

ELECTROCHEMICAL BEHAVIOR OF COPPER COMPLEXES IN MODEL ELECTROLYTE SOLUTIONS AND NATURAL WATERS

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Abstract

Several electrochemical techniques and methods were used to explore electrochemical behavior of copper while determining its complexation parameters in model electrolyte solutions, as well as in fresh, brackish and sea water. It was shown that adsorption of natural organic matter (NOM) strongly influences electrochemical reaction of copper during anodic stripping scan causing obstacles in obtaining proper copper complexing parameters. Experimental procedure setup that overcomes these difficulties is proposed.

Keywords : Trace Elements, Chemical Speciation, Organic Matter, Aeolian Arc, Metals.

The toxicity and bioavailability of metal ions to aquatic organisms is mainly related to concentrations of their free (hydrated) form - Free Ion Activity Model (FIAM)[1]. The chemical speciation of metals in natural water samples is determined by the net of chemical reactions of metal ions with inorganic and organic ligands existing in particular natural water [2]. Several physico-chemical methods are available for the determination of the chemical speciation of trace metals, among them anodic stripping voltammetry (ASV) satisfies requirements concerning sensitivity and selectivity, while keeping the benefit of low contamination risk and low alteration of original sample composition during analysis. However, ASV suffers from interferences during redox reactions, which could influence the determination of complexing parameters of investigated trace metal. In this work, electrochemical reactions of copper in model electrolyte solutions (sodium-chloride and sodium-perchlorate), as well as in fresh, brackish and sea water (river Gapeau, Hyères, France) were studied, in order to find the best parameters of experimental setup in obtaining reliable data, regarding copper complexation parameters. The methodology is based on pseudopolarographic measurements[3,4] and determination of copper complexing capacity (CuCC)[5] applying ASV method and a hanging mercury drop as a working electrode. Both methods yield data concerning complexing properties of copper.

- NOM) on the mercury surface[6]. As a consequence, a distorted shape of copper anodic peaks appears, which further leads to poorly developed pseudopolarograms. Moreover, incorrect data of copper complexing capacity parameters, ligand concentration and apparent stability constant, could be obtained.

Applying a.c. voltammetry, we found that only anodic stripping step is influenced by the adsorbed layer, and that the effect is more pronounced for longer accumulation times and accumulation potentials at electrocapillary maximum (around -0.6 V). At very negative potentials (<-1.4 V) most of the surface active substances are desorbed from the mercury surface giving well defined anodic stripping peak of copper. Desorption of SAS from the mercury electrode is relatively fast and only about 1% of total accumulation time at very negative potential (e.g. -1.6 V) is enough to remove practically all adsorbed SAS (Figure 1). The procedure to overcome this artifact is proposed and exploited to show its influence and consequences on copper pseudopolarographic measurements and determination of copper complexing capacity.

The influence of synthetic SAS Triton-X-100 on the electrochemical reaction of copper, the benefit of using Stripping Chronopotentiometry (SCP) and the importance of maintaining the original pH of the natural sample will be shown and discussed.

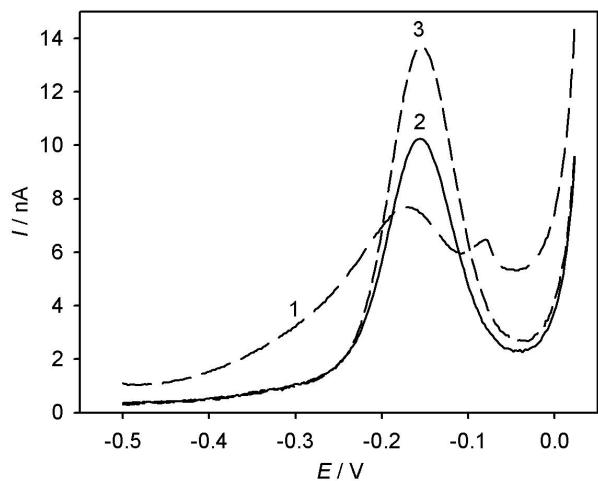


Fig. 1. DPAS voltammograms of copper in raw seawater sample obtained using different experimental parameters: (1) - $t_{dep} = 300$ s @ $E_{dep} = -0.45$ V; (2) - $t_{dep} = 297$ s @ $E_{dep} = -0.45$ V and $t_{dep} = 3$ s @ $E_{dep} = -1.6$ V; (3) - $t_{dep} = 300$ s @ $E_{dep} = -1.6$ V.

It is found that ASV of copper is strongly affected by the adsorption of surface active substances (SAS) of natural origin (natural organic matter

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