INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700  800/521-0600
METAL ION ANALYSIS BY DIFFUSIONAL MICROTITRATION:
ELECTROCHEMICAL GENERATION OF EDTA AT CARBON-FIBER
MICROELECTRODE ARRAYS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy
in the Graduate School of The Ohio State University

by

Larry J. Cain, B.S.

* * * * *

The Ohio State University
1998

Dissertation Committee:
Professor Larry B. Anderson, Advisor
Professor Richard L. McCreery
Professor Susan V. Olesik

Approved by

[Signature]
Advisor
Department of Chemistry
ABSTRACT

A carbon fiber microelectrode has been used to develop and investigate a novel method for the titration of metal ions and other electroactive species. Electrochemical shielding of the center fiber from the analyte, by the formation of titrant at the outer pair, allows a stoichiometric endpoint to be determined. A complexometric titration using amperometric endpoint detection is therefore possible using this type of electrode arrangement.

As a test case, electrogenerated EDTA was used to titrate Bi\(^{3+}\) solutions of a few to several hundred micromolar concentration. The central fiber of the array acted as the indicator (collector) electrode for uncomplexed Bi\(^{3+}\) by having its potential fixed sufficiently negative for reduction of Bi\(^{3+}\) but not for reduction of the BiEDTA\(^-\) complex. By controlling the reduction current applied to the generator fibers, the quantity of titrant is controlled precisely. An increase in the generator current liberates more titrant into solution where it shielded the collector from the analyte. The generator current which resulted in maximum shielding of the collector was shown to be proportional to the bulk concentration of analyte.

Because carbon-fiber microband arrays have been difficult to construct, they have not been frequently used. A simple, inexpensive, and relatively quick
procedure to construct these arrays has been developed and described. The electrodes are sufficiently reliable and rugged for repeated use and polishing, unlike electrode arrays formed by thin-film or vapor deposition techniques.

The qualitative relationships of the electrode and experimental variables to the analytical results are explored. The quality and characteristics of the electrode array are shown to affect the quality and characteristics of the analysis. In addition, the nature of the carbon surfaces requires that modified procedures be used to achieve adequate electrode response for solution concentrations less than approximately 20 μM. It is shown that the analysis is quick (endpoints typically reached in less than a minute), precise (1 to 5% RSD), and reliable.
I dedicate this work to my mother and family, who were always there to give support, and especially to the memory of my late father who was not able to see it completed.
ACKNOWLEDGMENTS

I wish to thank my advisor, Larry Anderson, for the ideas and discussions which made the work in this thesis possible.

I also thank Beth Groeber, Larry Cai, Husantha Jayaratna, and Hong Ren for their help with the problems which were too difficult to work out alone.

This research was supported by grants from the Lubrizol Co. and the U.S. Department of Education.
VITA

October 18, 1965 ................................................ Born- Kenosha, Wisconsin

1988 .............................................................. B.S. Chemistry,
University of Illinois,
Urbana, Illinois

1988 - 1991 ...................................................... Control Scientist,
Burroughs-Wellcome Co.,
Greenville, North Carolina

1991 - 1997 ...................................................... Graduate Teaching Associate
and Research Fellow, The Ohio
State University

1997 - present ................................................... Research Scientist, Wyeth-Ayerst
Research, Pearl River, New York

FIELDS OF STUDY

Major Field: Chemistry
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>Chapters:</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Experimental</td>
<td>7</td>
</tr>
<tr>
<td>2.1. Reagents</td>
<td>7</td>
</tr>
<tr>
<td>2.2. Electrode Fabrication</td>
<td>8</td>
</tr>
<tr>
<td>2.2.1. Plating of Carbon Fibers</td>
<td>8</td>
</tr>
<tr>
<td>2.2.2. Coating With Photoresist</td>
<td>10</td>
</tr>
<tr>
<td>2.2.3 Fiber Arrangement and Immobilization</td>
<td>11</td>
</tr>
<tr>
<td>2.2.4. Electrical Connections</td>
<td>14</td>
</tr>
<tr>
<td>2.2.5. Fiber Polishing</td>
<td>15</td>
</tr>
<tr>
<td>2.2.6. Electrode Characterization</td>
<td>15</td>
</tr>
<tr>
<td>2.2.7. Comments On Electrode Fabrication and Use</td>
<td>19</td>
</tr>
<tr>
<td>2.3. Apparatus</td>
<td>22</td>
</tr>
<tr>
<td>2.3.1. Instrumentation</td>
<td>22</td>
</tr>
<tr>
<td>2.3.2. Electrochemical Cell</td>
<td>25</td>
</tr>
<tr>
<td>2.4. Experimental Procedures</td>
<td>27</td>
</tr>
<tr>
<td>2.4.1. Preliminary cyclic voltammograms of metal ions</td>
<td>27</td>
</tr>
<tr>
<td>2.4.2. Electrochemical shielding experiments</td>
<td>29</td>
</tr>
</tbody>
</table>
3. Theory ........................................................................................................................................35

3.1. EDTA as a complexometric titrant .......................................................................................35
3.2. EDTA titrations using electrochemical endpoint detection ..............................................39
3.3. Electrochemical Shielding at triple-band microfiber arrays ..............................................42
3.4. Mass transport at the electrode surface ..............................................................................50

4. Results and Discussion ..........................................................................................................55

4.1. Reduction of metal ions and metal ion/EDTA complexes at carbon fibers ......................55
  4.1.1. Determination of reduction potentials ..........................................................................56
  4.1.2. Reduction overpotential and surface activity ..............................................................58
  4.1.3. Mechanical instability of deposits ..............................................................................60
4.2. Swept-current experiments with Bi³⁺/BiEDTA⁻ ..................................................................61
  4.2.1. High concentrations (greater than 20 μM Bi³⁺) ..........................................................62
  4.2.2. The relationship of experimental variables to analytical characteristics .....................67
  4.2.3. Predeposition to increase electrode activity ...............................................................78
  4.2.4. Analysis of low concentration Bi³⁺ solutions (less than 20 μM Bi³⁺) .........................84
4.3. Stepped-current experiments ..............................................................................................89
  4.3.1. Analysis results ...........................................................................................................90

5. Conclusions ...............................................................................................................................95

Bibliography ..............................................................................................................................100
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Pseudo steady-state reduction currents of 0.17 mM Bi^{3+} solution at individual fibers after successive polishings to expose fiber surface</td>
</tr>
<tr>
<td>3.1</td>
<td>Formation constants for various metal-EDTA complexes</td>
</tr>
<tr>
<td>3.2</td>
<td>Half-wave reduction potentials (volts) of metal ions before and after complexation with EDTA in different buffer solutions (potential vs. SCE)</td>
</tr>
<tr>
<td>3.3</td>
<td>Normalized currents at various triple-band geometries, showing the effect of shielding on a central generator flanked by two collectors</td>
</tr>
<tr>
<td>4.1</td>
<td>Approximate reduction potentials of metal ions and their EDTA complexes on carbon fiber surfaces in different buffers</td>
</tr>
<tr>
<td>4.2</td>
<td>Summary of experimental data for different electrode separations and generator sweep rates for the analysis of Bi^{3+} solutions from 14 to 500 µM concentration. Endpoint RSD statistics are for the highest concentration tested and analysis times reflect approximate time to reach a stable baseline</td>
</tr>
</tbody>
</table>
4.3 Data summary for the analysis of low concentration Bi$^{3+}$ solutions (3.4 to 17$\mu$M) at different generator sweep rates and gap widths. Endpoint RSD statistics are for the highest concentration tested and analysis times reflect approximate time to reach a stable baseline .................................................. 87
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Stepwise illustration of carbon fiber electrode construction</td>
</tr>
<tr>
<td>2.2</td>
<td>Photoresist-coated carbon fibers arranged and immobilized in photoresist on a Kel-F substrate. Viewed at 50° from normal. Undulations are due to photoresist beads along the length of the fibers</td>
</tr>
<tr>
<td>2.3</td>
<td>Copper deposits on a three-carbon-fiber array showing uniformity of deposits. Note the greater deposition at the outer edges</td>
</tr>
<tr>
<td>2.4</td>
<td>Crystalline bismuth deposits on carbon fiber surface after reduction of Bi^{3+}. Deposition to center fiber only</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic diagram of the variable current source used to supply the generator electrodes</td>
</tr>
<tr>
<td>2.6</td>
<td>Cell components for the electrochemical shielding experiments</td>
</tr>
<tr>
<td>2.7</td>
<td>Schematic diagram of cell components and instrument connections</td>
</tr>
</tbody>
</table>
2.8 Generator current for swept current (upper) and stepped current (lower) shielding trials ................................................................. 32

3.1 Indicator electrode response in a typical amperometric titration, with endpoint determined by extrapolation .................................................. 41

3.2 Cross-sectional illustration of the diffusion of electrochemically active species between bands at a triple-band electrode ......................................... 43

3.3 Evolution of the diffusion layers at a triple-band electrode after simultaneous potential steps at all three bands. Dashed and dotted lines represent the approximate growth of the layers with time .................... 45

3.4 Response for Bi$^{3+}$ reduction at the collector (center) electrode of a triple-band experiencing shielding by the generator electrodes. Electrochemical shielding alone (----) and with stepwise generation of EDTA (· · · · ·) . 49

4.1 Cyclic voltammograms of 1 mM Bi$^{3+}$ (-----) and 1 mM BiEDTA$^-$ (———) in pH 4.0 acetate buffer showing the overpotentials for deposition on the carbon fiber .............................................................................................................. 59

4.2 Titration of Bi$^{3+}$/BiEDTA$^-$ solutions in pH 4.0 acetate buffer. Bi$^{3+}$ concentrations: 0.014 mM (---), 0.057 mM (· · · · ·), 0.133 mM (··· ·· · ·), and 0.353 mM (——). Generator sweep rate: 8.9 nA/sec .... 63

4.3 Calibration plot using the endpoints determined from the data in Figure 4.2 ................................................................................................................................. 66
4.4 Calibration plots for the analysis of Bi\textsuperscript{3+} solution using different electrode geometries and generator sweep rates. Electrode A: 12 \(\mu\)m avg. spacing (8.9 nA/sec ——— ; 17.7 nA/sec • • • • • •); Electrode B: 18 \(\mu\)m avg. spacing (17.7 nA/sec — — — — ; 35.2 nA/sec — — ; 59.7 nA/sec • • • • • •) ................................. 68

4.5 Effect of predepositing bismuth on the carbon fibers in the analysis of Bi\textsuperscript{3+} ions. Bi\textsuperscript{3+} concentration: 17 \(\mu\)M; generator sweep rate: 35 nA/second; generators switched on at 8 seconds, sweep started at 10 seconds. Scan 1: no predeposition (———); Scan 2: after a single analysis, no deliberate predeposition (———); Scan 3: after deliberate predeposition (———); Scan 4: after further predeposition (• • • • • •)………81

4.6 The analysis of Bi\textsuperscript{3+} solutions from 3.4 to 17 \(\mu\)M. Predeposition used on all fibers before each analysis. Generator sweep rate: 17.8 nA/second. 3.4 \(\mu\)M (———); 13 \(\mu\)M (———); 17 \(\mu\)M (——••••••). Electrode gap width: 7 \(\mu\)m ................................................................. 86

4.7 Reproducibility of low concentration (3.4 \(\mu\)M) Bi\textsuperscript{3+} analyses at electrode with 7 \(\mu\)m spacing. Bi predeposition to all fibers before each scan. Generator sweep rate: 35.6 nA/second .............................. 88

4.8 Analysis of Bi\textsuperscript{3+} solutions using stepped generator current. Initial period of 60 seconds before applied current. Collector/generator gap width: 15 \(\mu\)m. Applied current: 43 nA/step. Bi\textsuperscript{3+} concentrations: 87 \(\mu\)M (• • • • •), 130 \(\mu\)M (———), 170 \(\mu\)M (———), and 220 \(\mu\)M (• • • • •) ....91

4.9 Calibration plot of Bi\textsuperscript{3+} for stepped generator current. Same conditions as Figure 4.8. Slope: 2877 nA/mM. Intercept: 91 nA ............................................ 92

xiii
Chapter 1

Introduction

Voltammetric microelectrodes have become widespread in their use as analytical sensors because of the many advantages they offer over conventional macroscopic electrodes.¹⁻⁵ Their smaller dimensions result in 1) smaller charging currents when used with varying potentials, reducing the magnitude of the background and increasing the ability to accurately quantitate very low concentrations; 2) lower currents that create less ohmic drop and iR distortion than do larger electrodes in similar experiments; 3) their use as probes of very small solution volumes; and 4) higher diffusional currents resulting from non-linear diffusion, that does not occur to a significant extent at macroelectrodes. A potential disadvantage is that the significantly smaller voltammetric currents may prove difficult to measure and may require special precautions such as shielding to reduce the level of environmental noise. Modern electronic instrumentation, however, is able to measure the level of electrical signals seen at electrodes of micrometer (and even nanometer) dimensions.

Several strategies have been devised to remedy the problem of smaller currents. As opposed to an electrode that is microscopic in all its dimensions, one
that has only a single microscopic dimension may be used to certain advantage. For example, microband and microcylinder electrodes, with lengths much greater than their width, possess some of the properties of true microelectrodes (size, enhanced diffusion) while also having some properties of macroelectrodes (substantially higher currents). Choosing the geometry of the electrode may allow one to select particularly desirable analytical characteristics. For a given technique or experiment, microband electrodes may have properties that are more useful than others. A second strategy to overcome the potential problem of low current is to create an array of microelectrodes. In this manner, microdisk electrodes have been arranged in both random and regular patterns at sufficient distance from each other so that each behaves as if it existed alone. The summed response for all the microdisks in the array is many times greater than the response for a single microdisk, but it exhibits the same characteristics as those for an individual microdisk.

Likewise, microband electrodes have been arranged in parallel arrays to take advantage of multiplicity. If the microbands are addressable individually or as discrete sets, separate potentials may be applied and the electrochemistry at one may be detected at the others following diffusion through the intervening solution. These collector/generator experiments have typically been performed at rotating ring-disk electrodes (RRDEs). The precise theoretical treatment of the hydrodynamics at an RRDE allows electrochemical parameters to be controlled and determined accurately. However, disadvantages such as instrumental complexity, sensitivity to mechanical irregularities, and the inability to experience
redox recycling may limit its application.\textsuperscript{13,14} A planar microband array, on the other hand, avoids some of the limitations. Diffusional mass transport is rapid enough for an analytical technique if the diffusion distance is small, and the instrumentation is considerably simpler than for RRDE's- a distinct advantage. The theory of simple diffusional mass transport at these arrays has been completed, and shows that communication and recycling of species between the bands is rapid and efficient if the bands have widths less than approximately 10\(\mu\text{m}\) and are separated by gaps less than this same amount.\textsuperscript{15}

In addition to normal redox cycling, where an electrochemical reaction product at one electrode undergoes the reverse reaction at the other, closely spaced collector/generator arrays allow electrochemically generated reactants to be used as a method of blocking or shielding the collector microband from a species in solution (the target of the reactant). By controlling the electrical input to the generator electrodes, the amount of reactant can be generated precisely. The ability to create an exact amount of reactant within the analyte solution itself provides advantages over conventional delivery.

Electrochemically generated titrants have had widespread use for many years. Reducing agents, oxidizing agents, precipitants, acids and bases, halogens such as bromine, and complexants have been reported.\textsuperscript{16-18} In particular, Reilly and Porterfield first described the coulometric titration of metal ions by the electrolysis of a mercury-EDTA chelate, where EDTA was released into solution to complex with free metal ions.\textsuperscript{19} The change in potential at a
working electrode gave a visual indication of the titration endpoint. Other researchers subsequently used the technique for the titration of other metal ions such as neodymium,\textsuperscript{20} barium,\textsuperscript{21} and cadmium.\textsuperscript{21} In all cases, the analysis was carried out with stirring to ensure the complete reaction of the analyte in the sample volume. A new sample solution was required for each analysis, and the time to generate sufficient EDTA to reach the endpoint was substantial (several to many minutes). Microcoulometric cells have been used to reduce the analysis time and sample volumes.\textsuperscript{22}

A microband electrode array can be used to perform the same analysis, but in a somewhat different manner. Rather than using the entire sample volume in the analysis of a substance, it is possible to restrict the titration to the volume of the diffusion layer. If stirring, convection, and migration are eliminated, the growth of a diffusion layer from an electrode is precisely defined and very reproducible. The electrochemical generation of a titrant from a precursor can be accomplished at the outer electrodes (generators) of a three-electrode array. Because of the proximity of the electrodes, the titrant diffuses away from the outer generators into the volume of solution immediately surrounding the central collector electrode, where it complexes or reacts with the analyte. The removal of the analyte from the collector causes a change in the collector response, which is measured as a function of generated reactant.

The complexometric titration of a metal ion using amperometric detection is possible by electrogenerating EDTA.\textsuperscript{23} If the collector is fixed at a potential where only the free metal ion is reduced, the generation of EDTA will remove the
free ion from the region of the collector. It will be effectively shielded, and the amount of EDTA required to shield it completely will be indicative of the analyte concentration.

It was therefore the goal of this work to determine the feasibility of performing such an analysis. Although most microband arrays have been gold or platinum produced by photolithography, we determined that carbon fibers were more suitable for this application. Carbon electrodes are advantageous in that they exhibit lower cathodic background currents and a larger negative potential limit than gold or platinum. The fibers also have much superior physical ruggedness than lithographically-produced thin-film arrays, and can be polished or pretreated many times without significant damage to the electrode.

However, the simple fabrication of carbon fiber arrays of dimensions of a few microns has not been reported. Carbon ring-disk microelectrodes have been developed, but they experience the small currents seen at microdisks. Carbon-based interdigitated arrays have been created by the etching of pyrolyzed polymer films, but they suffer from the same problem of ruggedness as their gold analogues. The fabrication of carbon-fiber interdigitated arrays of larger dimensions (60 μm) has been reported; however, the method of construction is not adaptable to smaller fibers at smaller spacings. Thus, the development of a technique for reliable, simple construction was necessary. A method involving the use of small photoresist spacers to keep the fibers separated was found to offer the precision necessary without the use of micropositioners or other
The three-fiber microband arrays produced by this method were used to develop and investigate a quick and simple technique for the analysis of metal ions in aqueous solution. Electrogenerated EDTA, formed by the controlled-current reduction of a metal-EDTA complex, is shown to be an effective agent for shielding the collector of the array. Bismuth ion, because of its desirable properties, was used as a test case to determine the characteristics of the technique. The amperometric endpoint (the generator current required to shield the collector completely) is shown to be proportional to the concentration of analyte. Properties of the analytical technique and the dependence of these properties on experimental variables such as the rate of complexant generation or array spacing are discussed.
CHAPTER 2

Experimental

2.1. Reagents

Aqueous solutions were prepared in either distilled or Nanopure (Sybron/Barnsted Co., Boston, MA) purified water. High-purity (99.99%) compressed nitrogen was used for deaerating solutions before analysis. Reagent-grade bismuth nitrate, Bi(NO$_3$)$_3$·5H$_2$O, copper nitrate, Cu(NO$_3$)$_2$·3H$_2$O, chromium nitrate, Cr(NO$_3$)$_3$·9H$_2$O, copper chloride, CuCl$_2$·2H$_2$O, potassium cyanide, KCN, and stannous chloride, SnCl$_2$·2H$_2$O (J.T. Baker Chemical Co., Phillipsburg, NJ); disodium dihydrogen ethylenediaminetetraacetate (EDTA), Na$_2$H$_2$(CH$_2$)$_2$N$_2$(CH$_3$COOH)$_4$·2H$_2$O (G. Frederick Smith Chemical Co., Columbus, OH); potassium acetate, KC$_2$H$_3$O$_2$, hydrochloric acid (Fisher Chemical Co., Fairlawn, NJ); glacial acetic acid, nitric acid, potassium hydroxide, KOH, iron nitrate, Fe(NO$_3$)$_3$·9H$_2$O, cadmium sulfate, 3CdSO$_4$·8H$_2$O, mercury acetate, Hg(C$_2$H$_3$O$_2$)$_2$, sodium carbonate, Na$_2$CO$_3$·H$_2$O, and zinc dust (Mallinckrodt, Inc., St. Louis, MO); calcium acetate, Ca(C$_2$H$_3$O$_2$)$_2$·H$_2$O (Spectrum Chemical Mfg. Corp., New York, NY); lead nitrate, Pb(NO$_3$)$_2$ (Allied Chemical Co., New York, NY); and thallium nitrate, TlNO$_3$ (K&K Labs, Plainview, NY) were used without any additional treatment.
2.2. Electrode Fabrication

Construction of the 3-fiber electrode array consists of several steps which prepare the fibers and immobilize them in an epoxy substrate (Figure 2.1).

2.2.1. Plating of carbon fibers

Direct electrical connection to the carbon fibers is not possible in the electrode arrangement used in these experiments. Attaching connecting wires to the fibers with only conductive silver epoxy (Tra-Con Adhesives, Medford, MA) was unreliable, presumably due to the coating of the fibers with the epoxy resin itself, insulating the fibers from contact with the silver grains. Instead, the connection was only feasible when a thick layer of copper was deposited electrolytically on one end of the fiber. Individual 7\(\mu\)m diameter carbon fibers (Thornel 50 or 300 PAN carbon fibers, Union Carbide Corp., Chicago, IL) of 3 to 4 cm length were affixed at one end to a small (1 cm x 2 cm) rectangular copper sheet using a small piece of transparent tape. A large alligator clip was attached to the copper to allow electrical connection to the voltage source. Approximately 1 cm of the free ends of the fibers were immersed in a 50 ml beaker containing 40 ml of copper plating solution (2.8 g CuCl\(_2\), 7 g KCN, and 1.4 g Na\(_2\)CO\(_3\) in 100 ml water and heated to approximately 60°C). The assembly of alligator clip/copper sheet/fibers was supported in a clamp on a ring stand for the duration of the plating. A potential of approximately 1.5 volts was applied between the fibers and
Figure 2.1. Stepwise illustration of carbon fiber electrode construction.
a plain copper wire that was also immersed in the solution and served as the anode. The progress of the plating was monitored visually and was stopped when it appeared that 1 to 2 fiber diameters of copper were deposited (5 to 10 minutes). Evolution of gases at the fibers is expected and any large bubbles clinging were removed by gentle tapping. The fibers were removed from the solution and followed by a quick dip in water to dissolve any remaining salts. Detachment from the copper and tape leaves a fiber 3-4 cm long with 1.0 cm of copper plated at one end.

2.2.2. Coating with photoresist

In order to reliably arrange fibers with micron-sized dimensions (without using micropositioners), tiny "spacers" are created along the length of the fibers to keep them separated during manipulation. Kodak Photoresist (KPR, Eastman Kodak Co., Rochester, NY) that is normally used for photolithography was found to be useful in this purpose. The copper-plated fibers were held by the copper end under a lighted magnifier, and the other half was "stroked" by a drop of photoresist suspended from the end of a disposable Pasteur pipet. The number of times the fiber is drawn through the drop of KPR controls the thickness of the coating. Several seconds between KPR strokes allowed the coating to dry somewhat before more KPR was added.

The growth of KPR on the fibers occurs as separated but uniform beads
rather than as a continuous layer. It was found that a total of 5 to 9 strokes produced beads of the necessary dimensions (between 5 and 10 μm thick). While there was some visual indication of the bead thickness as the coating progressed (scattering of light causing the fibers to become whiter), measurement under a microscope was the only reliable method.

After sufficient coating, the KPR beads were air-dried for 1 minute and hardened by exposing the fibers to long-wavelength ultraviolet light from a standard fluorescent black light for 5 minutes.

2.2.3. Fiber arrangement and immobilization

The fibers used for the electrode are trimmed to similar lengths (3-4 cm) and immobilized on a Kel-F substrate using a layer of KPR.

A small piece of Kel-F (0.25 cm x 2.5 cm x 5 cm) was prepared by first making the surface as flat as possible by scraping with the edge of a glass microscope slide. Next, the flat surface was polished with 0.3 μm alumina (Buehler Ltd., Lake Bluff, IL) using a felt polishing pad attached to an electric drill. Rinsing with water and soap solution removed contaminants from the surface.

A small fiber-manipulating tool was fabricated by breaking the tip off a dental probe, leaving a relatively flat surface. One side of the tip was then filed to create a flat spot. This shape worked well for pushing the fibers without breaking them.
The Kel-F substrate was placed under a large (6 inch) lighted magnifier which aided in positioning them. Two or three drops of filtered KPR were placed on the Kel-F using a disposable syringe fitted with a 0.45μm PTFE Acrodisk filter (Gelman Sciences) and spread uniformly over the surface with the side of a disposable Pasteur pipet. Depending on the thickness, this layer was found to dry in 3 to 5 minutes.

Three fibers, prepared as described above, were placed parallel in the layer of KPR about 0.5 cm apart. The tool described above was used to push the bead-coated portions of the fibers together while leaving the copper ends well separated. The fibers were repeatedly adjusted while the KPR layer dried and they drifted apart. After the layer was completely dry, the quality of the arrangement was determined by examining under a microscope. If the arrangement was acceptable, with unbroken and closely and uniformly spaced fibers, the KPR layer was polymerized by exposure to long-wavelength ultraviolet light for approximately 10 minutes. Immobilized fibers produced by this technique are shown in Figure 2.2.

The fiber arrangement was then transferred to a thick layer of Torr-Seal low vapor pressure epoxy (Varian Vacuum Products, Lexington, MA), which served as the electrode body. The epoxy resin and hardener were mixed in the appropriate ratio, and the mixture heated to approximately 80°C to allow it to flow easier and to help remove bubbles trapped during mixing. The hot epoxy
Figure 2.2. Photoresist-coated carbon fibers arranged and immobilized in photoresist on a Kel-F substrate. Viewed at 50° from normal. Undulations are due to photoresist beads along the length of the fibers.
was poured along the length of the fibers, creating an electrode body approximately 0.5 cm x 1.5 cm x 4 cm. The Kel-F with epoxy was placed in an 80°C oven for 1 hour to harden. After cooling, the Kel-F substrate can be gently flexed, popping the epoxy free along with the fibers.

2.2.4. Electrical Connections

The electroplated copper ends were exposed by polishing with 1.0 μm alumina (Buehler Ltd., Lake Bluff, IL) on a small felt polishing pad for several minutes (care must be taken not to polish the bare fibers and break them). When viewed under a low-power microscope with illumination at 45° to the electrode surface, the exposed and polished copper was easily identifiable. Also, a standard ohmmeter with small wire leads was used to verify exposure by the electrical conductivity of the copper. The electrode was then rinsed with water to remove polishing compound and dried.

Electrical connections were made with copper wire and conductive silver epoxy (Tra-Con Adhesives, Medford, MA). Short copper wires (5 cm) were dipped in the epoxy and attached to the exposed copper regions. The epoxy was hardened overnight at room temperature, or was alternatively heated to 80°C for several hours. The silver epoxy, exposed copper, and fiber regions not intended to be used as electrodes (such as any widely-spaced regions) were then covered and protected with Torr-Seal, which was also hardened at 80°C. The wire leads
were insulated by coating with silicone sealant.

2.2.5. Fiber polishing

The carbon fibers needed to be exposed by removing the KPR layer and beads which coat (and electrically insulate) them. A small felt pad with 0.05µm alumina (Buehler Ltd., Lake Bluff, IL) was used to polish the fibers and remove the KPR. Though they are imbedded in epoxy, the fibers remain fragile and all polishing was minimized and done with care.

The extent of polishing was determined initially by examination under a microscope. When the electrode body is held at approximately 30° to the illumination, the exposed fiber regions are easily distinguishable from coated regions. The different reflectivity of the epoxy and carbon fiber surfaces made discrimination simple. Electrochemical activity was also used to verify exposure of the fibers. Repeated polishing and testing in a known solution, such as Bi³⁺, gave increasing electrochemical response as the polishing progressed.

2.2.6. Electrode characterization

The suitability of this electrode fabrication process and newly constructed electrode assemblies was determined by electrochemical analysis of a solution of known composition and concentration. Comparison of the results with those expected or previously obtained allowed an evaluation of the electrode's
performance. In the case at hand, it is used to validate the construction technique.

Although ferricyanide ion is commonly used to demonstrate electrochemical activity, it was found to be not very useful due to its inherent sensitivity to the nature and condition of the carbon surface. The pseudo steady-state current for the deposition of bismuth from Bi$^{3+}$ solution seemed to offer better reliability, and was used as the typical method of evaluating electrode performance.

As an illustration, during polishing the individual fibers were tested by immersing in deaerated 0.17 mM Bi$^{3+}$ solution and applying a potential of -600 mV (vs. Ag/AgCl). After 30 seconds, the pseudo steady-state response for Bi$^{3+}$ reduction was measured. The sequence of polishing and testing was repeated several times. The results are shown in Table 2.1:

<table>
<thead>
<tr>
<th>Polishing Trial</th>
<th>Fiber 1 Current ($\mu$A)</th>
<th>Fiber 2 Current ($\mu$A)</th>
<th>Fiber 3 Current ($\mu$A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.08</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>0.165</td>
<td>0.217</td>
<td>0.230</td>
</tr>
<tr>
<td>3</td>
<td>0.215</td>
<td>0.217</td>
<td>0.228</td>
</tr>
<tr>
<td>4</td>
<td>0.217</td>
<td>0.214</td>
<td>0.230</td>
</tr>
</tbody>
</table>

Table 2.1. Pseudo steady-state reduction currents of 0.17 mM Bi$^{3+}$ solution at individual fibers after successive polishings to expose fiber surface.
An estimation of the electroactive surface area may be done empirically or theoretically. Copper, which forms bright deposits on the dark background of the fiber, was used to visually verify that the polishing technique was sufficient (Figure 2.3). Bismuth was also used as a visual indicator; however, its deposits are much darker, and much more was required before the deposits were visible.

The active surface area can also be estimated from the theoretical response of a band electrode under these conditions. The diffusion current at a planar band electrode is given by

\[ I(t) = nFDC_0A \left( \frac{1}{(\pi DT)^{1/2}} + \frac{1}{W} \right) \]  

(2.1)

for short times when

\[ 0 < (\pi DT)^2 < 1.2W \]  

(2.2)

or

\[ I(t) = nFDC_0L \left[ \frac{5.553}{\ln(4DT/W^2)} - \frac{6.791}{(\ln(4DT/W^2))^2} \right] \]  

(2.3)

at longer times when
Figure 2.3. Copper deposits on a three-carbon-fiber array showing uniformity of deposits. Note the greater deposition at the outer edges.
where

\[ \frac{1}{4.9W^2} < (\pi DT)^2 < 8.9W \]  

is the number of electrons

\( F \) is the Faraday constant

\( D \) is the diffusion constant of the electroactive species

\( C_0 \) is the species concentration in solution adjacent to the electrode surface

\( A \) is the electrode area

\( T \) is the elapsed time

\( W \) is the electrode width

\( L \) is the electrode length

While various experimental errors such as convective transport and uncertainty in the surface activity limit the accuracy of this approach, it was used with relatively good results and helped to confirm the two empirical approaches above. For the reduction of \( \text{Bi}^{3+} \) at the electrode used in the experiments in Table 2.1, equation 2.3 applies and gives a result of 194 nA, close to the values reported above. The slightly larger empirical result may be explained by the higher surface area created by the irregular bismuth deposits or by increased mass transport from convection.

2.2.7. Comments on electrode fabrication and use

Aside from the need for care in fiber handling and manipulation and the
elimination of dust (which caused irregular spacings), electrode construction was reasonably straightforward. However, several problems occurred repeatedly.

The usual way of removing deposited metals from the fibers was to reoxidize at a sufficiently positive potential. The fibers were also cycled from -1 to +1 volt in 0.5M HNO₃ to remove deposits. Although this usually happened without unexpected difficulty, some electrodes showed unusual behavior. When the fibers were used in repeated reduction/oxidation cycles (i.e., when metal was reduced, then reoxidized, more reduced, reoxidized again, etc.) the current during reoxidation would not decrease to zero, and would rise to higher levels on subsequent cycles. Clearly, the current was not due to reoxidation of deposited metal from the fiber surface. This behavior led to erratic results in testing. It is believed that incomplete hardening of the epoxy, especially the epoxy insulating the connections, may be responsible. Partial softening of the epoxy body was seen upon immersion in the aqueous solutions, supporting this hypothesis. There appeared to be some correlation between the two phenomena. Ensuring complete curing by correctly mixing and heating seemed to correct the problem. In addition, coating non-active portions of the electrode assembly with photoresist seemed to lend protection to the Torr-Seal body from the solutions.

Another significant problem was shorting of the collector and generator fibers due to the growth of long, crystalline deposits when significant amounts of metal were reduced. Of the different metals used, only bismuth showed this problem (Figure 2.4). The physical distance between the fibers, the solution
Figure 2.4. Crystalline bismuth deposits on carbon fiber surface after reduction of Bi$^{3+}$. Deposition to center fiber only.
concentration, length of experiment, and perhaps other unidentified factors all play a role. Also, metallic deposits are not removed completely by reoxidation even though the current returns to zero, especially for bismuth. This was seen repeatedly and must be due to electrical insulation of some of the deposits from the fiber surface. Fiber shorting is more common when these insulated deposits are present, and they must be physically removed by wiping or light polishing. Diluting the test solution may be used as an acceptable method for lowering the frequency of shorting, but the concentration and endpoint are not directly proportional in the type of experiment performed here (due to the presence of an intercept, see Chapter 4). Unless the quantitative relationship between the two is known (i.e., the equation of the calibration plot), an error is introduced if dilution by a factor of two is assumed to yield an endpoint reduced by a factor of two.

The insulation of the metal deposits from the fiber surface creates a problem when metal is predeposited to enhance sensitivity (see Chapter 4). The length of time needed to predeposit sufficient metal varies inversely with the solution concentration; thus, it is desirable to predeposit in a higher concentration solution and transfer the electrode to the lower concentration of interest. However, the process of transferring the electrode, presumably by exposure to air as well as physical agitation, disturbs the deposits and makes them partially inactive. The electrode then requires additional predeposition to restore its activity, although to a lower extent than if the fibers were completely free of deposits.
2.3. Apparatus

2.3.1. Instrumentation

Preliminary cyclic voltammograms using the carbon fibers and potential control of the collector electrode were performed with a BAS CV-1B cyclic voltammetric analyzer (Bioanalytical Systems, Inc., West Lafayette, IN). In some cases, a PAR Model 173 potentiostat/galvanostat with a Model 176 or 276 current-to-voltage converter interface was also used (Princeton Applied Research, Princeton, NJ). All applied potentials were relative to a BAS MF2063 Ag/AgCl reference electrode (Bioanalytical Systems, Inc., West Lafayette, IN).

Some preliminary data were recorded on a Hewlett-Packard 7044A X-Y recorder (Hewlett-Packard Co., Palo Alto, CA). Most, however, were recorded and stored on an IBM PC-compatible computer. Analog to digital conversion was performed by either a Keithley 199 digital multimeter (Keithley Instruments, Inc., Solon, OH) using GPIB software written in-lab, or by a homebuilt 12-bit analog to digital converter also controlled by software written in-lab. To increase the analytical signal and enhance signal-to-noise ratio, a homebuilt non-inverting op-amp amplifier with adjustable gain was used to collect all digitized data.

Control of the generator current was accomplished with a homebuilt current source (Figure 2.5). Although the PAR 173 galvanostat is capable of supplying nanoampere-level and higher currents, it could not be used in these
Figure 2.5. Schematic diagram of the variable current source used to supply the generator electrodes.
experiments because of the electrical communication and feedback between it and the BAS potentiostat used to control the potential of the collector electrode. The current source was therefore designed to be isolated from ground (and the other electrodes) by using its own auxiliary electrode and operates from four 9-volt batteries feeding through large output resistors. Current adjustment can be made by a continuously variable 10-turn potentiometer or in incremental steps by three 10-step switches affording 30-step resolution. The potentiometer was turned at a constant but adjustable rate by a peristaltic pump drive motor (Ismatec MS-Reglo, Cole-Parmer Instrument Co., Chicago, IL) attached to the shaft. A cell switch disconnects the attached auxiliary and working electrodes from the internal circuitry of the source.

2.3.2 Electrochemical Cell

A small 2-oz. polyethylene bottle with the neck removed (or, alternately, a 50 ml Pyrex beaker) was used as the sample container. A 5 cm Teflon disk machined to fit the sample container was used as a lid. The electrode assembly (consisting of the collector and generator working electrodes), collector reference and platinum auxiliary electrodes, and generator platinum auxiliary electrodes were held in holes drilled in the Teflon lid. In addition separate holes were added for the nitrogen purge and bubbler. A one-into-two valve was used to allow nitrogen gas to first be bubbled through the solution to remove dissolved oxygen,
Figure 2.6. Cell components for the electrochemical shielding experiments.
and then turned to allow a slow purge above the solution to prevent oxygen from entering the cell. See Figure 2.6 for cell diagram.

The BAS CV-1B potentiostat was connected by attaching the working electrode lead to the collector (center) fiber of the array, the reference lead to the Ag/AgCl electrode, and the auxiliary lead to one of the two platinum electrodes. For the shielding experiments involving EDTA, the negative lead of the current source was connected to the generator (outer) fibers of the array, and the positive lead connected to the second platinum electrode. The need to keep the current source and potentiostat electrically isolated from one another is satisfied by this arrangement (Figure 2.7).

2.4. Experimental Procedures

2.4.1. Preliminary cyclic voltammograms of metal ions

A fundamental investigation on the reduction potentials of various metal ions and metal ion/EDTA complexes on carbon fiber was completed. In most cases, the metal ion solutions of 1 mM were prepared by dissolving a suitable quantity of soluble salt in 100.0 ml of pH 4.0 acetate buffer. Bismuth solution was prepared by dissolving the bismuth nitrate salt in approx. 2 ml of nitric acid and readjusting the solution to pH 4.0 with KOH. Tin solution was prepared by dissolving SnCl₂ first in 0.5 ml HCl and readjusting to pH 4.0 with KOH. Zinc
Figure 2.7. Schematic diagram of cell components and instrument connections.
solution was prepared by dissolving zinc dust in a few milliliters of HNO$_3$ and readjusting the pH. The 1mM metal ion/EDTA solutions were prepared similarly, except with the addition of 40.9 mg of Na$_2$H$_2$EDTA$\cdot$2H$_2$O, which is in 10% excess and ensures complexation. The pH 4.0 acetate buffer was prepared by adjusting the pH of a 0.1 M KC$_2$H$_3$O$_2$ solution by addition of glacial acetic acid.

Cyclic voltammograms of the background electrolyte and metal ion solutions were obtained by filling the cell and deaerating for at least 10 minutes by bubbling nitrogen through the solution. After bubbling, a nitrogen purge was used to blanket the solution and prevent leakage of oxygen into the cell. A one minute wait before the experiment allowed the solution to become quiescent. The CV was acquired by scanning between appropriate potentials, based on the reduction of interest and the background limit of the aqueous solution. The negative potential limit of the pH 4.0 acetate buffer was approximately -1.2 V (vs. Ag/AgCl), resulting in scans from approx. +500 mV to -1.2 V in most cases. Scan rates were 100 mV/sec and at a sensitivity of 10 µA/V, unless otherwise specified.

2.4.2 Electrochemical shielding experiments

Solution Preparation

Two types of shielding experiments were carried out: those involving
swept generator current and those using current steps. While the procedures for
the two are different, the solution preparations are similar. Solutions containing
varying concentrations of Bi\(^{3+}\) and several-fold excesses of BiEDTA\(^{-}\) were
prepared by serial dilution of a stock Bi/BiEDTA solution. A general scheme
follows. A 2.0 mM Bi\(^{3+}\) solution and a 2.0 mM EDTA\(^{4+}\) solution in pH 4.0 acetate
buffer were prepared separately. When mixed in a ratio of 5 parts Bi\(^{3+}\) solution to
4 parts EDTA\(^{4+}\), the resulting solution has a composition of 0.22 mM Bi\(^{3+}\) and 0.88
mM BiEDTA\(^{-}\). Serial dilution of this stock solution with pH 4.0 acetate buffer
yielded others of lower Bi\(^{3+}\) concentration, while maintaining the Bi/BiEDTA ratio.
The nature of the shielding process requires an excess of the EDTA complex; the
actual needed is dependent upon the collection efficiency of the array, which is
largely controlled by the fiber spacing. It was determined that three or higher-fold
excesses were sufficient to ensure maximum shielding.

**Swept Generator Current Procedure**

The swept current procedure was started with assembling the cell and
deaerating the solution by bubbling with nitrogen for a minimum of 10 minutes.
Both the potentiostat and current source cell switches were initially off, the
potentiostat was set to the necessary collector potential (-400 mV vs. Ag/AgCl for
Bi\(^{3+}\)) and the current source was set to zero generator current. In addition, the
current source drive motor was off, but set to the appropriate sweep rate. The
output range of the current source (low, medium, or high) was predetermined based on the expected concentrations of metal ion. Most experiments were performed with the "high" range setting, allowing up to approximately 3400 nA of generator current. After deaerating, the bubbler was turned off and the purge started. The cell assembly was tapped lightly to dislodge any bubbles clinging to the cell walls or electrodes, and allowed to sit undisturbed for at least 1 minute to ensure a quiescent solution. The potentiostat cell switch, data collection program, and a stopwatch were all started simultaneously. At 28 seconds (8 seconds for some trials), the current source cell switch was turned "on". The length of time before the cell was switched depended on the rate of return of the collector to steady-state. Two seconds later (at 30 seconds or 10 seconds, respectively), the generator current drive was started (Figure 2.8, upper). After the collector current had returned to a flat baseline, the potentiostat and current source cell switches were turned off and the data saved to disk. Depending on the nature of the experiment, the deposited bismuth was sometimes removed from the fibers by oxidation at +400 mV after each trial. For the higher concentration solutions where fiber shorting was a problem, the reoxidation was followed by a gentle swabbing of the fibers using a cotton-tipped applicator. Subsequent trials were generally completed immediately after.
Figure 2.8. Generator current for swept current (upper) and stepped current (lower) shielding trials.
**Stepped Generator Current Procedure**

The procedure for the stepped current trials was very similar to that for current sweep. After deaerating the solution, the current source was set appropriately and the experiment started by simultaneously flipping the potentiostat cell switch and starting the computer data collection and stopwatch. After a suitable length of time to allow the collector response to return to steady-state (28 or 58 seconds), the current source cell was switched. Two seconds later, the generator current steps were incremented by turning the control switch one position every time interval (15 or 30 seconds, Figure 2.8, lower). The length of time between steps was chosen by the return of the collector response to approximate steady-state. This was generally satisfied in 30 seconds, although some experiments used a 15 second interval. The generator current was incremented until the collector response dropped to a reliable baseline, at which time the experiment was stopped by turning the potentiostat and current source off. As above, the deposited metal was usually reoxidized at +400 mV between experiments, and swabbing was needed in some cases to prevent shorting of the collector and generator fibers.

**Experiments Using Predeposition**

Predeposition of metal on the fibers was used to increase fiber response in
experiments involving low concentrations of uncomplexed metal ion. Before the analysis procedure was performed, the potentiostat was used to apply a potential to the collector and generator electrodes sufficiently negative to cause reduction. The cathodic current was monitored by a digital multimeter. Periodic and gentle stirring allowed bulk solution to be brought to the electrode surface, increasing the rate of deposition. The length of time necessary depended on the concentration of the solution and ranged from one to several minutes. The current level, as measured by the voltmeter, gradually increased as more metal was deposited. Predeposition was continued until the level reached for each fiber was approximately a factor of 10 higher than the expected shielding level seen in the experiments. While this depended on the electrode dimensions and geometry as well as the solution concentration, it was typically reached at approximately 5 to 15 nA for each fiber. The normal analysis procedure (given above) was then completed.

It was found that predeposition was necessary between successive trials as well as different solutions. When several different concentrations were analyzed in succession, the highest concentration was generally tested first and the metal not reoxidized between trials or solutions. Thus, the metal deposited at higher concentration was helpful in maintaining electrode response at lower ones. In practice this required that the electrodes have any excess solution removed before transfer to the next solution by gentle dabbing with a KimWipe tissue, without disturbing the fibers or deposits.
CHAPTER 3

Theory

3.1. EDTA as a complexometric titrant

Ethylenediamine tetraacetate (EDTA),

\[
\text{H}_2\text{EDTA} \rightleftharpoons \text{H}^+ + \text{H}_3\text{EDTA}^- \quad \text{pK}_1 = 2.0
\]

\[
\text{H}_3\text{EDTA}^- \rightleftharpoons \text{H}^+ + \text{H}_2\text{EDTA}^{2-} \quad \text{pK}_2 = 2.76
\]
\[ H_2\text{EDTA}^2- \rightleftharpoons H^+ + \text{HEDTA}^2- \quad pK_3 = 6.16 \]

\[ \text{HEDTA}^3- \rightleftharpoons H^+ + \text{EDTA}^4- \quad pK_4 = 10.26 \]

Loss of the first two protons occurs quite easily in solutions of moderate to low acidity, but EDTA exists as the unprotonated tetraanion primarily only in alkaline solutions.

The affinity of a metal ion, M^{n+}, for EDTA^{n-} to form the complex MEDTA^{n-4} is quantitatively described by its formation or stability constant, \( K_{\text{MEDTA}} \). The value of \( K_{\text{MEDTA}} \) is dependent upon the size and charge of the metal ion, with small, highly charged metal ions generally bound most strongly (Table 3.1). It is also dependent on the solution pH, which controls the fraction of EDTA existing as the unprotonated form. At low pH, the shift in equilibrium toward protonated forms results in a competition for EDTA between the metal ion and protons and lowers the effective formation constant for the complex. Similarly, alkaline solutions contain a higher proportion of unprotonated EDTA, leading to a higher effective formation constant. Control of solution acidity is one method of gaining selectivity in complexation.\(^{35,36}\)

The strong complexes formed with many metal ions makes EDTA a useful and effective titrant. In addition to those using colorimetric endpoint detection, metal ion titrations may be performed using electrochemical means such as potentiometry, coulometry, or amperometry.\(^{38}\) The metal ion is stabilized by
<table>
<thead>
<tr>
<th>Cation</th>
<th>Complex</th>
<th>log $K_{\text{MEDTA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>MgEDTA$^{2-}$</td>
<td>8.69</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>CaEDTA$^{2-}$</td>
<td>10.96</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>NiEDTA$^{2-}$</td>
<td>18.62</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>CuEDTA$^{2-}$</td>
<td>18.80</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>HgEDTA$^{2-}$</td>
<td>21.80</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>PbEDTA$^{2-}$</td>
<td>18.04</td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>BiEDTA$^{-}$</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table 3.1. Formation constants for various metal-EDTA complexes.\(^{37}\)

Complexation, which raises the free energy for reduction. The degree of stabilization is proportional to the magnitude of the stability constant, $K_{\text{MEDTA}}$. In general, for the reversible reduction of a complex metal ion,

$$MX_p + ne \rightleftharpoons M^0 + pX$$

the voltammetric half-wave potential is\(^ {38}\)

$$E_{1/2}^C = E_M^0 + \frac{RT}{nF} \ln K_d + \frac{RT}{nF} \ln C_x + \frac{RT}{nF} \ln \frac{m_A}{m_c}$$
where

$E^o_M$ is the formal potential of the free metal ion

$K_d$ is the dissociation constant of the complex

$C^*_{X}$ is the bulk concentration of the ligand

$m_A/m_c$ is the ratio of mass transport coefficients for free to complexed ion

The difference in reduction potential between the uncomplexed and complexed forms allows for the detection of the endpoint by electrochemical means. A shift of the voltammetric wave by several hundred millivolts is sufficient to ensure discrimination of the two species.

Appropriate selection of pH, which alters the value of the stability and dissociation constants, can be used to shift the reduction potential in either direction (Table 3.2). If the complexed ion exhibits a reduction potential outside the range of the solvent limit, lowering the solution pH weakens the complex and shifts the potential to more positive values. Insufficient separation between the free and complexed forms may be corrected by raising the pH, increasing the fraction of unprotonated EDTA and strengthening the complex.
Table 3.2. Half-wave reduction potentials (volts) of metal ions before and after complexation with EDTA in different buffer solutions (potential vs. SCE).40

<table>
<thead>
<tr>
<th>Metal</th>
<th>(E_a(V))</th>
<th>(E_a(\text{EDTA}))</th>
<th>(E_{a}(V))</th>
<th>(E_{a}(\text{EDTA}))</th>
<th>(E_{a}(V))</th>
<th>(E_{a}(\text{EDTA}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>-0.38</td>
<td>-0.77</td>
<td>-0.43</td>
<td>disappears</td>
<td>-</td>
<td>disappears</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>+0.02</td>
<td>-0.13</td>
<td>-0.02</td>
<td>-0.32</td>
<td>-0.29</td>
<td>-0.56</td>
</tr>
<tr>
<td>Bi(^{3+})</td>
<td>0</td>
<td>-0.47</td>
<td>-0.14</td>
<td>-0.63</td>
<td>-</td>
<td>-0.74</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>-0.6</td>
<td>-0.89</td>
<td>-0.61</td>
<td>disappears</td>
<td>-0.67</td>
<td>disappears</td>
</tr>
<tr>
<td>Ti(^{3+})</td>
<td>-0.46</td>
<td>-0.46</td>
<td>-0.46</td>
<td>-0.46</td>
<td>-0.48</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

3.2. EDTA titrations using electrochemical endpoint detection

The typically large shift in half-reaction reduction potentials caused by complexation with EDTA provides a convenient method for determining titration endpoints. A complexometric titration by the addition of EDTA proceeds until the metal ion exists solely as the bound form. As is the case for most conventional acid-base titrations, the excess titrant present after the endpoint may be detected visually by using an appropriate indicator.41 However, the stabilization of the oxidized form of the metal ion (a consequence of complexation) allows detection by potentiometric and amperometric means as well.

The technique of amperometric endpoint detection is most commonly accomplished by fixing a working electrode at a potential sufficient for oxidation or
reduction of the analyte.$^{42}$ In the case of most complexometric metal ion titrations, the potential is sufficiently negative for reduction of the metal ion to the element but not for reduction of the complexed ion. As titrant is added to the analyte solution and the free metal ions are converted to inactive complexes, the reduction current at the working electrode decreases. The addition of a stoichiometric amount of complexant results in the complete conversion of metal ions, and the reduction current drops to zero. The extrapolated transition between the flat regions of titration curve and baseline is the endpoint, which is proportional to the total amount of analyte in the sample solution (Figure 3.1).

The addition of titrant can be by direct addition of complexant solution or by the electrochemical reaction of a precursor in the solution itself. If the titrant is generated at a constant rate by controlling current as opposed to potential, the time required to reach the endpoint is directly proportional to the amount of analyte in solution. This latter technique is known as a coulometric titration. Bromine, cerium (IV), and EDTA are examples of coulometric titrants.$^{16-18}$

The use of EDTA as an electrogenerated complexant is based on the reduction of a metal-EDTA precursor, which deposits the metal on the working electrode and liberates exact quantities of EDTA.$^{43}$ The free complexant then reacts with any unassociated analyte and prevents its detection at the indicator electrode. This requires knowledge of the precursor and analyte EDTA complex formation constants. Clearly, if the precursor complex is less stable than the analyte complex, the bound EDTA will not remain entirely with the precursor.
Figure 3.1. Indicator electrode response in a typical amperometric titration, with endpoint determined by extrapolation.
fraction of EDTA which transfers to the analyte is dependent on the values of the formation constants. If a coulometric titration was then performed, the analysis would give falsely low results due to the premature reaction in solution. If the precursor was significantly less stable than the analyte complex, the reaction would go to completion, yielding a solution with no free analyte. The subsequent titration would show almost no analyte. Thus, the choice of precursor requires a stability constant greater than that for the nearest possible analyte by at least several orders of magnitude. For this reason HgEDTA\(^2\) (log $K = 21.8$) has typically been used as the source of chelating agent.

3.3. Electrochemical shielding at triple-band microfiber arrays

A triple-band electrode is simply three parallel band electrodes closely spaced to allow species generated at one band to diffuse to adjacent bands (Figure 3.2). This overlap of diffusion layers of the individual bands alters the response from what is seen at isolated bands. If significant overlap occurs, the electrode is commonly referred to as a collector-generator arrangement, for the reason described above.

A single band electrode exhibits a voltammetric response dependent upon its dimensions. Typically, the length of the band is much greater than the width. If the width of the electrode is of microscopic dimensions (usually taken as less
Figure 3.2. Cross-sectional illustration of the diffusion of electrochemically active species between bands at a triple-band electrode.
than 10 μm), diffusional mass transport is significantly non-linear. The theoretical
treatment of the current at a single microband electrode during a potential step
has been performed and shows that the behavior must be described as a
consequence of the time scale of the experiment (Figure 3.3). At short times, it
experiences enhanced currents relative to a Cottrell experiment due to increased
mass transport at the edges:

$$I(t) = nFDC_0A\left(\frac{1}{\pi Dt^{1/2}} + \frac{1}{W}\right)$$  \hspace{1cm} (3.1)

where $I(t)$ is the current at time $t$
$n$ is the number of electrons
$F$ is the Faraday constant
$D$ is the species diffusion coefficient
$C_0$ is the species concentration near the electrode
$A$ is the electrode area
$W$ is the band width

The diffusion of species to the electrode surface occurs not only in
directions normal to the surface, but also parallel. Radial diffusion to the edges
combines with planar diffusion to give enhanced currents. At longer times, the
diffusion layer has grown to approach that of a hemicylinder. Although microdisk
electrodes, with two microscopic dimensions, show a steady-state behavior at
long times, microband electrodes exhibit pseudo-steady-state currents:
Figure 3.3. Evolution of the diffusion layers at a triple-band electrode after simultaneous potential steps at all three bands. Dashed and dotted lines represent the approximate growth of the layers with time.
\[ I(t) = nFDCL\left[ \frac{5.553}{\ln(4D/tW^2)} - \frac{6.791}{(\ln(4D/tW^2))^2} \right] \]  

(3.2)

with a gradual $1/\ln(t)$ decrease in current.

The growth of the diffusion layers in directions parallel to the electrode surface is important if the microbands lie close to one another. In the case of a triple-band electrode, the diffusion layers of the two outer bands may cover the center band. The extent of the coverage depends on the length of the experiment, which determines the thickness of the diffusion layers, and on the widths of the electrode gaps and the electrodes themselves. By keeping the center electrode at a different potential than the two outer ones, what is generated at the two can be detected at the center band, and vice versa. This is referred to as collector-generator mode.

The collection efficiency of a collector/generator array describes the amount of species collected relative to the amount generated. For a single generator flanked by two collectors (all of equal width), the quasi-steady-state collection efficiency is

\[ \phi_{ss} = 0.095 + 0.33 \log \theta_{\text{GAP}} - 0.035 (\log \theta_{\text{GAP}})^2 \]  

(3.3)

where $\theta_{\text{GAP}} = 4D/T/W_{\text{GAP}}^2$. It can be seen that the diffusion of a species between
electrodes is highly dependent on the gap width between the electrodes, and quick response requires small spacings as expected. In addition, digital simulation shows that collection efficiency depends on electrode widths, with wider electrodes offering somewhat better collection.\textsuperscript{11}

If the central collector of the three-band electrode is held at the same potential as the two outer generators, it will become shielded from electroactive species. The depletion layers originating from the generator pair will grow in thickness as the experiment proceeds and will eventually deplete material near the collector. The collector current, measured as a function of time, will decrease as the diffusion layers coalesce and expand. Analogous to collection efficiency, the \textit{shielding factor} of the array describes the current of the collector in this mode relative to the current at an equivalent, unshielded band. Again, digital simulation has shown that the effectiveness of the shielding is dependent on the electrode gaps and widths (Table 3.3). Higher shielding is a result of greater overlap of the adjacent diffusion layers, which is increased by increasing the widths of the two flanking bands and decreasing the gap size.

While shielding reduces the amount of electroactive species the collector can sense, the reduction is not complete. Only for arrays in which the outer bands are very near and many times wider than the collector can shielding approach completion.\textsuperscript{10} An alternate approach involves the simultaneous electrochemical generation of a species at the outer bands which will react with
### Table 3.3. Theoretical relative currents at various triple-band geometries, showing the effect of shielding on a central generator flanked by two collectors.

(Currents are normalized to that predicted for a single generator, 0.50.)

<table>
<thead>
<tr>
<th>gap width, μm</th>
<th>electrode width, μm</th>
<th>Relative currents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>generator</td>
<td>collector</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The titration of a chemical species requires precise control of the amount of added titrant. To control the amount of EDTA produced at the generator electrodes, it is necessary to regulate the current rather than potential. An increasing generator current will liberate increasing amounts of EDTA, which is free to diffuse into the region of solution surrounding the collector. If the current efficiency of EDTA generation is 100%, the applied generator current is directly...
Figure 3.4. Response for Bi$^{3+}$ reduction at the collector (center) electrode of a triple-band experiencing shielding by the generator electrodes. Electrochemical shielding alone (———) and with stepwise generation of EDTA (· · · · ·).
proportional to the amount liberated. In this way the amperometric titration of a metal ion may be completed within the diffusion layer of the electrode array. Addition of a slight excess of metal-EDTA complex to the analyte solution provides a source of complexant. The choice of complex ion to use as the EDTA precursor depends on the complex formation constants. For reasons discussed above, the complexant must have sufficient affinity for the analyte to shift its reduction potential, but must not bind more strongly than the source complex. With their large formation constants, complexes such as HgEDTA\(^2-\) or BiEDTA\(^-\) are acceptable for most analyses.

3.4. Mass transport at the electrode surface

The diffusion of species at a triple-band array during this type of experiment is complex. It was not the goal of this research to develop an exact mathematical solution to the problem of mass transport, but rather an understanding of the qualitative relationships between the experimental variables and results. In addition to the diffusion of the various ions between the collector and generator electrodes, we have the added complexities of potentiostatic control of the collector but galvanostatic control of the generators, and also the time rate of change of the applied current. A description of mass transport to and from the electrode surfaces is necessary.

Initially, before any applied potentials, the solution near the electrode
surface is that of the bulk, which is composed of free metal ions with a severalfold excess of complexed ion, which is the source of EDTA^2-. For simplicity, let the analyte be Bi^{3+} and the complex be BiEDTA^−, although other situations are possible. The analysis is started with the application of a fixed potential to the collector, a potential chosen so that only uncomplexed metal ions are reduced (about -300 mV vs. Ag/AgCl for Bi^{3+} + 3e¬ → Bi^0). The measured current rises rapidly and within a short time reaches its pseudo-steady-state value, where it remains until the generator electrodes are switched on (the actual time required to reach steady-state is dependent upon the Bi^{3+} concentration and the activity of the carbon fiber surface, which is related to the amount of predeposited bismuth (see chapter 4) and the electrode potential). The hemicylindrical diffusion layer grows outward from the collector and overlaps the adjacent generator electrodes. The concentration of Bi^{3+} at the surface of the collector reaches equilibrium as the depletion of ion is balanced by inward flux.

After a predetermined delay, the generator electrodes are switched on, and the current source is started immediately after (for example, 8 and 10 seconds, respectively). The current source must apply a potential to the generators sufficiently negative to maintain the desired current. Although its concentration is already low as a result of the growth of the diffusion layer from the collector, Bi^{3+} is reduced first due to its lower reduction potential. The depletion layers from the generators grow and lower the Bi^{3+} level near the collector even further, producing a concurrent drop in the collector response. Depending on the separation of the fibers and the diffusion coefficient
approximately $0.4 \times 10^{-5}$ cm$^2$/s for Bi$^{3+}$ in acetate$^{56}$, the communication time between electrodes is several seconds.

The deposition of bismuth on the generator fibers from Bi$^{3+}$ in solution continues until the flux of Bi$^{3+}$ is insufficient to meet the applied current from the source. At this point, the source potential becomes more negative until another electrochemical reaction replaces the reduction of Bi$^{3+}$. In this case the reduction of BiEDTA$^-$ begins, liberating EDTA$^-$ which diffuses into solution. The freed EDTA$^-$ immediately binds to any Bi$^{3+}$ ion it encounters, creating an additional flux of Bi$^{3+}$ away from the collector, and lowering the collector current proportionally. This newly created BiEDTA$^-$ is able to diffuse back to the generators, where it will be reduced, liberating EDTA$^-$ and repeating the cycle of Bi$^{3+}$ removal. The combination of the increase in generator current and the depletion of Bi$^{3+}$ near the electrode surface causes growth of the uncomplexed EDTA$^-$ diffusion layer.

Eventually, the collector response drops to a pseudo-steady-state value near zero (reflecting maximum shielding) and remains near that value until the end of the analysis. The length of time required to reach this baseline depends on the bulk analyte concentration; width and spacing of the electrodes; diffusion coefficients of the analyte, complex, and complexant; and the time rate of change of the generator current. The residual current at the baseline is indicative of incomplete shielding and "leakage" of Bi$^{3+}$ to the collector.

In general, the above experiment can be characterized by the following relationships:
Collector Response

For the reaction $\text{Bi}^{3+} + 3e^- \rightarrow \text{Bi}^0$,

$$i_{(coll,t)} = nkFC_{(Bi^{3+},t)} LW$$

where $i_{(coll,t)}$ is the collector current at time $t$

$k$ is a mass transport coefficient for $\text{Bi}^{3+}$

$C_{(Bi^{3+},t)}$ is the near-surface ($x = \delta$) concentration at the collector at time $t$

$L$ and $W$ are the collector length and width

and where

$$C_{(Bi^{3+},t)} = C_{Bi^{3+}} - \Delta C_{EDTA} - \Delta C_{red}$$

where $C_{Bi^{3+}}$ is the bulk concentration of analyte, $\text{Bi}^{3+}$

$\Delta C_{EDTA}$ is the change in $\text{Bi}^{3+}$ concentration at the collector due to EDTA complexation

$\Delta C_{red}$ is the change in $\text{Bi}^{3+}$ concentration near the collector due to deposition on the fibers

53
Generator Behavior

For the reactions

\[ \text{Bi}^{3+} + 3e^- \rightleftharpoons \text{Bi}^{0} \]
\[ \text{BiEDTA}^- + 3e^- \rightleftharpoons \text{Bi}^{0} + \text{EDTA}^+ \]
\[ \text{Bi}^{3+} + \text{EDTA}^+ \rightleftharpoons \text{BiEDTA}^- \]

\[ i_{gen}^{\text{app}} = A + Bt = nFLWk_{\text{Bi}}C_{(\text{Bi}^{3+}\text{gen})} \]

at short times (several seconds, typically)

\[ = nFLW(k_{\text{Bi}^{3+}}C_{(\text{Bi}^{3+}\text{gen})} + k_{\text{BiEDTA}}C_{(\text{BiEDTA}_{\text{gen}})}) \]

at longer times

where

\[ i_{gen}^{\text{app}} \] is the applied current

\[ A \] is the initial applied current

\[ B \] is the sweep rate

\[ k_{\text{Bi}} \] is the mass transport coefficient for \( \text{Bi}^{3+} \)

\[ k_{\text{BiEDTA}} \] is the mass transport coefficient for \( \text{BiEDTA}^- \)

\[ C_{(\text{Bi}^{3+}\text{gen})} \] is the concentration of \( \text{Bi}^{3+} \) at the generator

\[ C_{(\text{BiEDTA}_{\text{gen}})} \] is the concentration of \( \text{BiEDTA}^- \) at the generator
4.1. Reduction of metal ions and metal ion/EDTA complexes at carbon fibers.

While the reduction of most metal ions and their complexes has been thoroughly studied by polarography, the use of solid electrodes is less frequent. This is especially true for the deposition of these species at carbon surfaces. Complicating the situation further is the fact that the most commonly used type of carbon electrode is glassy carbon, which may bear some similarities to carbon fibers but is not identical. The variability in the voltammetric response at carbon surfaces has been widely reported, and has been shown to be a consequence of the surface treatment as well as the material itself. Depending on the degree of heating, carbon fibers may not be completely graphitized. The polishing of a fiber along its axis will expose graphitic edge planes; the number and orientation of the edge planes will depend upon the degree of graphitization. The voltammetry of a species will (to some extent) thus depend on the nature of the material. Overpotentials for the deposition of metals at various solid electrodes have been reported, along with the uncertainty in the
surface activity of freshly deposited metal. For these reasons, it was felt that a preliminary study of the deposition of various metals on carbon fibers would be necessary.

4.1.1. Determination of reduction potentials

Cyclic voltammetry was used to determine the reduction potentials for the various ions. Solutions were prepared in 0.1M acetate buffer (pH 4.0) and scanned between the potential limits for this buffer. The background current and potential limits for the solution were determined by cyclic voltammetry of the buffer solution alone. Negligible activity was seen between +1.2 and -1.2V (vs. Ag/AgCl). In some cases, the cathodic limit was extended to more negative potentials.

While pretreatment of the carbon surface was shown to be important in other situations, it was found that it made little difference on the reduction potentials and currents for the background or the metal ions. The pretreatment investigated here involved both polishing and electrochemical methods (cycling for several minutes in 1M HNO₃ or 1M H₃PO₄ from the anodic to the cathodic limits). Light polishing was helpful, however, in removing deposits from the fiber surfaces when reoxidation alone was insufficient.

The reduction potentials for the ions and their EDTA complexes in pH 4.0
<table>
<thead>
<tr>
<th>Ion</th>
<th>$M^{n+}$</th>
<th>MEDTA</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{3+}$</td>
<td>N/A</td>
<td>N/A</td>
<td>pH 4.0 acetate</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>N/A</td>
<td>N/A</td>
<td>&quot;</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>N/A</td>
<td>N/A</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>-0.55</td>
<td>-1.10</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>-0.80</td>
<td>-1.00</td>
<td>&quot;</td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>-0.20</td>
<td>-0.70</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn$^{2+}$</td>
<td>-0.60</td>
<td>-1.00</td>
<td>&quot; (slight ppt.)</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>0.25*</td>
<td>0.15*</td>
<td>pH 4.0 acetate</td>
</tr>
<tr>
<td></td>
<td>0.25*</td>
<td>0.10*</td>
<td>pH 4.0 NH$_4$NO$_3$</td>
</tr>
<tr>
<td></td>
<td>0.10*</td>
<td>0.10*</td>
<td>pH 7.0 NH$_4$NO$_3$</td>
</tr>
<tr>
<td></td>
<td>0.05*</td>
<td>0.05*</td>
<td>pH 8.5 NH$_4$NO$_3$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-0.75</td>
<td>-0.80</td>
<td>pH 4.0 acetate</td>
</tr>
<tr>
<td></td>
<td>-0.15</td>
<td>-0.80</td>
<td>w/o acetate, pH 4.0 KNO$_3$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>N/A</td>
<td>N/A</td>
<td>pH 4.0 acetate</td>
</tr>
<tr>
<td></td>
<td>slight activity</td>
<td></td>
<td>0.1M KClO$_4$</td>
</tr>
<tr>
<td>Ti$^+$</td>
<td>-0.85</td>
<td>-0.85</td>
<td>pH 4.0 acetate</td>
</tr>
<tr>
<td></td>
<td>-0.85</td>
<td>-1.40</td>
<td>pH 10.0 phosphate</td>
</tr>
</tbody>
</table>

* formed unstable deposits

Table 4.1. Approximate reduction potentials of metal ions and their EDTA complexes on carbon fiber surfaces in different buffers.
acetate buffer are shown in Table 4.1. When specified, no activity indicates no apparent reduction within the background potential limits.

4.1.2. Reduction overpotential and surface activity

Of the metal ions tested that showed reduction, all exhibited an unexpected characteristic: the onset of reduction in the cathodic scan direction was significantly more negative than the potential at which reduction stopped on the return scan (Figure 4.1). The voltammograms show that the freshly deposited metal has a higher surface activity than the plain carbon surface. The metal deposited during the early stages of the reduction cycle enhances further deposition, and a pseudo-steady-state current is established.

The question of the surface activity of metallic deposits has been raised in regard to the theoretical treatment of voltammetry at solid electrodes. In this situation, however, the issue is mainly empirical. The use of these fibers may be possible only after a sufficient amount of the metal has been predeposited. The relatively large concentrations used here (1 mM) allow for this to happen rather quickly. The cyclic voltammograms show that an amount sufficient to give acceptable electroactivity deposits in a period of several to many seconds. If significantly lower concentrations are used, the time required increases and special procedures are necessary to maintain the electrode activity (see section 4.2).
Figure 4.1. Cyclic voltammograms of 1 mM Bi$^{3+}$ (---) and 1 mM BiEDTA$^{-}$ (-----) in pH 4.0 acetate buffer showing the overpotentials for deposition on the carbon fiber.
4.1.3. Mechanical instability of deposits

The metal deposited on the fibers usually showed some form of mechanical instability, which complicates the use of carbon fibers as electrodes. Experiments with Hg\(^{2+}\) were very erratic and unreliable due to a rapidly fluctuating current. Although the nature of mercury on carbon was investigated before,\(^{25}\) most work involved the formation of droplets larger than seen here, and on carbon surfaces of larger area. The explanations offered to explain the instability included inadequate wetting of the carbon by the mercury, and the subsequent growth of the droplet until it was too large to be supported on the fiber. Microscopic examination of the droplets in the experiments presented here showed small spheres (approximately 100 nm diameter) distributed over the fiber surface. It was these deposits that yielded fluctuating reduction currents, preventing a reliable steady-state from being established. The cause is suspected to be the creation and destruction of a tenuous electrical contact between the fibers and the mercury. The larger activity of the droplets than the carbon thus creates a "noise" in the reduction current. A second and perhaps related explanation is the much larger perimeter-to-area ratio for the fibers used in these experiments. The radial diffusion at these narrower fibers cause significantly higher deposition at the outer edges relative to the interior surface (see Figure 2.3, for example). This may exaggerate the cause suggested above.

Solid deposits also showed problems with instability, although in a different
manner. As discussed in Chapter 2, the reoxidation of deposited metal did not happen to completion. When an oxidizing potential was applied, the anodic current dropped to zero faster than expected, but still after a time roughly proportional to the amount of material deposited. Examination under a microscope revealed the presence of unoxidized metal on the fiber surface. In Figure 2.4, potential was applied to only the center fiber. The deposits on the two outer fibers are remaining from a previous reduction/reoxidation cycle. Clearly, there is a loss of electrochemical response which prevents the dissolution of these deposits. Transferring an electrode from one solution to another has a similar effect on the deposits, and lowers their electrochemical response (see section 4.2). Additional metal plated on the surface seems to restore the activity, however, possibly by reestablishing electrical contact with the carbon fiber.

4.2. Swept current experiments with Bi/BiEDTA

The analysis of Bi$^{3+}$ solutions containing several-fold excesses of BiEDTA$^-$ was found to require special procedures and techniques when the analyte concentration was relatively low or relatively high. For this reason, the results and discussion will be presented separately based on concentration.
4.2.1. High concentrations (greater than 20μM Bi^{3+})

An analysis of several bismuth solutions is shown in Figure 4.2. Upon application of the collector potential at zero seconds, the cathodic current rises as bismuth begins to deposit on the carbon surface. Although a pseudo-steady-state current should be established fairly rapidly at an electrode of this dimension, it can be seen that the actual time is largely dependent on the analyte concentration. For the lowest levels of bismuth, the rise is quite slow but increases as more is deposited. In contrast, the highest concentration reaches steady-state rapidly, within several seconds.

The last trial repeat of the 0.353 mM solution also shows the effect of incomplete reoxidation of prior deposits. Its response is almost immediate, and does reach a true steady-state rapidly. The initial rise and slight fall seen in the first several seconds is likely due to the characteristics of the deposit. As seen before (Figure 2.4), bismuth deposits as a very irregular surface. The slight peak may be caused by the reduction of Bi^{3+} ions in solution trapped in the convolutions of the surface. After it is depleted, the diffusion layer grows out from the electrode toward the bulk solution, as is expected for a typical microband electrode.

At 28 seconds, the generator fibers are switched on, but with zero applied current. At 30 seconds, the current source drive is started, and a steadily increasing cathodic current is applied. Initially, as the potential of the generator
Fig. 4.2. Titration of Bi$^{3+}$/BiEDTA$^-$ solutions in pH 4.0 acetate buffer. Bi$^{3+}$
concentrations: 0.014mM (-----), 0.057mM (.........), 0.133mM (..................), and
0.353mM (---------). Generator sweep rate: 8.9 nA/sec.
electrodes becomes more negative, Bi^{3+} is reduced and deposited. The generator current rises until reduction of Bi^{3+} alone is insufficient. The potential applied to the generators becomes more negative and the onset of BiEDTA⁻ reduction is reached.

The collector does not respond immediately to the application of current to the generators. For the data shown in Figure 4.2, the delay in response is approximately 11 seconds. This represents in part the communication time between the collector and generator electrodes and is dependent upon any factors which alter the transit time between them, including fiber spacing and diffusion coefficient. In addition, there is a delay in the response of the generators themselves. Until sufficient bismuth has been deposited, they do not respond effectively. This is especially true for low concentrations, as can be seen. In the present case there is little difference between the delay for the high and low concentrations, and it may be assumed that a delay in generator response is not a significant factor.

The slope of the collector decay can be seen to become slightly more negative after it starts. More apparent in the highest concentration of Figure 4.2 (at approximately 60 seconds), the transition may reflect the beginning of BiEDTA⁻ reduction.

After the collector begins to respond to the increasing generator current, its signal drops steadily until it reaches a baseline which corresponds to maximum shielding by electrogenerated EDTA. The level of baseline current reflects the amount of Bi^{3+} leakage between the generator fibers due to
incomplete shielding. For the highest concentration of Figure 4.2, the baseline is
approximately 15nA. With an initial current of approximately 750 nA, this
corresponds to a overall shielding level of 98%.

The endpoint of the titration is determined by the intersection of the
extrapolated linear portions of the collector response and baseline. A calibration
plot (endpoint vs. concentration) for the data in Figure 4.2 is shown in Figure 4.3.
Within the range of concentrations tested, the data show good linearity. The
precision appears to be lower for the higher concentrations (4% RSD); this may
be due to residual stirring or convection of the solution. It may also be due to
uncertainty in the estimation of the endpoints. At longer times, such as for the
higher concentrations, the endpoint region may be broader and less well defined
than for low concentrations.

In order to maximize the analytical sensitivity of the technique, it is
necessary to minimize the level of the baseline. In this way the separation
between endpoints (and the slope of the calibration plot) is maximized. It follows
from the above discussion that maximizing the shielding of the collector is
important for maximizing sensitivity.

The calibration plot also shows a non-zero intercept, corresponding to an
endpoint current of approximately 180nA for zero analyte concentration. While
this may seem unusual, it is in part a consequence of the diffusional nature of the
technique. For a normal titration using colorimetric or potentiometric endpoint
detection a zero-zero intercept is normal; otherwise, an interferant or systematic
error may be suspected. When a blank solution containing only BiEDTA− in pH
Figure 4.3. Calibration plot using the endpoints determined from the data in Figure 4.2.

\[ y = (3792 \text{ nA/mM})x + 183 \text{ nA} \]

\[ r = 0.996 \]
4.0 acetate is analyzed, no signal is seen at the collector. In the type of amperometric titration performed here, however, the response is seen at the collector only after diffusional communication from the generators. During the delay caused by the transport of species across the gap width, the continually increasing generator current has changed. Thus, the endpoint reflects not only the amount of analyte present, but also the diffusion time between the electrodes. The delay is constant for a given electrode and set of experimental conditions and is not dependent on the concentrations, so it manifests itself as a vertical offset of the calibration curve. This same type of intercept was seen in other types of diffusional titrations (see discussion below). As is the case for the response delay discussed above, any factor which changes the time of diffusion between the collector and generator electrodes will change the intercept. In addition, because the changing generator current creates the offset between the response and generation, the intercept will also depend on the sweep rate of the current source.

4.2.2. Relationship of Experimental Variables to Analytical Characteristics

The analyses were performed with varying sweep rates and different collector/generator spacings to determine the qualitative effect on the characteristics of the calibration plot (Figure 4.4 and Table 4.2). In the following trials, similar concentration solutions were used to prevent unidentified
Figure 4.4. Calibration plots for the analysis of Bi$^{3+}$ solution using different electrode geometries and generator sweep rates. Electrode A: 12 µm avg. spacing (8.9 nA/sec — ; 17.7 nA/sec • • • • •); Electrode B: 18 µm avg. spacing (17.7 nA/sec — — ; 35.2 nA/sec — — ; 59.7 nA/sec • • • • •)
### Calibration Plot

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Avg. Fiber spacing (μm)</th>
<th>Generator Sweep Rate (nA/s)</th>
<th>Analysis Time (seconds)</th>
<th>Slope (nA/mM)</th>
<th>Intercept (nA)</th>
<th>Avg. Endpoint RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>12</td>
<td>8.9</td>
<td>250</td>
<td>3792±123</td>
<td>183±12</td>
<td>3.5</td>
</tr>
<tr>
<td>A</td>
<td>12</td>
<td>17.7</td>
<td>175</td>
<td>3784±79</td>
<td>297±18</td>
<td>1.3</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>17.7</td>
<td>200</td>
<td>3044±90</td>
<td>348±23</td>
<td>2.2</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>35.2</td>
<td>150</td>
<td>3672±112</td>
<td>392±29</td>
<td>3.3</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>59.7</td>
<td>80</td>
<td>4050±67</td>
<td>360±36</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

**Table 4.2.** Summary of experimental data for different electrode separations and generator sweep rates for the analysis of four Bi^{3+} solutions from 14 to 500μM concentration. Slope and intercept 95% confidence limits are from six individual data sets (n=6) for each condition. Endpoint RSD statistics are for the highest concentration tested and analysis times reflect approximate time to reach a stable baseline.
concentration-related factors from affecting the results.

**The Effect of Generator Sweep Rate**

The discussion on the collector response and calibration plot above suggested that a change in the generator sweep rate will alter not only the speed of the analysis but also the characteristics of the calibration plot. In particular, the intercept and precision were highlighted as parameters which would be expected to be directly affected. However, the results in Table 4.2 also show that the analysis sensitivity is dependent on the rate.

**Analysis Precision**

For each of the two electrodes, an increase in the sweep rate lowers the analysis time proportionally. A more rapidly decreasing collector response sharpens the endpoint transition, making extrapolation of the linear portions of the response easier and less subjective. Thus, the increase in scan rate tends to increase the precision of the endpoint determination. Most of these experiments were performed on different days and without any deliberate temperature control. Because the cell was not thermostatted, daily temperature fluctuations of an estimated ±2°C certainly contribute to the variability. The titration is a diffusional process and it is not unreasonable to expect a certain amount of temperature
dependence of the results. If it is assumed that the diffusion coefficients vary by 2%/degree$^{52}$ and the change in collector response is linearly related to the diffusion coefficients, temperature effects may be responsible for most of the observed variability.

The increase in precision with sweep rate is especially important for the lower concentration solutions, for which the overall change in collector response is less. The analysis of low concentrations is necessarily more uncertain than high concentrations because the relative error is much higher. In any of these experiments, the minimum estimated error in the endpoints is $\pm 1$ second and is determined by the sharpness of the transition. An increase in the scan rate lowers the uncertainty, although the extent of shielding also plays a role (see below).

**Calibration Plot Offset**

The intercept of the calibration plot has been attributed to the change in generator current during the communication time between the generator and collector. This time does not represent the diffusion of a single species; it represents the combined effect of a sequence of individual diffusion events. In the case of an analysis of Bi$^{3+}$ with BiEDTA$^-$ the interdependent processes include the diffusion of BiEDTA to the generator, the liberation of EDTA into solution where it complexes with Bi$^{3+}$, and ultimately the diffusion of Bi$^{3+}$ away from the collector. Any change in the applied generator current during the period of
communication time between the fibers should induce a similar change in the intercept of the calibration plot offset. The data for the two electrodes support this conclusion.

While not directly proportional, the sweep rate and plot intercept do seem to be dependent. Electrode A shows an intercept of 183 nA for a sweep rate of 8.9 nA/sec. This experiment showed a communication time of 11 seconds (Figure 4.2), and during this time the generator current changed by (11 sec * 8.9 nA) or about 98 nA. Thus, 98 nA of the intercept is due to the increase in applied current, and the remainder of approximately 90 nA is due to other factors. The lack of a direct proportionality suggests that one or more other phenomena may contribute (an interferent in the solution or perhaps a systematic error). Care was taken to eliminate contamination, high-purity reagents and water were used, and deaerating and purging with nitrogen for at least 10 minutes was shown in additional trials to be sufficient for removing dissolved oxygen.

The theory of diffusional microtitration\textsuperscript{53-55} may yield additional insight into the nature of the intercept. In this type of analysis, the reagent is diffused through a membrane into the sample volume, where it reacts with the analyte. The quantity of reagent delivered through the membrane as a function of time is\textsuperscript{55}

\[
R(t) = \frac{D}{l_m} \left( r c r^2 A_m t + \frac{2 c A_m l_m}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} (1 - e^{-D./n^2 \pi^2 ut^2}) \right)
\]  

(4.1)
where $D_r$ is the diffusion coefficient of the reagent in the membrane

c is the concentration of reagent

$l_m$ is the membrane thickness

$A_m$ is the membrane area

At long times, the second term of eqn. 4.1 is non-zero and represents the amount of reagent that must be added to the sample to establish a steady concentration gradient across the membrane after its initial equilibrium. If the collector/generator gap is taken as an analogy of a membrane, the non-zero intercept can be interpreted to mean the amount of cathodic current at the generators necessary to create an equilibrium concentration profile from the generators to the collector. (Unlike the diffusion of a reagent through a membrane, however, the movement here is essentially opposite, corresponding to the diffusion of the analyte Bi$^{3+}$ away from the collector.)

Relative to the magnitude of the endpoint currents, the intercept seen in these experiments is small. It does not seem to significantly affect the results of the analysis. It does present complications if the analysis is to be performed by way of standard addition, though, because the magnitude of the intercept must be known at least approximately before the concentration can be calculated.
Analysis Sensitivity

An important consequence of increasing the generator sweep rate is the increase in analytical sensitivity. In order to be useful as an quantitative analytical technique, a procedure must have adequate sensitivity to the level of analyte present. In the case of a titration or other technique where an applied stimulus causes a measurable response, sensitivity is usually defined as the ratio of change in response to change in stimulus, which is the slope of the calibration plot. Maximum sensitivity results from the appropriate choice of experimental variables. The data in Table 4.2 show that the sensitivity of this technique is at least partly dependent on the sweep rate. Electrode B exhibits a 33% increase in calibration plot slope for a tripling of the sweep rate. However, Electrode A does not show a similar increase. The significantly larger spacing of Electrode B suggests that sweep rate plays a larger role in determining sensitivity of lower quality electrodes than for electrodes of closer and more uniform spacing.

The relationship between sensitivity and sweep rate seems to be another consequence of the diffusional nature of the analysis. Although the analogy of diffusional titration provides a possible explanation for the intercept, it is less helpful in this case. From eqn. 4.1, the slope of the calibration plot (the change in time for a change in reagent amount) is given by the reciprocal of the first term, $l_m/D_r c_r A_m$. Thus, thicker membranes would yield the higher sensitivity. An increase in the generator sweep rate would seem to be analogous to a thinner membrane,
however, as the production of EDTA is faster. For this reason the membrane
analogy fails, and suggests that a more complex phenomenon is responsible. The
sensitivity may be dependent on the concentration gradient of EDTA, which
determines the gradient of Bi$^{3+}$. At higher speeds, the localization of the analysis
to the region immediately surrounding the fibers may result in higher sensitivity,
as opposed to low speeds where the diffusion layers are much broader. The data
for an increase in collector/generator spacing also seem to support this (see
discussion below).

While the increase in sweep rate increases the sensitivity of moderate to
high concentrations, it does not allow lower concentrations to be analyzed. The
data above are for a concentration range of 14 to 500 μM Bi$^{3+}$. Even for 14 μM
Bi$^{3+}$ solutions, there was a distinct lack of sensitivity in the electrode response. At
very low levels, insufficient free metal is present in solution to achieve adequate
sensitivity. The discussion of Section 4.1.2 illustrates the need for "predeposition"
of the metal ion to give the carbon surface sufficient activity. Analysis of Bi$^{3+}$
solutions less than approximately 20 μM was found to require this type of
pretreatment. (Conversely, gold and platinum electrodes have been shown to
exhibit underpotential deposition of metals onto their surfaces until a monolayer is
formed. This has been attributed to the entropy requirement for arrangement of
the deposited atoms into crystals.$^{51}$)
The Effect of Collector/Generator Spacing

The experimental results of Table 4.2 and Figure 4.4 show that the collector/generator gap width also plays a role in the analytical characteristics. In addition to the average distance between the fibers, the uniformity of the gap is important.

Precision of the Analysis

The relative standard deviation (RSD) of the analysis data shows a general decrease in precision for an increase in the average fiber spacing. This can be explained as a consequence of increased shielding of the collector.

The determination of the endpoint is significantly affected by the sharpness of the transition. This, in turn, is related to the shielding efficiency of the generator electrodes. For a triple-band of the type used here, a lower gap width allows the outer generator electrodes to more effectively shield the collector. An electrode with higher shielding produces a faster rate of decline of the collector response than one with lower. In addition the baseline residual current after the endpoint has a slope which depends on the degree of shielding. The slow growth of the depletion layers out from the electrodes is insufficient to completely prevent the incoming Bi$^{3+}$ from reaching the collector in the time scale of the experiment. The
result is a negatively-sloping, non-horizontal baseline as the Bi$^{3+}$ depletion layer grows. Thus, lower shielding creates gradual, less distinct endpoints.

An electrode with non-uniform fiber spacing experiences a slightly more complex situation where the combination of regions creates a distorted endpoint. In general, blocking or inactivating these regions (by covering with epoxy) improves electrode response. Although the maximum currents are less (due to the lower surface area), the increase in endpoint sharpness increases the overall precision.

Calibration Plot Offset

The non-zero intercept was described as a consequence of the communication time between the generator and collector. Accordingly, the sweep rate has been shown to be one factor that affects its magnitude. An increase in electrode gap width would also be expected to affect the value of the intercept, and the data in Table 4.2 confirm this. As discussed above, the increase is not directly proportional to the increase in spacing, further suggesting that experimental errors or an unidentified factor of the intercept also play a role, in addition to sweep rate and fiber spacing.
Analysis Sensitivity

Although the sweep rate and calibration plot slope are shown to have a definite relationship, the cause is unclear. An increase in fiber spacing, such as shown by Electrode B relative to Electrode A, decreases the analytical sensitivity for somewhat clearer reasons. The decrease in shielding creates a higher baseline current and less sharp collector response, driving the endpoints together at longer times. Above, it was suggested that increasing the sweep rate may increase the sensitivity because it decreases the thickness of the diffusion layer, creating a higher concentration gradient; if the same argument is applied here, it is concluded that reducing the fiber spacing also reduces the diffusion layer thickness.

4.2.3. Predeposition to Increase Electrode Activity

The data from the above trials show that solutions of lower than approximately 20μM concentration do not have adequate response at the carbon fiber surface. The low activity of the carbon surface results in low reduction currents, which limits the ability to discriminate at low concentrations. Because the sharpness of the endpoint transition also depends on the fiber response, any increase of the fiber activity will in general make the endpoint more reliable. For
these reasons, the analysis of lower concentrations requires additional procedures to predeposit metal on the carbon surface.

The cyclic voltammograms show that a significant overpotential for Bi\(^{3+}\) reduction exists for the carbon fiber electrodes (Figure 4.1). To eliminate this problem, the fibers were held at -400 mV (vs. Ag/AgCl) for a time sufficient to allow a pseudo-steady-state current of at least approximately 10 nA. The time required to reach this level depended significantly on the Bi\(^{3+}\) concentration, as expected, and ranged from several minutes to approximately 10 minutes. Solutions were generally analyzed in order from highest to lowest concentration to take advantage of Bi deposited previously and thereby reduce the necessary time. However, the transfer of the electrode from one solution to another seemed to reduce the activity, and more deposition was required. This loss of sensitivity when the electrode is transferred from one solution to another indicates that the deposits are physically unstable, and may be damaged or somehow compromised in the process. Microscopic examination shows that the deposits are not actually removed, but rather only made non-electroactive. A slight amount of additional metal is needed to restore their activity.

The influence on the solution composition is negligible, even after repeated and extended predeposition. A typical analysis of 30ml of 3.0 \(\mu\)M Bi\(^{3+}\) solution, requiring 10 minutes of deposition at an average current of 10 nA, experiences a deposition of \(2.07\times10^{-11}\) moles Bi\(^{3+}\). This changes the original solution composition by only 0.02%, which allows multiple analyses without introducing error.
The effect of predeposition on carbon fiber response is shown in Figure 4.5. With no pretreatment and clean carbon surfaces, the collector shows very little response, as was seen previously for low concentrations (Figure 4.2). After the initial analysis, however, dramatic changes in the response can be seen. An analysis immediately following the first (without any additional predeposition) shows a slightly higher initial collector current which increases significantly when the current source switch is flipped at 8 seconds. The current sweep is started at 10 seconds, and the collector response rises a short time more before eventually returning to a stable baseline.

The increase in the initial current is due to the increased activity of the collector resulting from the bismuth deposited during the prior analysis. However, the relatively small increase between the first two analyses suggests that the amount deposited during a single analysis is not very large, as one would expect from the shielding of the collector (i.e., most Bi\(^{3+}\) reduction occurs at the outer edges of the generator fibers). The much larger rise in initial current for the third and fourth analyses is a direct result of the deliberate predeposition before each analysis. Note that the baseline response increases as well; if the shielding efficiency is approximately constant, the baseline response is directly proportional to the collector activity. The initial current is approximately the same in the last two analyses, which suggests that the maximum response has been achieved.

The theoretical response of a 7 µm x 1.0 cm band to a 17 µM Bi\(^{3+}\) solution is approximately 14nA (see Chapter 3), and is very close to that seen in Figure 4.5.
Figure 4.5. Effect of predepositing bismuth on the carbon fibers in the analysis of Bi$^{3+}$ ions. Bi$^{3+}$ concentration: 17$\mu$M; generator sweep rate: 35 nA/second; generators switched on at 8 seconds, sweep started at 10 seconds. Scan 1: no predeposition (---); Scan 2: after a single analysis, no deliberate predeposition (-----); Scan 3: after deliberate predeposition (----); Scan 4: after further predeposition (-----).
The large rise in collector current at 8 seconds, when the current source switch is flipped, seems to be feedback as a consequence of the electrode properties and the instrument design. When performed without any predeposited bismuth (scan 1, Figure 4.5), the analysis proceeds as expected, with only a slight distortion at 8 seconds. However, the subsequent analyses all show a large but relatively constant increase in current. The slight difference in initial current between the first two analyses suggests that the amount of bismuth on the collector after the first is small; hence, additional predeposition was needed to increase its response for the third and fourth. The large current increase at 8 seconds of scan 2 can therefore be taken to show that it is the amount of material deposited on the generator fibers which is (at least partly) responsible. The appearance of the third and fourth analyses confirm this; although the initial current is much higher than in the second, the size and shape of the peak are very similar. Considering that the concentration of BiEDTA\(^-\) is several times higher than Bi\(^{3+}\), that both BiEDTA\(^-\) and Bi\(^{3+}\) are reduced at the generators, and that the generators are less shielded than the central collector and therefore exposed to larger diffusional flux, it is not surprising that the generators reach maximum activity after a single analysis.

In contrast, the collector requires much more predeposition to achieve maximum activity. After an analysis, after the collector had reached maximum activity, it was found that the response was usually lower than before the analysis (i.e., the act of performing an analysis lessens the effect of predeposited
bismuth.) The response of the collector needed to be checked before each analysis, and additional metal reduced if the activity was low. Whether material is actually removed from the surface or just losing electrical contact is unknown. The generator fibers were also checked before each analysis but did not show the same problem, perhaps because of the greater amount of metal present.

The cause of the peaks is thought to be a consequence of the combined effects of the predeposited material and the nature/design of the instrumentation and electrochemical cell. The analyses of high concentration solutions did not show the feedback, but they were performed after reoxidizing or physically removing the deposits (Chapter 2). The <cell> switch of the current source serves only to remove the electrodes from electrical connection of the interior circuit (Figure 2.5). Because of the design of the circuit, a high (but not infinite) resistance pathway is created between the generator working and auxiliary electrodes when the switch is closed, even with zero applied current. It is speculated that a slight current loop is established from the collector to the generator, through the current source and to the auxiliary electrodes. Potential applied to the collector will be communicated through the current source and result in a cathodic current. With this explanation, the dependence of the magnitude of the peak on the activity of the generator fibers is clear. Also, additional data suggests that the level of feedback is lower for electrodes with larger gap widths, agreeing with the proposed explanation. The eventual decrease of the feedback current after the start of the generator current sweep is also easily explained: the increase in generator potential balances and reverses.
the feedback current. A closer examination of the response after the feedback maximum in the last two analyses in Figure 4.5 shows a two-stage decay. The second stage, which is proposed as the onset of EDTA$^{4-}$ production, occurs slightly below the initial response level of the collector. A comparison of the collector decay in Figure 4.2 shows a nonlinear response in the same region.

Although there is some uncertainty in the cause of the feedback, the data suggest that it doesn't have a significant impact on the outcome of an analysis. Indeed, its presence is indicative of high surface activity, which has been shown to yield better results. The data in Figure 4.5 are representative of the characteristics and nature of the analysis; other analyses also show that differing degrees of response yield essentially the same titration endpoint (also see results below). However, the sharpness of the endpoint and therefore the precision with which it can be determined is greater at higher electrode activities. It follows that the feedback phenomenon may even be somewhat beneficial to the analysis of low concentration solutions.

It may be possible to eliminate or reduce the feedback phenomenon with a different galvanostat design. Although a passive circuit was used here (for reasons of simplicity), an active design incorporating an op-amp output may effectively screen the feedback. However, the need to have the galvanostat isolated from ground (to eliminate potential conflicts with the potentiostat) must still be met.
4.2.4. Analysis of Low Concentration Bi^{3+} Solutions (less than 20μM)

The collector response in the titration of low concentration Bi^{3+} solutions is shown in Figure 4.6, with analysis data summarized in Table 4.3. As described above, predeposition of Bi onto all three fibers was used to increase sensitivity. In general, the data support the observations made for the 20 to 500 μM solutions.

Although the initial and feedback currents of the 17 μM Bi^{3+} solution are less than those of the 13 μM, the endpoint is at a higher generator current. This is additional evidence that the feedback phenomenon does not significantly affect the titration, even if it occurs to different extents. The endpoints of the analyses were determined by extrapolating the lower linear portion of the response (the portion immediately before the endpoint as seen in Figure 4.6). If the lower portion is caused by the shielding of the collector with electrogenerated EDTA, as proposed, it is this portion which contains useful quantitative information.

The analysis sensitivity is seen to be dependent upon both the generator sweep rate and on the fiber spacing for these low concentration analyses, just as they were for the higher concentrations. Electrode D, with a smaller spacing and a higher uniformity than that of either Electrodes A or B, shows the highest sensitivity seen in these experiments. The smaller spacing also lowers the intercept for the same reasons as above.

The error in estimating the endpoint limits the precision of measurements in this low concentration range. Even with a very uniform, closely spaced
Figure 4.6. The analysis of Bi\textsuperscript{3+} solutions from 3.4 to 17 μM. Predeposition used on all fibers before each analysis. Generator sweep rate: 17.8 nA/second. 3.4 μM (---); 13 μM (---); 17 μM (-----). Electrode gap width: 7μm.
Table 4.3. Data summary for the analysis of four low concentration Bi$^{3+}$ solutions (3.4 to 17μM) at different generator sweep rates and gap widths. Slope and intercept 95% confidence limits for each set of conditions are calculated from six individual data sets (n=6). Endpoint RSD statistics are for the highest concentration tested and analysis times reflect approximate time to reach a stable baseline.
Figure 4.7. Reproducibility of low concentration (3.4 $\mu$M) Bi$^{3+}$ analyses at electrode with 7$\mu$m spacing. Bi predeposition to all fibers before each scan. Generator sweep rate: 35.6 nA/second.
electrode, the shape of the endpoint and seemingly inevitable experiment-to-experiment variability limit the precision to ±1 second (Figure 4.7). Considering that this represents a 4μM change in solution composition, the accuracy of the analysis is somewhat uncertain at these low concentrations.

The scans of figure 4.7 show that the endpoint transition is not as sharp as would be desired; in a large part, this is the reason for the uncertainty of the analysis. Also note that some of the analyses have a slightly distorted baseline, appearing as if a second titration is occurring. The cause of these distortions is not known, although they may be due to stirring of the solution. They do not occur reproducibly (the same solution and electrode was used for all the scans in Figure 4.7), and the peak-shaped appearance cannot be explained by the current understanding of the processes at the collector and generator electrodes. Other electrodes and solutions had shown negative peaks in the same region. However, this happened only rarely. Their occurrence doesn't seem to affect the titration results if the baseline distortions are not large.

The limit of quantitation of this analytical method is primarily controlled by the endpoint uncertainty. Although the 3 μM Bi³⁺ solution in Figure 4.7 gives a large, clearly identifiable drop in collector response, making it easily detectable, the ability to quantitate it is more difficult. Electrode spacing less than the 7 μm used above is likely necessary for effective discrimination of lower concentrations, and especially so at levels below 1 μM. A further decrease in the collector/generator gap width will make the endpoints less broad, but the data
above show that the sensitivity will also be enhanced. Higher generator scan rates are also likely to be of benefit. Together, the combined effects will increase the resolution of closely spaced concentrations and allow quantitation at lower levels.

4.3. Stepped Current Experiments

In addition to a steadily increasing generator current, the analysis of Bi$^{3+}$ solutions was carried out using current steps. These experiments give similar information to those for current sweeps and help support the previous observations.

4.3.1. Analysis Results

Typical results of Bi$^{3+}$ analyses are given in Figures 4.8 and 4.9.

The collector response in Figure 4.8 is as expected for discrete current steps to the generator electrodes. 60 seconds after potential is applied to the collector, currents steps of approximately 43 nA are applied to the generators each 30 seconds. The time to reach a near steady-state after each step is less than 30 seconds. Thus, the collector current at the end of each is due to the balance of the incoming Bi$^{3+}$ flux and the generation of EDTA$^-$. The magnitude of
Figure 4.8. Analysis of Bi$^{3+}$ solutions using stepped generator current. Initial period of 60 seconds before applied current. Collector/generator gap width: 15 μm. Applied current: 43 nA/step. Bi$^{3+}$ concentrations: 87 μM (· · · ·), 130 μM (—), 170 μM (— — ), and 220 μM (— · · ·).
Figure 4.9. Calibration plot of Bi^{3+} for stepped generator current. Same conditions as Figure 4.8. Slope: 2877 nA/mM. Intercept: 91 nA.
the decrease with each step is related to the shielding efficiency of the electrode: higher shielding is expected for closer electrodes, and the drop in collector response will be greater. For the data in Figure 4.8, the drop of 25 nA/step compared to the applied step size (43 nA/step) gives a shielding efficiency of 58% for the generated EDTA. As the endpoint is approached, the collector response decreases for each applied step. A similar calculation applied to the data in Figure 4.2 shows a collector response of -4.5 nA/second for an applied current of 8.9 nA/second, a shielding efficiency of 51% for EDTA.

The endpoint of each analysis is determined by the extrapolation of the collector current at the end of each step to the baseline after the endpoint, in a manner analogous to that for swept-current. The calibration plot from this data is shown in Figure 4.9.

When compared to the data in section 4.2, the characteristics of the plot become clear. Each current measured is essentially at steady-state and any time related effects should disappear. Thus, the intercept of Figure 4.9 (91 nA) does not include the effect of changing generator current, and is smaller than those given in Table 4.2, even though the fiber spacing is larger in this case. The 91 nA intercept seen here may reflect other processes, such as those explained previously.

The lower slope of the stepped-current calibration plot is not surprising, given the slightly larger electrode spacing and the rate dependence of the slope for the swept-current case. Here, the realization of steady-state with each change in generator current should result in a collector response which changes from
only the shielding by the generators. The discussion of section 4.2.2 on the 
dependence of sensitivity on sweep rate suggested that an increase in the 
concentration gradient of generated EDTA was responsible; establishment of a 
steady-state with each change in generator current would minimize such a 
gradient and lower the sensitivity. The data in Figure 4.9 support this hypothesis.

Not surprisingly, the variability of the high-concentration endpoints is worse 
for the present case of stepped-current. The steady-state current at each 
generator step results from diffusional mass transport. At long times, 
electrochemical experiments may experience density gradients or vibration-
induced convection, both of which create enhanced transport to the electrode 
surface. Without any precautions to inhibit these effects, substantially longer 
analysis times are likely to be affected. The lower concentrations of Figure 4.9 do 
not appear to suffer from the same problem. In addition, the absence of these 
effects for the much shorter times of the swept-current analyses may be partially 
responsible for their higher precision.
Conclusions

The analytical results show that the quantitative analysis of metal ions using carbon fiber microband arrays is quick and relatively precise. Analysis of metal ion solutions is possible in several minutes and over a relatively wide range of concentration, and without sample destruction. Amperometric generation of a reactant such as EDTA from a precursor complex allows accurate titrations to be performed, without the need for standardization of the titer. Although electrogeneration of reactants has been widely reported in the past, the utilization of carbon fiber microband arrays allows a much quicker analysis, without large sample or reagent volumes. In fact, the type of experiment described here takes place in the diffusion layer near the electrode surface. Even a small sample volume of less than a milliliter can be analyzed many times, giving greater precision and accuracy.

A fast, simple, and inexpensive procedure for fabricating these carbon fiber arrays was developed. Up to now, no other technique for producing
microfiber arrays has been described. Other than a few materials and tools, nothing special is required. Their ruggedness and electrochemical properties make them more suitable than comparable photolithographically-produced gold or platinum arrays for the routine use described here. Unlike metal thin-film arrays, these arrays can be lightly polished many times before suffering damage and the materials of their construction are sufficiently inert and unaffected by exposure to the chemicals used. While the arrays used were composed of three fibers, construction of an electrode of five or seven fibers would offer advantages. Electrodes with additional fibers were produced, but it was found that three offered sufficient sensitivity for these experiments. An increase to five or seven fibers is expected to increase the signal-to-noise ratio and also sharpen the endpoint, increasing the precision. While not needed in the experiments described here, increases in signal and precision would be necessary for the analysis of significantly lower concentrations.

The timescale of the analysis is a result of the communication time (and consequently the distance) between the generator and collector electrodes. When mass transport of chemical species is restricted to diffusion, it is seen that a decrease in the distance between the electrodes decreases the communication time and therefore the time required for analysis.

The precision of the analysis is also seen to be related to the separation of the fibers. A wide spacing results in a thicker diffusion layer before the endpoint is reached, and the sharpness of the transition is reduced. Also, the lower shielding efficiency which results from a wide electrode spacing is responsible for a sloping
baseline after the endpoint, making the endpoint determination subject to greater error. In experiments with closely and uniformly spaced electrodes, the data showed less than a few percent RSD. Higher quality electrode arrays (with separations of less than 5 microns), an increase in the number of fibers, and better control of experimental variables such as temperature can be expected to reduce the uncertainty further.

The precision is somewhat affected by the rate of increase of reactant generation (EDTA). In the swept-current experiments, a faster generation of EDTA was generally shown to increase precision. This was proposed to be a result of the increase in the sharpness of the endpoint transition, allowing easier estimation.

Analytical sensitivity is seen to be dependent upon both the electrode spacing and the rate of increase of EDTA generation. The slope of the calibration plot increases for lower spacings and higher sweep rates. While the cause is not entirely clear, it is supposed that the sensitivity is a function of the concentration gradient near the collector. At large spacings and low sweep rates, the diffusion layer is thicker and has a lower gradient than for small spacings and high sweep rates.

The diffusional nature of the titration is exhibited as a positive offset of the calibration plot, giving a non-zero intercept for zero analyte concentration. Two components are proposed to be largely responsible for the offset. First, a change in generator current during the communication or diffusion time between the electrodes is seen to be an inevitable consequence of the swept-current
experiments, and is responsible for a portion of the offset. Decreasing the electrode gap or the sweep rate reduces the offset, as expected. Second, a portion of the offset is proposed to be due to the amount of current necessary for the creation of a concentration gradient, a phenomenon seen for diffusional microtitrations. Analyses using stepped current show offsets less than for swept current; the offset in those cases is presumed due to the second component alone, as the first component is absent.

In order to analyze Bi\(^{3+}\) solutions of concentrations less than a few \(\mu\)M, it is necessary to predeposit Bi onto the fiber surface to increase response. The insufficient activity of the carbon to Bi\(^{3+}\) reduction was evident for only these lower concentrations. Pretreating the fibers in this manner extends the analysis time, but was reliable and gave reproducible results. Although they weren't investigated here, it is expected that the titration of other metal ions will also require similar pretreatment to enhance sensitivity at lower concentrations. Data presented here for the deposition of many metals onto these carbon electrodes supports this prediction.

Finally, it must be mentioned that the titration of other metal ions is possible, depending on the choice of titrant. In general, the choice of titrant precursor and possible analytes is based on two criteria. First, the precursor complex must be more stable than the analyte complex (\(K_f\) larger by several orders of magnitude). BiEDTA\(^-\) has a formation constant larger than most other metal ions \((10^{23})\). Second, the precursor must be electroactive at a potential more
extreme than that for the analyte. Thus, BiEDTA\textsuperscript{-} would be a possible titrant for metal ions which are reduced at potentials more positive of approx. -0.7 volts (vs. Ag/AgCl). Although not investigated here, BiEDTA\textsuperscript{-} may be used as the precursor for the analytes Pb\textsuperscript{2+}, Hg\textsuperscript{2+}, and Cu\textsuperscript{2+}. Adjustment of pH and buffer composition will influence the reduction potentials of the free and complexed metal ions; therefore these may yield additional selectivity for the titratable species. For example, a mixture of lead and copper could be analyzed with BiEDTA\textsuperscript{-} by the use of an acetate buffer, which will selectively complex copper and shift its reduction potential.

The new electroanalytical technique presented here will allow the quick, accurate, and precise determination of metal ions in solution. Although electrochemical techniques in general suffer from potential interference problems, they are useful for analysis of solutions in which the number of electrochemically active species is limited. The technique presented here is one of a more general utility, however, and is not limited to electrogeneration of EDTA. The shielding of the collector can theoretically be accomplished with any reagent that can be formed at the generator electrodes, depending upon appropriate selection of the precursor and electrode potentials. In this manner, the titration of non-electroactive species is possible by the detection of excess electroactive titrant, such as bromine, iodine, or redox reagents.
BIBLIOGRAPHY


