

A novel, ultra-fast electrochemical tool to study speciation of trace metals in aqueous solution

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Trace metals play important roles in biological and ecological systems. In biology, trace metals act as catalytic or structural cofactors and regulate biochemical processes. In the environment, natural and anthropogenic sources of trace metals mobilized into natural waters where they can create harmful and persistent pollution. Trace metal chemistry in physiological and environmental systems can fluctuate rapidly which makes it difficult to clearly define trace metals' roles in these systems with traditional analytical methods. Furthermore, these systems are often chemically harsh and physically delicate (e.g. the brain), factors that add to the challenge of analysis in real systems. Fast scan cyclic voltammetry (FSCV) is explored in the context of rapid, minimally invasive and robust analysis of Cu²⁺ in aqueous samples with carbon fiber microelectrodes (CFMs). Unique Cu²⁺-specific waveform was generated with an optimized potential window and scan rate to provide sub-second analysis of Cu²⁺. An array of electrochemical and spectroscopic techniques was employed to discover the underlying mechanisms of the ultra-fast FSCV response. Adsorption was explained as the fundamental mechanism for the rapid FSCV signal and the thermodynamic properties of adsorption of Cu²⁺ onto CFMs were evaluated with fast scan controlled adsorption voltammetry (FSCAV) in different matrices.

In aquatic systems and soils, metals commonly exist in complexed forms with organic and inorganic ligands. It is generally the free, unbound metal that is the most toxic, thus metal speciation is a critical factor when considering metal pollution. Free Cu²⁺ concentrations and the solution formation constant (K_f), provide valuable speciation information. We show that FSCV and FSCAV can be utilized to study copper speciation. Mathematical relationships (Equation 1) were constructed from experimental data to predict free Cu²⁺ concentrations and the overall K_f of a solution with a range of model ligands, representing a range of Cu²⁺- ligand K_f expected to be encountered naturally. These findings showcase the power of FSCV as a real-time biocompatible, eco-friendly speciation sensor with excellent sensitivity and a temporal resolution of milliseconds.

Equation 1:

$$\log_{10}(K_f) = 12.21 - (5.49 \times 10^7) \times [\text{Cu}^{2+}]_{\text{free}} + (0.12) \times \text{Current} + (1.74 \times 10^5) \times [\text{Cu}^{2+}]_{\text{free}}^2 \times \text{Current} + (8.82 \times 10^{11}) \times [\text{Cu}^{2+}]_{\text{free}}^2 - (4.21 \times 10^{-4}) \times \text{Current}^2$$

Keywords: Fast scan cyclic voltammetry, Fast scan controlled adsorption voltammetry, Metal speciation, Complexation, Formation constants