire shape of the pseudopolarographic curve, which provides a scanning image (fingerprint) of the investigated electrochemical reactions. It was shown that thermodynamic stability constant of the inert metal complex can be obtained from the difference between the standard

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potentials of the redox reactions of the free and of the inert complexed metals [10]. This theoretical concept is empirically used for the determination of stability constants of inert metal complexes using pseudopolarographic half-wave potentials, and is successfully applied for trace metals speciation of unknown natural aquatic systems [18,19,28,29]. From the ratio of the limiting currents of the labile and inert metal complexes (using known side reaction data) the calculation of the stability constant is possible, as well. The parameters relative to the redox reaction, such as the transfer coefficient and the rate constant, can be obtained through the analysis of the shape of pseudopolarographic wave [34,35].

Theoretical background for the pseudopolarography has been developed for the hanging mercury drop electrode [4,7], for the thin film electrode under different conditions [8,11,36] and for the mercury ultramicroelectrode [9]. The automation of the pseudopolarographic measurement is crucial for its wider employment and has been achieved with the nowadays instrumentation and the existing software [23].

There is often a considerable discrepancy when measuring and examining model solutions with well-defined composition and the measuring of the samples of natural, polluted or pore waters. This is true already when the working electrode is a mercury hanging drop electrode, with the surface renewed for every cycle of the measurement, but if instead, the working electrode is a solid electrode, more problems could be encountered, something to be worried about. In that case it cannot be counted on single “clear” effects, one by one thoroughly elaborated in the literature, to appear one at a time, instead a superposition of various effects should be expected. Anyhow, voltammetric in situ measurements are restricted to the solid electrodes that can be moved vertically to characterize depth profiles, or they can follow the evolution in time of a single sampling site either by simple repeating of measurements or by gradually changing one of the parameters of the method as in the case of pseudopolarography.

Lead is a toxic, nonessential element, thus its increased concentrations in the media affect living organisms inducing negative physiological effects [37]. During the early diagenetic processes, iron oxides were reduced, which lead to releasing Pb^{2+} into pore waters, while the production of sulphides tended to (co)precipitation of Pb^{2+} (mainly as PbS or Pb associated with FeS_2) [38,39]. Nevertheless, partial redissolution might occur at the oxic–anoxic interfaces [40,41,38], especially when the concentration of lead in high contaminated sediments reaches nearly 1 g kg^{-1} . Moreover, significant enrichment of trace elements in interstitial waters has been explained by the effect of complexing by organic substances [42]. This explains why the concentrations of most of the trace elements in interstitial waters were significantly higher than could have been predicted from their sulphide solubility [38,43]. On the other hand, lead is a classical element to be investigated by voltammetry and a mercury drop as a working electrode as it forms amalgams, and even a large number of pseudopolarographic measurements were

made in model and natural solutions with lead as the analyte [3,8,10,12,21,24,27,29–31,34].

Pseudopolarograms obtained in the experiments described in this work differ from the theoretical assumptions and calculations, or at least they represent a combination of several ones. Shifts of half-wave potentials and changes in the slope due to the complexation, changes in reversibility and metal–ligand ratios have been elaborated theoretically [7–11,30,32,36], as well as the existence and the effects of the combinations of electrode reactions (E) with coupled homogeneous chemical reactions (C), such as the CEC preceding and following reactions [44].

Since pseudopolarography is here considered as a kind of fingerprint of the measured sample, or the place near the electrode put in situ, retrieving more complex information from this composite voltammetric method by tracing not only the peak-height and the peak-area, but also the peak-potential and the half-peak width versus deposition potential is proposed.

2. Experimental

2.1. Electrode preparation

The experiments were performed with an Ir microelectrode, designed as described elsewhere [45] for the similar Au and Ag microelectrodes. This electrode was $75 \mu\text{m}$ in diameter and the procedure of surface activation differed from the previous works in the part related to the application of mercury. Mercury was applied electrochemically from a 0.01 M solution of $\text{Hg}(\text{NO}_3)_2$ at -0.4 V versus Ag/AgCl , $[\text{KCl}] = 3 \text{ mol L}^{-1}$. A very thin film of mercury was deposited in order to avoid memory effect, which was observed with a hemispheric mercury drop. Under the microscope neither the mercury layer nor the mercury drops were observed. Kept in distilled water, the electrode was stable for several days. The sensitivity of the electrode was checked by the standard addition method with lead (II) and cadmium (II), before and after the experiments.

2.2. Instrument and chemicals

A $\mu\text{Autolab 2}$, multimode polarograph with the software package GPES 4.8 (Ecochemie, Utrecht) was used. A Metrohm Stand 663 was used for mercury deposit and calibration steps, where a facility for proper purging with nitrogen was needed. Purging with nitrogen was also applied when measuring the interstitial water samples in order to prevent any oxidation of the medium. Stirring the solution was not applied in order to approach in situ conditions, cell volume was 20 ml , and supporting electrolyte for calibration measurements was filtered seawater of 31 salinity. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt wire. The reference electrode for in situ measurement was a Unisense Ag/AgCl electrode and the counter electrode was a robust Pt rod electrode. The applied methods were

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