OP 4.2

Determination of trace metal speciation parameters by using screen-printed sensors in stripping chronopotentiometry

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Electrochemical techniques, especially stripping methods, are of particular relevance for studies on metal ion speciation. They provide adequate sensitivity and the analytical signals inherently can contain direct speciation information. In particular, these methods are sensitive to the lability which is characterized by a shift of the characteristic potential, and, for unequal diffusion coefficients, by the magnitude of the analytical signal [1]. However, lability is an experimentally defined parameter that depends on the effective time scale of the analytical technique. The analytical challenge is therefore to develop a technique able to determine parameters that describe the lability such as the stability, and rates of association and dissociation. The stripping chronopotentiometry (SCP) method appears as the most appropriate for ion speciation studies because it leads to minimize adsorption effects under conditions approaching complete depletion [2]. Moreover, Van Leeuwen and Town (2002) have demonstrated that the stripping chronopotentiometry at scanned deposition potential (SSCP) allows a straightforward description of the lability [3]. Ideally, such measurement should be made in situ to avoid sampling and sample handling artifacts [4]. The purpose of this work has been therefore to develop the SSCP for screen-printed sensors.

First, analytical parameters of SCP have been optimized to approach conditions of complete depletion. This regime has been reached for a stripping current higher than 3 µA. However, it was demonstrated that a stripping current of 10 µA allowed to skip the sample deoxygenating step which is liable for change the pH sample and therefore speciation [5]. Then, the adsorption effects on the working surface of the screen printed sensor have been investigated in a Cd solution containing a complexing ligand, the pyridine-2,6-dicarboxylic acid (PDCA). It has been shown that SCP measurements at screen-printed sensors were essentially free from adsorption effects whatever the electrodeposition time used. Finally, the SSCP has been applied to a range of ligand concentrations (from 10^{-4} to 10^{-5} mol L^{-1}). The experimental curves have been successfully compared to those calculated, which allowed to determine the stability constants of the Cd complex. The SSCP at screen-printed sensors appears therefore as a promise tool for the in situ determination of the lability criteria in order to provide the information required to the ecotoxicological risk assessment.

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