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### Fiber Optic Spectroelectrochemical Sensing for *in situ* Determination of Metal Ions

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## Fiber Optic Spectroelectrochemical Sensing for *in situ* Determination of Metal Ions

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**Abstract:** *In situ* chemical sensing techniques are increasingly used for a variety of applications, including industrial process control, on-site environmental assessment, and detection of explosives and chemical and biological weapons. A common category of sensors for such purposes entails the use of optical fibers for making spectral measurements of target compounds or species derived from these compounds via physical, chemical, enzymatic, or immunologic reactions. A less common but potentially advantageous approach involves the electrochemical conversion of the analyte subsequent to its spectroscopic detection. These spectroelectrochemical schemes represent versatile, essentially reagent-free analyses that could provide superior alternatives to existing methods. Reported here is a summary of progress made by the authors' group toward the development of fiber optic spectroelectrochemical sensors for *in situ* measurements. The aqueous copper (II)/copper (0) couple was chosen as a model system to investigate the merit of an analytical scheme involving (i) cathodic preconcentration of  $\text{Cu}^{2+}$  as  $\text{Cu}^0$  followed by (ii) anodic stripping of  $\text{Cu}^0$  to  $\text{Cu}^{2+}$ , (iii) complexation of  $\text{Cu}^{2+}$  by an appropriate ligand, and finally (iv) absorbance determination of the copper–ligand complex or fluorescence determination of the unbound ligand. Results are encouraging and indicate the need for further

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refinement of the sensor's design and the experimental protocol in order to improve the method's sensitivity.

**Keywords:** Fiber optic sensors, heavy metals, spectroelectrochemistry

## INTRODUCTION

Since their introduction in the mid-1960s,<sup>[1]</sup> spectroelectrochemical (SEC) techniques have been extensively applied to fundamental studies of electrode processes and related phenomena, and they have become well-established tools for a wide variety of investigations.<sup>[2]</sup> To date, however, SEC methods have seen relatively few applications for purely analytical purposes (i.e., measurement of analyte concentration). As illustrated in the bulk of the existing literature summarized below, one particularly attractive trait of an SEC assay is the enhanced selectivity afforded by simultaneous control of both the analytical wavelength and the electrolysis potential. Spectral interferants are thus of no consequence if they are not electrochemically active at the employed electrolysis potential because it is the *change* in optical signal that is measured. Sample components that are electrochemically active at potentials very close to the analyte's redox potential ("electrochemical interferants") likewise pose no problem to determination of the analyte if they do not absorb at the wavelength of interest: that is, if they are not also spectral interferants. For components that are both electrochemical and spectral interferants, more elaborate data acquisition and analysis procedures (multiwavelength measurements, spectral deconvolution, etc.) may be required.

The seminal body of work on the potential utility of SEC techniques for analytical purposes is perhaps that produced by West, Tyson, and other. The first report by West involved preliminary studies on the determination of electrogenerated hydrated metal "atoms" via atomic absorbance and fluorescence spectrometry.<sup>[3]</sup> More specific demonstrations of the general analytical utility of SEC for metal ions<sup>[4]</sup> and organic compounds<sup>[5]</sup> were subsequently reported by Tyson and West. In these studies, and in a later report by Tyson<sup>[6]</sup> that included preliminary results for anodic stripping SEC, a bulk electrochemical cell was employed that permitted parallel or grazing angle sampling of solution adjacent to a planar working electrode. One report by West and McLeod<sup>[7]</sup> involved fluorescence SEC determination of alkaloids using a thin-layer flow cell modified with a gold minigrid working electrode.

Xie and Dong reported the derivation of theoretical relations and experimental verification of analytical SEC determination for analytes involved in simple, reversible electrode processes,<sup>[8]</sup> electrocatalytic electrode reactions,<sup>[9]</sup> and electrodeposition processes (anodic stripping). Yao et al. have reported a general theoretical and experimental treatment of potential-step chronoabsorptometric determination of reversible analytes,<sup>[10]</sup> and have

published specific descriptions of the SEC determination of trace iron<sup>[11]</sup> and copper.<sup>[12]</sup>

Most recently, Heineman et al. have published an extensive series of articles detailing various applications of a SEC sensor employing attenuated total reflectance sampling of optically transparent electrodes. Since its initial demonstration of concept report,<sup>[13]</sup> this group has investigated diverse aspects of the sensor as described in nearly two dozen journal articles.<sup>[14]</sup>

Fiber optic-based chemical sensors have been increasingly used over the past decade for a wide variety of applications. These sensors typically involve either direct spectral measurement of the analyte or similar measurement of another chemical species linked to the analyte via some transduction mechanism that serves to enhance the measurement's selectivity. Common transduction schemes include chemical, enzymatic, and immunologic reactions of the analyte with appropriate reagents immobilized on or near an optical fiber terminus.<sup>[15]</sup> Because of their promise for solving a wide variety of *in situ* measurement problems, the development of new sensors and sensing protocols represents a most active area of research as described in several recent review articles.<sup>[16–18]</sup>

Fiber optic spectroelectrochemical (FOSEC) sensors employ electrochemical cells to serve the same function as the immobilized reagents (indicators, enzymes, antibodies, etc.) of more conventional fiber optic probes (i.e., to induce a change in the sensor signal related to the concentration of analyte species). The transduction mechanism in such sensors is thus the reduction or oxidation of the analyte by the sensor's working electrode. Although there have been many reports on the use of fiber optics to monitor processes in conventional electrochemical cells, to date there have been only a few publications on true FOSEC sensors as described in the following paragraphs.

Van Dyke and Cheng have described FOSEC sensor designs for diffuse reflectance<sup>[19]</sup> and luminescence<sup>[20]</sup> measurements in various biological media. These designs were somewhat incomplete, however, in that the employed reference and auxiliary electrodes were physically separate from the sensor, thus complicating *in situ* measurements. Although applications were demonstrated, the sensors' analytical performance was not rigorously evaluated, and no subsequent reports have appeared.

Egashira et al. have described a sensor that exploits the electrochemiluminescent behavior of the  $\text{Ru}(\text{bpy})_3^{2+/3+}$  couple for measurement of oxalate<sup>[21]</sup> and have reported its application to such determinations in a variety of vegetables.<sup>[22]</sup> Results obtained in this latter study were in general rather poorly correlated with those obtained by ion chromatography.

Gunasingham et al. have reported on the performance of a fiber optic glucose sensor employing tetrathiafulvalene (TTF) as both a redox mediator and an optical indicator.<sup>[23]</sup> Compared with the amperometric method, the FOSEC sensor exhibits an inferior linear range and detection limit but does possess slight advantages in terms of discrimination against chemical interferences.

Based on the successes of previous feasibility studies<sup>[24]</sup> and apparatus development,<sup>[25]</sup> Carrabba and co-workers have developed a FOSEC sensor for analysis of organics in water based on surface-enhanced Raman (SER) spectrometry.<sup>[26]</sup> This sensor promises to afford sensitive and selective screening for a variety of organic contaminants in surface and subsurface environmental waters, though field measurements using this SER sensor have not yet been reported.

Work in the authors' laboratory is directed toward the development of FOSEC sensors suitable for *in situ* measurements, with a current focus on heavy metal ions of environmental concern. Most recently, the modification of commercially available fiber optic flow cells to yield FOSEC sensors permitting spectral detection of species derived from analyte electrolysis has been investigated. Aqueous copper (II)/copper (0) has been used as a model system in the development of analytical schemes involving (i) cathodic preconcentration of  $\text{Cu}^{2+}$  as  $\text{Cu}^0$  followed by (ii) anodic stripping of  $\text{Cu}^0$  to  $\text{Cu}^{2+}$ , (iii) complexation of  $\text{Cu}^{2+}$  by an appropriate ligand, and finally (iv) absorbance determination of the copper–ligand complex or fluorescence determination of the unbound ligand. This paper provides a summary of the current status of this work.

## MATERIALS AND METHODS

### Reagents

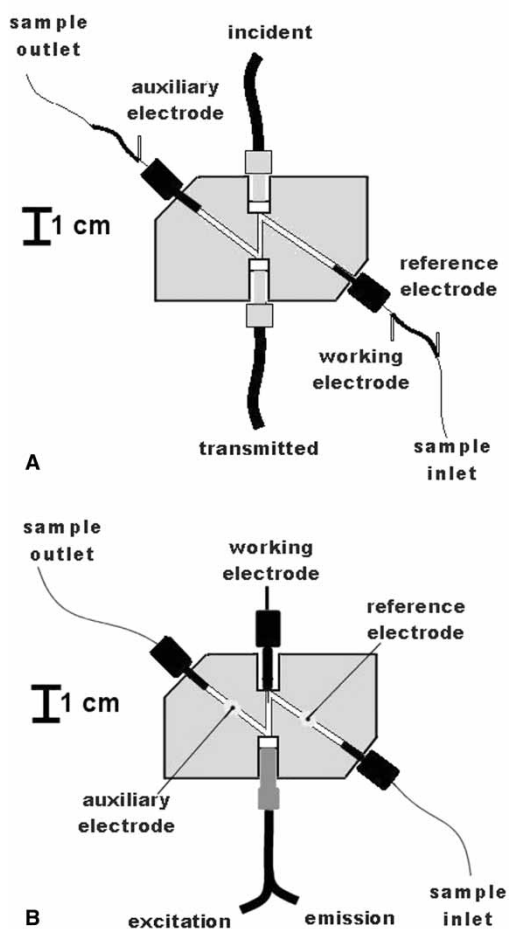
The following reagent grade chemicals were used as received from Fisher Scientific (Pittsburgh, PA, USA): calcein,  $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_{13}$  (1461-15-0); copper sulfate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (7758-99-8); disodium ethylenediaminetetraacetic acid dihydrate (EDTA),  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  (6381-92-6); hydrochloric acid,  $\text{HCl}$  (7647-01-0); potassium ferricyanide,  $\text{K}_3\text{Fe}(\text{CN})_6$  (13746-66-2); potassium nitrate,  $\text{KNO}_3$  (7757-79-1); sodium bicarbonate,  $\text{NaHCO}_3$  (144-55-8); sodium carbonate,  $\text{Na}_2\text{CO}_3$  (497-19-8); sodium hydroxide,  $\text{NaOH}$  (1310-73-2); sodium monohydrogen phosphate heptahydrate,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  (7782-85-6).

Solutions were typically prepared using deionized water, stored in tightly capped polyethylene or polycarbonate bottles, and used within a few days of preparation. All solutions were prepared using 1 M  $\text{KNO}_3$  as the supporting electrolyte. Absorbance FOSEC measurements employed a 0.2 M EDTA solution buffered to pH 10 with 0.1 M  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ . A 0.01 M calcein solution buffered to pH 8 with 0.05 M  $\text{Na}_2\text{HPO}_4$  was used for fluorescence measurements.

### FOSEC Sensor Construction

The FOSEC sensors were fabricated by incorporation of working, reference, and auxiliary electrodes into a commercially available fiber optic flow cell

(model SMA-Z, FIALab Instruments, Inc.). Working and auxiliary electrodes were typically wires or rods of Pt, Au, or glassy carbon (Alfa-Aesar, Karlsruhe, Germany), and miniature AgCl/Ag reference electrodes were prepared according to the procedure reported by Nolan et al.<sup>[27]</sup> Initial work involved absorbance measurements using separate fiber optic cables (RRU-171-1-SS, Multimode Fiber Optics, Inc.) with electrodes epoxy-sealed into the sample inlet and outlet tubing as illustrated in Fig. 1A. In hopes of improving sensitivity, subsequent efforts were focused on fluorescence measurements using a bifurcated fiber optic bundle (RBU-171-1-S, Multimode) coupled to one of the flow cell's optical ports, but problems with sample leakage due to poor adhesion of the epoxy to the PTFE tubing prompted an alternative modification



**Figure 1.** Illustrations of FOSEC sensors for absorbance (A) and fluorescence (B) measurements.

(Fig. 1B). This design includes reference and auxiliary electrodes epoxy-sealed into small holes drilled into the flow path of the cell body and a working electrode epoxy-sealed into a ferrule and subsequently bushing-sealed into the cell's unused optical port.

### Instrumentation

Electrochemical measurement and control were accomplished using either a model CV-50 W or CV-27 voltammograph, or a model LC-E3 potentiostat (Bioanalytical Systems, Inc., West Lafayette, IN, USA). Absorbance measurements were made with a model 8453 diode array spectrometer (Agilent Technologies, Santa Clara, CA, USA) and fluorescence measurements with a model USB2000-FLG CCD spectrometer in conjunction with a model LS-450 LED light source (Ocean Optics, Inc., Dunedin, FL, USA). Sample flow was achieved by either a variable speed, programmable syringe pump (model BS-8000, Braintree Scientific, Braintree, MA, USA) or a variable flow peristaltic pump (Fisher Scientific, Pittsburgh, PA, USA).

### Procedure

A typical experiment was conducted by first assembling the sensor, flushing thoroughly with deionized water to remove air, and then filling with the sample solution of interest. Voltammetric measurements were made under static conditions (i.e., without sample flow). Fluorescence calibration measurements were made by monitoring the sensor's optical signal while making sequential, measured additions of analyte stock solution to a beaker containing solvent that was recirculated through the sensor via a peristaltic pump. Absorbance and fluorescence spectroelectrochemical measurements using the copper (II)/copper (0) system generally entailed a three-step procedure:

1. Electrodeposition of  $\text{Cu}^{2+}$  as  $\text{Cu}^0$  while flowing the sample solution through the sensor at 0.5 mL/min for a measured time interval with the working electrode held at a reducing potential.
2. Replacement of the sample with a buffered solution of complexing ligand.
3. Monitoring the optical signal during the anodic stripping of  $\text{Cu}^0$  to  $\text{Cu}^{2+}$  while flowing ligand solution through the sensor with the working electrode held at an oxidizing potential.

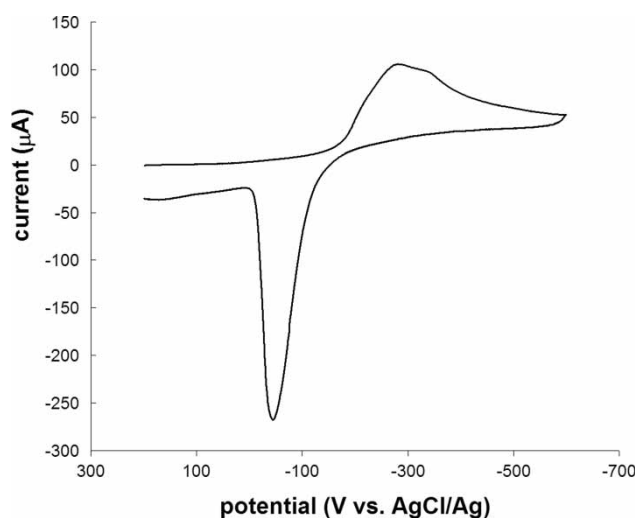
### RESULTS AND DISCUSSION

After incorporation of electrodes into a flow cell, the electrochemical performance of the modified cell was evaluated to ensure that adequate working

electrode control with minimal ohmic distortion was possible. Cyclic voltammograms of 3 mM potassium ferricyanide were measured over scan rates ranging from 5 to 100 mV/s using a glassy carbon rod working electrode ( $\sim 3 \text{ mm} \times 1 \text{ mm}$  o.d.). The expected dependence of peak current on scan rate was observed, and a moderate cell resistance was indicated by a peak potential separation that increased from approximately 80 to 120 mV over this range of scan rates. Similar results were obtained using platinum and gold working electrodes.

A cyclic voltammogram for 5 mM copper sulfate measured at a platinum working electrode is shown in Fig. 2 and exhibits the characteristic sharp, symmetric anodic feature attributable to electrolysis of an electrode surface-bound species. Using these data, suitable values of deposition and stripping potentials for a spectroelectrochemical analysis to determine copper (i.e., steps 1 and 3 noted previously) were identified as  $-500 \text{ mV}$  and  $+200 \text{ mV}$ , respectively.

Initial work on developing such an analysis was directed toward absorbance measurements of the copper-EDTA complex. As demonstration of this approach, several series of copper standard solutions in the millimolar concentration range were prepared and analyzed per the three-step scheme described above using a 10-min deposition time. Calibration curves generated by plotting peak absorbance of the signal transients versus concentration over the 0–6 mM range were reasonably linear ( $R^2 > 0.9$ ) and exhibited near-zero y-intercepts and slopes (sensitivities) of  $\sim 60 \text{ mau/mM}$ . Considering the baseline noise in the measured absorbance signal transients, the detection limit for copper under the employed experimental conditions



**Figure 2.** Cyclic voltammogram for 5 mM copper sulfate measured with a platinum electrode at a scan rate of 20 mV/s.

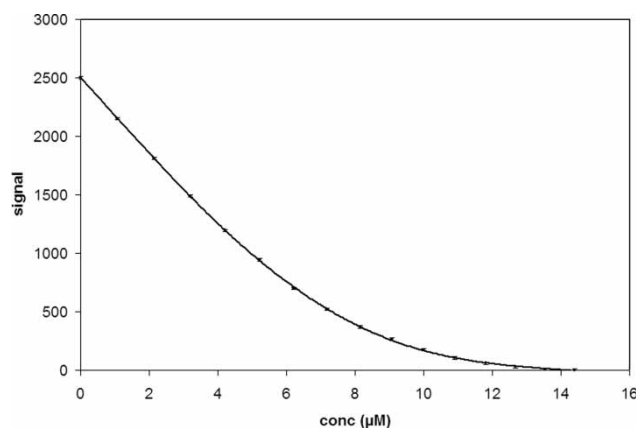


was estimated per the  $S/N > 3$  criterion<sup>[28]</sup> to be of the order  $10^{-4}$  M. Though these preliminary data represented a successful proof of concept for the FOSEC sensing strategy, the demonstrated sensitivity and detection limit were not sufficient for the planned environmental applications to trace heavy metal determinations.

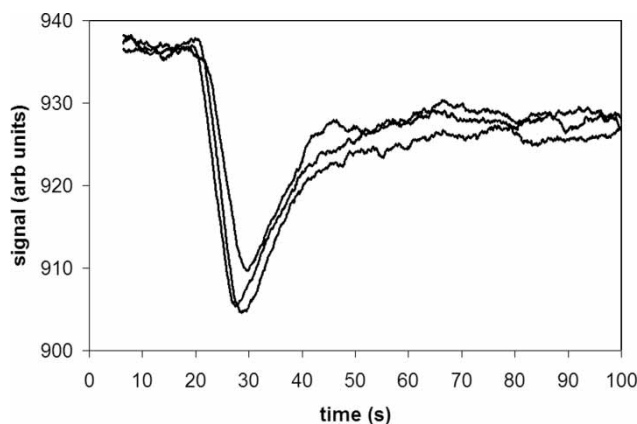
In pursuit of greater sensitivity, an approach was developed similar to that reported by Buffle et al.<sup>[29]</sup> in which copper was determined via its quenching of the fluorescence of a fluorochromic ligand, calcein, following its preconcentration by selective extraction using a permeation liquid membrane. In contrast, the FOSEC scheme reported here will accomplish analyte preconcentration via electrodeposition. To examine the feasibility of this method, the FOSEC sensor was first calibrated to assess its optical sensitivity and detection limit for copper (II). Measuring fluorescence signals for calcein standards suggested a linear range of approximately 0–10  $\mu\text{M}$ , hence a solution of  $\sim 10$   $\mu\text{M}$  was used to calibrate the sensor for determination of copper via fluorescence quenching. The results of these calibration measurements were in good agreement with previously published data,<sup>[29]</sup> and indicated a detection limit of the order 10 nM (Fig. 3). These results suggest that a FOSEC assay of the sort described above should be suitable for trace or, considering the cathodic preconcentration step, even ultratrace level analyses.

As an initial demonstration of the fluorescence FOSEC measurement approach, relatively concentrated (i.e., millimolar) copper sulfate solutions have been subjected to the three-step analysis described above. For example, one series of triplicate measurements using a 3 mM copper sulfate solution and a 5-min deposition time generated the data shown in Fig. 4.

While these results demonstrate proof of concept, a number of issues must be addressed in order to develop a useful method for trace level heavy metal



**Figure 3.** Calibration curve for determination of copper (II) by fluorescence quenching of an  $\sim 12$   $\mu\text{M}$  calcein solution (450-nm excitation, 517-nm emission).



**Figure 4.** Signal transients for triplicate fluorescence FOSEC measurements of a 3 mM copper sulfate standard (450-nm excitation, 517-nm emission).

analysis. Based on the data presented in Fig. 4, the detection limit does not appear to be significantly lower than that observed for absorbance measurements. Additionally, the fluorescence FOSEC measurements have to-date exhibited a rather poor repeatability, perhaps due in part to occasional solubility problems as evidenced by precipitate formation in the sensor effluent.

## CONCLUSIONS

In summary, the concept of fiber optic spectroelectrochemical sensing for *in situ* heavy metal ion determinations has been successfully demonstrated, though a number of issues have been identified as areas in need of investigation and improvement. The potentially high sensitivity of fluorescence FOSEC measurements has not yet been realized, perhaps a result of chemical complications (e.g., analyte precipitation) or other unidentified factors. Current work is being directed toward understanding the solubility issues associated with the analysis scheme, in addition to optimizing the sensor's working electrode characteristics (material, geometry, etc.), in hopes of resolving the sensitivity and repeatability problems. Subsequently, the effects of various experimental parameters such as deposition time, sample flow rate, and the presence of interferants may be examined in the course of developing a robust method suitable for *in situ* determination of heavy metal ions.

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