

Fast-scan Cyclic Voltammetry for Continuous, Ultra-Fast Measurements of Trace Metals in Natural Water Systems

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Trace metal contamination of natural waters is hazardous to the environment and to the public. The adverse effects of trace metals are well known and potent metal mitigations systems have been developed. To efficiently implement the systems however, more information is needed about dynamic metal behavior in natural systems. This necessitates an *in-situ* analytical device that is portable and low-cost while providing a continuous measurement output. While electrochemistry has shown promise for this goal it has been limited by its temporal resolution and concerns about Hg toxicity. This paper describes a novel electrochemical technique that can perform Hg free, real-time trace metal analysis at carbon fiber microelectrodes. The application of this method to Cu (II) and Pb (II) measurements is described.

Introduction

Pollution of natural waters and foods by trace metals is detrimental to the environment and to the public. Trace metals leach into natural waters from industrial and consumer wastes^[1] and bioaccumulate in plants and animals^[2, 3]. The toxic effects of trace metals are well documented^[4]; as such several methods have been developed to interdict their impact. For example, passive treatment systems such as rain gardens and bioswales^[5, 6] as well as active systems employing chelation and amendements^[7, 8]. These methods are low energy, inexpensive approaches with great promise for sustainability^[5, 6] but in many instances they cannot be applied effectively. Aqueous metal chemistry is complex, especially during events such as storms where solution chemistry is not in equilibrium^[9]. In these circumstances, because trace metals fluctuate dynamically, it is difficult to follow their transport to assess when and how to apply mitigation^[10, 11]. To better understand metal transport, it is necessary to rapidly quantify the interactions of metals with organic ligands and soils because these reactions have rapid kinetics (\leq seconds)^[12]. The experimental information needed to understand rapid metal transport is critically uncharacterized. This is because analytical methods that allow scientists to accurately understand the kinetics of trace metals in environmental contexts continuously and in real-time are limited.

Rapid environmental events occur on a fast temporal resolution (seconds). Spectroscopic techniques provide high sensitivity but they require sample collection and manipulation^[13, 14]. Sample collection introduces temporal limitations and likely alters metal speciation^[15]. To bypass this, a compact submersible or integrated device, capable of sampling its immediate environment while minimally altering it, would be ideal. Electrochemistry has previously been explored in this context because reactions occur on a portable, fashionable and submersible surface. Ion-Selective Electrodes (ISEs) have a temporal resolution of seconds, however, issues with stability have limited their applicability *in-situ*^[16, 17]. Voltammetric methods such as Anodic Stripping Voltammetry (ASV) have also been explored^[18]. ASV applies a negative potential to an electrode for several minutes such that positively charged metal ions electrodeposit on the surface. The metal is then 'stripped' off during a positive sweep and the current generated quantifies the metal. ASV is capable of parts per trillion sensitivity and has been used in a device that researchers have taken to sample off-shore waters with readings every 3 minutes^[18].

The extreme sensitivity of ASV hinges upon two critical factors that paradoxically limit its environmental applications. First, electrodeposition is unstable on most substrates. Hg electrodes significantly stabilize deposition by creating an amalgam with the depositing metal.

Because Hg itself is environmentally hazardous, Hg electrodes are not suited for environmental studies. A safer electrode such as the Bismuth Film Electrode (BFE) is more appropriate to monitor the environment. Unfortunately, the BFE is limited by a narrow anodic range that makes it impossible to detect metal ions with oxidation potentials more positive than Bi (e.g., Cu)^[19]. Second, electrodes are held at a negative potential for several minutes to ‘pre-concentrate’ the metal and create high sensitivity^[20]; this process prevents high temporal resolution analysis. Hence, there is great interest in creating an electrochemical method that is Hg-free and requires little or no pre-concentration.

Carbon Fiber Microelectrodes (CFMs) for Hg-free Metal Analysis

Carbon fibers are inexpensive, inert and green electrode materials. In addition, they display excellent stability, sensitivity and fast electrode kinetics. We apply Hg-free CFMs to fast metal analysis^[21, 22]. Construction of CFMs is described in detail elsewhere^[21, 22]. Briefly single carbon fibers of 5-7 μm in diameter are aspirated into fine glass capillaries. These glass capillaries are pulled apart under heat and gravity to form a glass seal around the carbon fiber. The exposed carbon fiber is then cut to a length of 100-150 μm under an optical microscope. A zoomed-in view of the carbon fiber surface is shown in the Scanning Electron Microscope (SEM) image in Figure 1. There are horizontal carbon striations that run the length of the carbon fiber, providing a rich surface area for electrochemistry. CFMs are electrochemically pretreated before experimentation by over-oxidization at 1.3V^[23]. Like other activated carbons, activated CFM surfaces

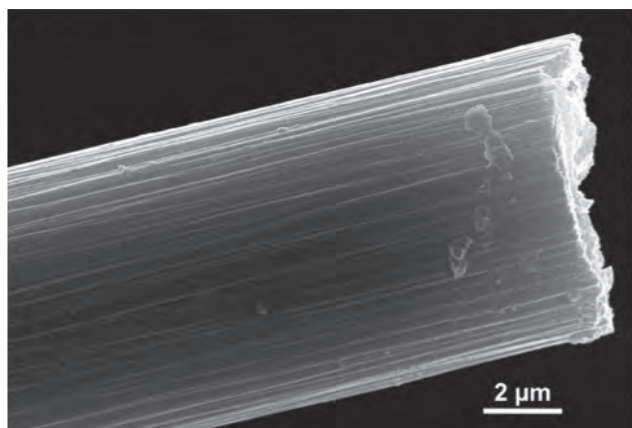


Figure 1—Scanning electron microscopic image of CFM surface.

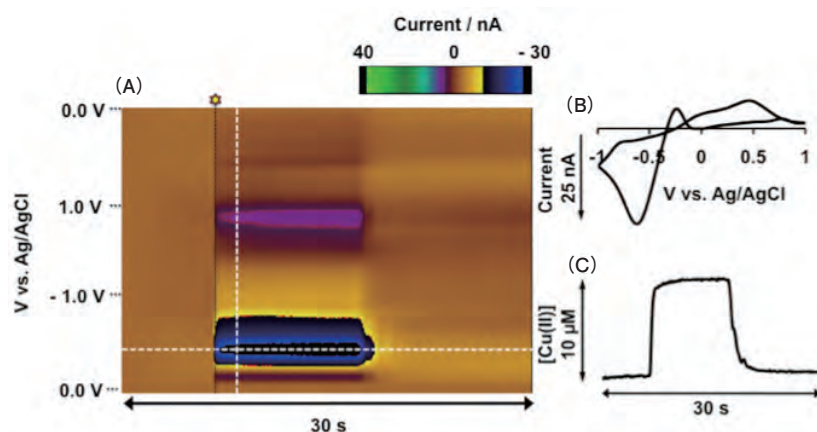


Figure 2—(A): Color plot of CVs collected for 30 s during Cu (II) injection. (B)—CV taken from vertical dashed line on the color plot. (C)—Concentration vs. time extrapolated from (C).

have a highly adsorptive surface. Whereas traditional metal voltammetry on other electrode surfaces is slow (minutes), metal electrochemistry on CFMs is adsorption controlled. This adsorption is a very dynamic process therefore ultra fast-scan rates can be employed to rapidly collect voltammograms. We call our method Fast Metal Voltammetry (FMV). This method can continuously quantify metals, is low cost, robust and environmentally green.

Figure 2 shows the response of the method that we created for Cu (II) analysis, to Cu (NO₃)₂ (10 μM) in a flow injection analysis (FIA) system. FIA introduces a fast bolus of analyte into a buffer stream and therefore can mimic rapid environmental events. The star indicates analyte injection time. The color plot in (A) is a topographic representation of Cyclic Voltammograms (CVs) collected every 100 ms for 30 s. Time is plotted on the x-axis and potential on the y-axis. Current is displayed in false color on the z-axis. (B) shows one CV, taken at the time indicated by a white vertical dashed line from the color plot. Current is measured at the peak reduction potential for Cu (II) (horizontal white dashed line) and is converted to concentration with time (C) with calibration curves. While Cu has previously been characterized with slow-scan voltammetry, it is the information in (C), real-time concentration, that is fundamentally novel.

Fast Cu Analysis

Copper (Cu) is a trace metal that is essential to human life^[24]. Inorganic copper easily bypasses the liver and directly enters the free copper pool of the blood. This copper is potentially hazardous as it may penetrate the blood/brain barrier. In the brain, copper can be particularly toxic, being implicated in Alzheimer’s and Wilson’s diseases amongst other neurodegenerative

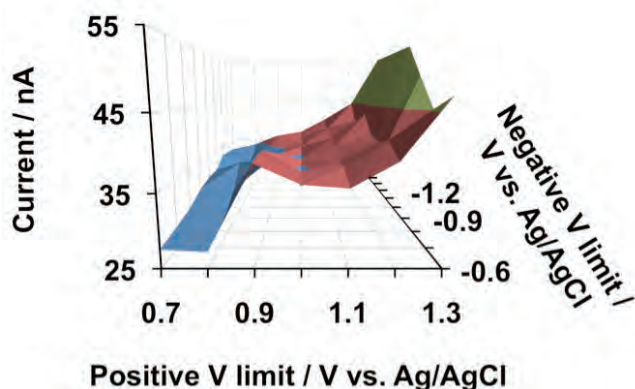


Figure 3—Current response with different combinations of positive and negative potential limit taken from^[21].

disorders^[25, 26]. Furthermore, Cu electrochemistry is well-established therefore we first optimized FMV for copper analysis^[21].

An electrochemical waveform is the ‘instruction’ to the electrode surface and comprises of a positive potential limit, a negative potential limit, a resting potential and a scan rate. To optimize FMV for Cu, it was necessary to modify and optimize the waveform. We first assessed the

FMV current response (i.e. the sensitivity) by varying the positive and negative potential limits. Figure 3 shows the averaged current response to Cu (II) (10 μM). Every point on this contour is the averaged current response at a particular combination of positive and negative limit. The current is increased with increasing negative potential but there is a more defined trend with increasing positive limit. There is an exponential increase after 1.2 V, a phenomenon previously observed for neurotransmitters. This is due to over-oxidation of the carbon surface that creates more adsorptive oxygen functionalities, thus increasing sensitivity^[23]. Additionally, the carbon fiber surface is regenerated with each scan, providing a fresh surface between scans^[27]. We, therefore, took the optimal potential limits as -1.4 V to 1.3 V vs. Ag/AgCl. Through similar experimentations, we determined that the optimal resting potential was 0 V and the optimal scan rate was 600 Vs^{-1} . With this optimized waveform we experimentally followed Cu (II) levels in real-time.

The power of real-time continuous copper detection is demonstrated in Figure 4. In this experiment, the CFM was immersed into a well-stirred solution of Cu (II). Ethylenediaminetetraacetic acid (EDTA), a well-known

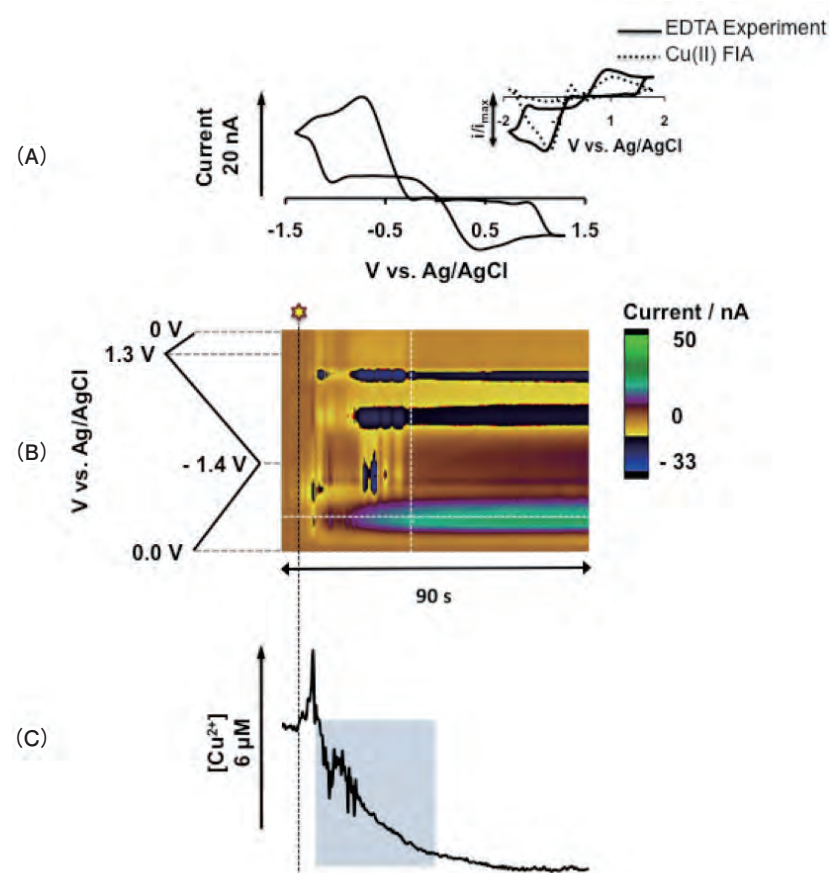


Figure 4(A)—CVs taken from the white vertical dashed line from the color plot (B). Inset—CV, reversed in current, of Cu (II) (10 μM) collected *in vitro* (dashed) superimposed on CV taken from white vertical dashed line on (B). (B) Color plot of Cu (II) upon addition of EDTA. (C) Concentration of Cu (II) vs. time taken. Taken from^[21].

and potent chelator of metal ions including Cu (II) was added to this solution at the time point indicated by the star and the vertical dashed black line. It can be seen from the color plot in (B) that immediately upon addition of EDTA, there is an electrochemical event. We previously tested EDTA with the Cu (II) specific waveform and found very little electroactivity therefore this change is only mediated by EDTA. The close agreement of the CV obtained during this event with an *in vitro* injection of Cu (II) confirms a reduction in the Cu (II) levels. This is to be expected since EDTA is a potent chelator of Cu (II). It can be seen in (C) that Cu (II) levels rapidly fall, reaching an equilibrium level after several seconds. This reading is fully quantitative. Cu-EDTA interactions are routinely performed during titrations, where EDTA additions can be evaluated after equilibrium has been reached. However the real-time data showing real-time binding of Cu by EDTA in (C) has not been observed before^[21]. We are currently using this type of experiment to assess the kinetic binding constants

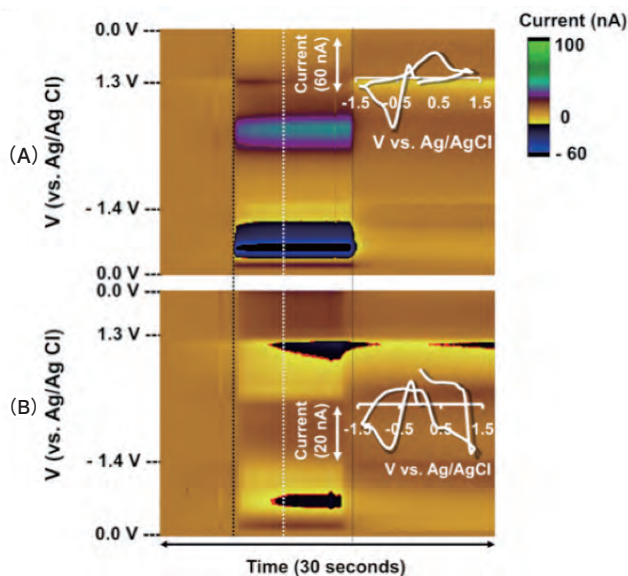


Figure 5(A)—Color plot with inset CV of Cu (II) injection with Cu (II) specific waveform. (B)—Color plot and inset CV of Pb (II) injection with Cu (II) specific waveform. Taken from^[22].

of different metal chelators.

Fast Pb Analysis

Lead (Pb) has a variety of important uses in industry and was used extensively in gasoline prior to the 1990s. Lead poisoning predominantly affects the central nervous system, especially in children. Long-term exposure to Pb causes more severe symptoms such as soft tissue damage and bone weakness. We therefore next optimized our FMV method for Pb detection^[22].

There were two challenges for Pb detection. Firstly Pb is relatively insoluble in most test solutions, therefore researchers have traditionally used test solutions at low pH^[28, 29] or those with non-environmentally relevant

compositions^[30, 31]. Secondly, the waveform that we had previously optimized for Cu (II) was not suitable for Pb detection. This can be seen in Figure 5. In this experiment, a Cu (II) injection with the Cu (II) specific waveform (A) is compared to a Pb (II) injection with the same waveform (B). While the Cu (II) CV has well-defined redox peaks, the Pb CV does not contain a recognizable redox process. This shows that different kinetics govern the Pb (II) response and that a different electrochemical waveform is required. We hence created a novel solution, that mimics stormwater as an environmentally relevant test solution and used this to optimize a novel waveform for Pb (II) detection^[22].

We used a geochemical model PHREEQc to create a test-solution that mimics stormwater. Our first solution was not stable, and precipitates formed, we therefore adjusted this solution in order to keep it at equilibrium^[22]. Additionally, Pb was stable in this second solution at an environmentally relevant pH. We used this solution to optimize a waveform for Pb (II) detection and were able to find reproducible and well defined redox peaks^[22].

This robust experimental model for quantifying Pb fluctuations in real-time is invaluable for studying metals in laboratory solutions. However, we wanted to test the feasibility of our method for studying Pb in real environmental samples of unknown composition. We therefore collected real stormwater samples after a storm event in January 2012. This was used as the buffer in our FIA system and also spiked with three different Pb (II) concentrations ((A): 20 μ M, (B): 50 μ M, (C): 100 μ M) (Figure 6). Each concentration was injected into the FIA system and the signal was evaluated. This is shown in Figure 6. The top panel of Figure 6 shows color plots. CVs collected from the vertical white dashed lines are displayed in the bottom panel. It can be seen that the

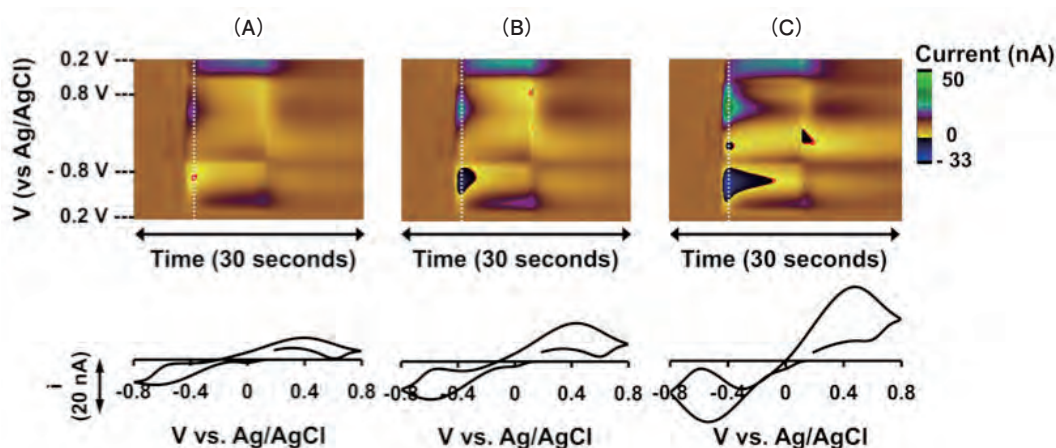


Figure 6(A)—Color plot and CVs for real stormwater samples spiked with different levels of Pb (II). Taken from^[22].

FMV signal increases with increasing Pb concentration. We therefore showed proof of concept that our FMV method can be applied in authentic environmental systems to measure dynamically fluctuating Pb.

Conclusions

There is public concern about trace metal pollution of natural water systems and its effects on the environment and on human health. As such metal mitigation systems have been developed to reduce the negative impact of metals. Unfortunately these systems are not currently used at their maximum efficiency due to lack of experimental knowledge about dynamic metal behavior in natural systems. A portable analytical method, capable of providing a continuous and real-time output of metal concentrations is necessary to provide experimental environmental data. Electrochemical methods have previously shown promise for this due to their low costs and portability but have been limited by their temporal resolution and potential toxicity. In this paper, we described a novel electrochemical method, FMV, which can perform real-time, green Cu and Pb analysis at CFMs. We described the application of FMV to real-time Cu (II) binding by EDTA and to measuring Pb (II) in real environmental samples.

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