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The use of Nafion-coated thin mercury film electrodes for the determination of the dissolved copper speciation in estuarine water

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Abstract

Differential pulse anodic stripping voltammetry (DPASV) using a Nafion-coated thin mercury film electrode (NCTMFE) was implemented to determine the dissolved copper speciation in saline estuarine waters containing high concentrations of dissolved organic matter (DOM). The study used model ligands and estuarine water from San Francisco Bay, California, USA to demonstrate that the NCTMFE is more effective at distinguishing between electrochemically inert and labile copper species when compared to the conventional thin mercury film electrode (TMFE). Copper titration results verify that the NCTMFE better deals with high concentrations of DOM by creating a size-exclusion barrier that prevents DOM from interacting with the mercury electrode when performing copper speciation measurements. Pseudovoltammograms were used to illustrate that copper complexes found in natural waters were more apt to be electrochemically inert at the NCTMFE relative to the TMFE when subjected to high negative overpotentials. Copper speciation results using the NCTMFE from samples collected in San Francisco Bay estimated that >99.9% of all copper was bound to strong copper-binding ligands. These L_1-class ligands exceeded the concentration of total dissolved copper in all samples tested and control the equilibrium of ambient [Cu^{2+}] in the San Francisco Bay estuary.

Keywords: Nafion-coated thin mercury electrode; Rotating disk electrode; Anodic stripping voltammetry; Copper speciation; San Francisco Bay

1. Introduction

Trace metals in natural waters are capable of controlling growth rates of phytoplankton either as a limiting nutrient or by causing a toxic response [1,2]. To better understand the role of trace metals, one must be able to determine the various chemical forms or species and their respective concentrations in order to accurately assess the impact they may have on an aquatic system. In the case of copper, toxicity to marine phytoplankton has been demonstrated to be a function of the hydrated free cupric ion concentration, denoted here as [Cu^{2+}], rather than the total dissolved copper concentration or [Cu_T] [3]. For this reason, analytical methods with the ability to directly or indirectly measure [Cu^{2+}] supply information necessary to evaluate the health of a highly impacted urban estuary such as San Francisco Bay.

Estuaries are recognized in having high dissolved organic matter (DOM) content that presents an analytical challenge in determining trace metal speciation. Like most estuaries, the DOM in San Francisco Bay varies both spatially and temporally [4]. The primary source of DOM is from the upper estuary and concentrations decrease with increasing salinity. The use of mercury electrodes to measure copper speciation in natural waters has become a mainstay over the last three decades, but they have difficulties in obtaining reproducible signals in the presence of high concentrations of DOM [5–7]. The fouling of mercury electrodes by DOM adsorption is brought about by an entropy-driven reaction where hydrophobic portions of the macromolecules displace ordered water molecules at the surface of the electrode [8]. There is a special need to employ a method that can deal with the presence of DOM and measure labile copper in solution.

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This research presents the use of the Nafion-coated thin mercury film electrode (NCTMFE) as a means to deal with the organic-rich seawater matrix within estuaries such as the San Francisco Bay. The thin membrane of Nafion polymer can be cast onto a glassy carbon-rotating disk electrode (GC-RDE) and a mercury film is deposited through the permeable membrane onto the glassy carbon. The original research using Nafion-coated electrodes as an analytical tool demonstrated that the NCTMFE possessed anti-fouling properties when determining total dissolved copper, cadmium, and lead concentrations in biological samples that included blood, urine, and sweat [9]. However, the use of the NCTMFE in estuarine samples containing high DOM has not been fully examined. Copper speciation studies have also been limited [10], with Morrison and Florence (1989) employing the NCTMFE to measure the ASV-labile fraction of copper in samples within a coastal seawater matrix. They focused on the copper complexation capacity of the water sample, comparing the NCTMFE to other polymer-coated membranes, differential pulse polarography, and bioassay results. This study is more directed at the thermodynamic characterization of the strong copper-binding ligands (L_1) and weaker, more kinetically labile ligands that potentially dominate the equilibrium concentration of copper species in such systems [11]. An estimate of the kinetic contributions from the dissociation of copper-organic complexes is included. The objective is to show the advantages of this NCTMFE approach as compared to the conventional TMFE, demonstrating the effects of DOM on the performance of the mercury electrodes during copper speciation measurements and to what extent the Nafion barrier is able to prevent fouling of the electrode surface.

Copper speciation data from San Francisco Bay has been collected over the past two decades using various analytical approaches [12–15]. These studies were spurred by the fact that many areas within San Francisco Bay exceeded the total dissolved copper concentration limit set by the United States Environmental Protection Agency national saltwater quality criteria [16]. Differential pulse anodic stripping voltammetry (DPASV) using both a thin mercury film glassy carbon-rotating disk electrode (TMF-GC-RDE) and hanging mercury drop electrode (HMDE), competitive ligand equilibration–adsorptive cathodic stripping voltammetry (CLE–ACSV) using 8-hydroxyquinoline as a competing ligand, and chelating resin column partitioning–graphite furnace atomic absorption spectrometry (CRCP–GFAAS) were employed to determine the copper speciation of two samples collected in 1991 from South San Francisco Bay [12]. The study revealed that 80–92% of the copper existed in the form of relatively inert organic complexes. More recently, studies using salicylaldoxime as a competing ligand in CLE–ACSV [13,14] and supported liquid membranes (SLM) [15] have suggested that an increasing amount of copper-binding ligands and a decreasing amount of total dissolved copper are present in the estuarine waters relative to the initial copper speciation study in 1991.

Anodic stripping methods are especially useful in estimating the extent of metal complexation by distinguishing between electrochemically labile and inert complexes. The NCTMFE in conjunction with the DPASV technique makes use of the chemical properties of the mercury film, where electrochemically labile species of copper become reduced and amalgamated when adequate negative potentials are applied to the working electrode. The approach possesses sub-nanomolar detection limits and measures labile copper directly. But DPASV is a nonequilibrium technique, where the lability measurement is influenced by the dissociation rates of metal complexes. The technique can only estimate equilibrium conditions if the metal complexes are relatively electrochemically inert, meaning that the residence time of the species within the diffusion layer is significantly less than the dissociation rate [17]. However, more rapid rotation of the RDE results in the creation of a thinner diffusion layer that minimizes the residence time and increasing the fraction of organic ligands that are operationally defined as electrochemically inert. There will still likely be metal complexes that dissociate given their respective dissociation rate constants and diffusion coefficients [18], but one could argue that the metal complexes in this category are also likely to be labile to a microorganism with a similar diffusion layer thickness.

1.1. Nafion-coated thin mercury film electrode

The Nafion polymer is ideal for use in electroanalysis for aqueous solutions given that it is water insoluble, hydrophilic, nonelectroactive, permeable with size-exclusion properties, and chemically inert. It has also been shown to stabilize the mercury droplets that constitute the thin film at the glassy carbon surface by creating a scaffold for mechanical support [19]. The structure of Nafion itself is a perfluorosulfonated ionomer with negatively-charged sulfonic groups at $pH > 5$. However, the anionic properties of the polymer at near-neutral pH have been suggested to be negated in solutions with an ionic strength greater than 0.10 [20]. Under these conditions, it is likely that the principles of Donnan exclusion no longer apply and results in the Nafion membrane losing its permselectivity properties [21]. Consequently, there is an increase in the permeability of both anions and cations through the membrane. The net effect from this increase of ions is that the preconcentration of copper at the electrode surface is diminished, simplifying the potentially complex nature of a charged electrode surface and minimizing the polymer coating to merely a size-exclusion barrier.

The structure and thickness of the polymer film contribute to the electrochemical selectivity of labile species. The effect of solvent polarity on the structure of recasted Nafion films has been investigated and it has been suggested that the polymer structure experiences an inversion when in contact with a polar solvent, where the resulting structure has the negatively-charged sulfonic groups interacting with an aque-