

# SPECIATION OF DISSOLVED TRACE METALS IN THE MARINE ENVIRONMENT BY PSEUDOPOLAROGRAPHY

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## Abstract

The speciation of dissolved trace metals has been studied in model solutions and in natural water samples using a pseudopolarographic method, with a static mercury drop electrode (SMDE) and a thin mercury film glassy carbon disk electrode (TMFGCDE). The stability constants of the labile lead(II) complexes with chloride ions were determined from the shift of the half-wave potential of automatically measured pseudopolarograms. In the solution of constant ionic strength of 4 M ((4-X) M NaClO<sub>4</sub> + X M NaCl) and a concentration of lead(II) ions of 5x10<sup>-8</sup> M at pH = 2. It has been established that copper in seawater exists mainly in the form of strong inert complexes (>95%).

**Keywords:** chemical speciation, trace elements

## Introduction

Pseudopolarography (repetitive anodic stripping voltammetric measurements with changing accumulation potential) is a relatively new electroanalytical approach for species the analyzing of dissolved trace metals at low metal concentration in natural and polluted water (<10<sup>-8</sup> M) [1-8]. The anodic peak current-accumulation potential curves are polarographically-shaped and named pseudopolarograms [1,3] and it is very useful for the determination of both labile and inert metal stability constants [1-4,6-8]. The electrochemical characteristic of labile complexes is a shift of the half-wave potential of the complexed species towards negative values as compared to the "free" metal. The reduction half-wave potential of inert metal complexes is well separated from the reduction potential of free and labile metal complexes and is shifted towards more negative value. This shift depends on the stability constants of the inert metal complex. The DeFord-Hume method for the determination of the consecutive stability constants of labile metal complexes was based on the shift of the polarographic (cathodic) half-wave potential with changing ligand concentration at relatively high metal concentrations (>10<sup>-5</sup> M). It is also applicable for the irreversible processes [9]. As the half-wave potential of the pseudopolarogram is dependent on the half-wave potential of the accumulation cathodic process, it is possible to use this method, following the same procedure, for the determination of stability constants of labile metal complexes at very low metal concentrations [1-3].

## Materials and methods

An EcoChemie  $\mu$ AUTOLAB potentiostat was used. The working electrodes were PAR 303A SMDE and a home-made thin mercury film glassy carbon disk electrode (TMFGCDE). The auxiliary electrode was platinum wire and the reference electrode was Ag|AgCl|NaCl(sat). The chemicals used were either of "suprapur" grade, concentrated HNO<sub>3</sub>, or of "analytical-reagent" grade: NaCl, Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, HgCl<sub>2</sub>, EDTA, NaOH, H<sub>3</sub>BO<sub>3</sub> (all MERCK, Darmstadt) and T-X-100 (Rohm and Haas). Sea water sample was taken from Krka river estuary (Sibenik) and stored at 4°C before analysis. Milli-Q water was used in all experiments.

## Results and discussion

Figure 1 shows the determination of the consecutive stability constants of the lead-chloro complexes using pseudopolarography. The entire procedure (the addition of chloride ions and pseudopolarographic measurements) was automatically managed. In the solution of ionic strength 4 M ((4-X) M NaClO<sub>4</sub> + X M NaCl) and 5x10<sup>-8</sup> M lead(II) by pH = 2, the apparent stability constants are determined as: log $\beta$ <sub>1</sub> = 0.61±0.05, log $\beta$ <sub>2</sub> = 1.77±0.02, log $\beta$ <sub>3</sub> = 2.18±0.02, log $\beta$ <sub>4</sub> = 1.85±0.02.

The pseudopolarographic determination of dissolved copper species in seawater samples exemplifies the possibilities of this speciation analysis of trace metals in natural systems. In the analyzed natural seawater sample (Figure 2) pseudopolarographic measurements show that copper(II) occurs mainly in the form of inert complexes (>95%).

Pseudopolarographic determination of the labile copper and inert complex (CuEDTA) in model solution (0.55 M NaCl, pH = 8.1) shows two well separated waves both using SMDE and TMFGCDE. First of them at the potential of about -0.35 V corresponds to the reversible copper reduction and a more negative wave (about -1.0 V) to the reduction of the inert CuEDTA complex. In chloride solutions copper is reduced as copper(I). The successful separation of two waves (labile copper and CuEDTA complex) using SMDE are obtained by addition of 1 mg T-X-100/L. Triton (T-X-100) adsorbed on the mercury drop surface shift the reduction potential of CuEDTA complex to more negative values. Using TMFGCDE with thinner mercury film separation of two waves (labile copper and CuEDTA complex) is achieved without addition of Triton. Pseudopolarography is the first and essential step for the metal complexing capacity determination using anodic stripping voltammetry at the actual metal concentration level in pristine seawater. These measurements enable the determination of the convenient accumulation potential range where free/labile metal complexes are separately reduced from inert metal complexes [10].

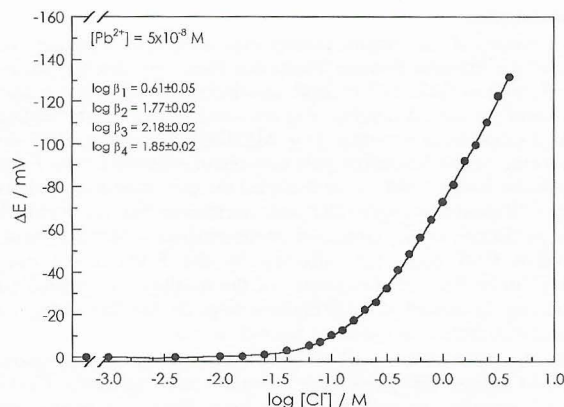


Figure 1. Shift of the half-wave potentials of the pseudopolarograms as a function of concentration of Cl<sup>-</sup> ions.

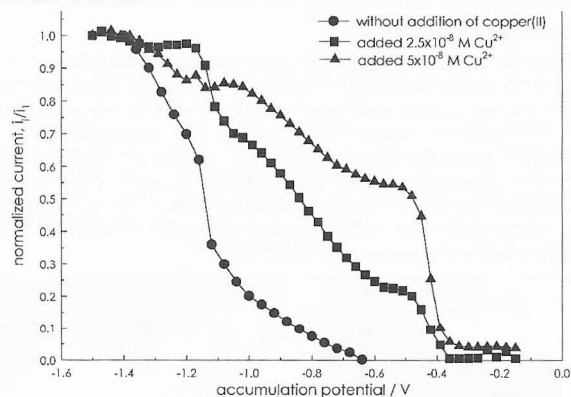


Figure 2. Pseudopolarogram of copper in seawater sample (S = 38 ‰, pH = 8,2)

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