Development of a Microelectrode Array Sensing System for Water Quality Monitoring

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DEVELOPMENT OF A MICROELECTRODE ARRAY SENSING SYSTEM FOR WATER QUALITY MONITORING

by

Robert D. Gardner

A thesis submitted in partial fulfillment Of the requirements for the degree of

MASTER OF SCIENCE in

Biological Engineering

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ABSTRACT

Development of a Microelectrode Array Sensing System for Water Quality Monitoring

by

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Utah State University, 2008

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This thesis reports the design and fabrication of a low-cost reliable microelectrode array sensing platform and its application toward water quality monitoring, including heavy metal ion detection. Individually addressable microelectrodes were designed in a planar array on a nonconductive glass substrate by a photolithography method. The size, shape, composition, and functionality of the microelectrodes were theoretically explored in order to maximize performance.

The microelectrode array sensing platform was proven and characterized in the K$_3$Fe(CN)$_6$ electrochemical standard using cyclic voltammetry. The sensor platform exhibited well defined voltammograms and had increased sensitivity relative to a commercially available microelectrode of similar size. Feasibility for application to heavy metal ions, copper and lead, detection in aqueous solutions was demonstrated utilizing the electrochemical method of anodic stripping voltammetry. Well defined voltammograms for the copper and lead ions were obtained with individual microelectrodes of the sensor platform, and compared against the similar sized commercially available microelectrode; increased sensitivity was observed.
Finally, a piecewise proving technique was done to prove the feasibility for future coupling of the microelectrode array sensor platform with a previously developed homemade electrochemical device. By analyzing the response of the homemade electrochemical device compared to that of a commercially available electrochemical analyzer, feasibility was demonstrated.
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CHAPTER I

PROJECT INTRODUCTION

1.1 Problem Description

Charged species identification and quantification is very important to analytical chemistry experiments in industrial, environmental, and academic experimentation. Many systems and environments require testing for trace levels of ions or molecules that reside, contaminate, or transform through some reaction. Salinity is an important criterion of water control both in agricultural and municipal water supplies. Salts are strong electrolytes consisting of metal cations and counter ions that disassociate in aqueous solutions. These metal cation contaminants such as copper, lead, zinc, and cadmium can be present in foods, beverages, drinking water, and aquatic environments.\(^1\)-\(^4\) High levels of charged species raise levels of concern and, therefore, accurately monitoring or quantifying them is desired.

Traditionally environment or industrial process samples are taken on site and removed to laboratory facilities where electrochemical, chromatographic, and spectroscopic methods are employed to detect, observe, and quantify any ions or ionic species within the sample. Examples of typical methods utilized include inductively coupled plasma - mass spectrometry (ICP-MS), differential pulse anodic stripping Voltammetry (DPASV), graphite furnace atomic absorption spectrometry (GF-AAS), cold vapor atomic absorption spectrometry (CV-AAS), and cold vapor atomic fluorescence spectrometry (CV-AFS).\(^5\)-\(^7\) However, these test methods vary in sensitivity to the charged species of interest (dependent on method employed), take an undesirable amount of time to obtain results, and the samples have a greater probability of contamination or loss due to the handling and transport prior to testing.\(^1\) Advantages of new analytical tools that are capable of real
time process monitoring or real time environmental monitoring include improved process control, minimization of environmental impact, and ability for continuous monitoring with options for early detection.\textsuperscript{1,2} Where, the greatest advantage is the rapid return on the test results, enabling quick action responses.

Charged species of concern can be monitored on site with an appropriately designed sensor capable of all of the aforementioned advantages. Additionally, due to advances and trends towards cleaner (green) analytical chemistry, a new sensor system should be capable of monitoring an environment without polluting the system or affecting it in any adverse manner.\textsuperscript{1} This can be a main constraint parameter on new sensor system development and must be considered.

This thesis is the summary of the work completed to develop a low cost reliable sensor that is sensitive and selective to the heavy metal ions, including copper and lead, which act as contaminants in aqueous systems. Parameters and characterization of the sensor are proven along with the operating theory and justification of design and usage.

1.2 Overview of the Solution

Electrochemical (EC) methods offer great promise for ion detection. Features like independence from an optical path length and high sensitivity, approaching that of fluorescence, along with low power requirements, low cost, ability to be miniaturized, and adaptability with advanced micromachining and microfabrication technologies, make EC method very appealing.\textsuperscript{1} Voltammetry, one of the most widely used electrochemical methods in the detection of ions, is used to examine the kinetics of electrode processes for which current is monitored as the applied potential is changed. Alternatively chronopotentiometry, another electrochemical method, explores the kinetics of electrode processes for which the potential is monitored as the current is changed; this method is not
explored herein. The overpotential measured can be directly related to the concentration of the analyte in solution. Traditionally, sensor electrodes used in voltammetric and/or chronopotentiometric experiments have typically been relatively large electrodes on the millimeter scale. However, since the advent of microelectrodes, there is no longer a reason to rely on bulky electrodes or difficult electrochemical cells; fast, easy, environmentally friendly electrochemical systems can be obtained.\textsuperscript{1}

1.2.1 Stripping Voltammetry Analysis

Stripping analysis has proven extremely powerful for identification of trace metals in environmental, clinical, or industrial samples.\textsuperscript{1,4,9,10} Due to the coupling of a preconcentrating step with a sensitive electrochemical measurement technique, higher sensitivity can be obtained.\textsuperscript{1,4,9} Furthermore, since stripping analysis utilizes only low power and the instrumentation needed for implementation is small and portable, its feasibility increases as a reliable on-site trace metal sensing system.\textsuperscript{1} As an example, Giacomino reports, in a 2008 study on the parameters affecting determination of mercury using anodic stripping voltammetry on a gold electrode, that the US Environmental Protection Agency (EPA) has recommended adopting stripping analysis for the quantification of mercury.\textsuperscript{6}

Anodic stripping voltammetry (ASV) is a form of stripping voltammetry where an under potential is set for a period of time, the preconcentrating step, allowing the positive charged metal ions to be reduced and electroplated on the electrode surface. Then the potential is swept towards an overpotential effectively oxidizing the metal species, releasing the ions and electrons from the electrode surface. This preconcentration effectively increases the amount of metal ions at the electrode surface, with respect to the concentration in solution, and allows a favorable signal-to-background ratio.\textsuperscript{4} Current is
monitored during a second phase sweeping step and is dependent on the concentration of charged species accumulated at the electrode and the time preconcentrating is allowed.\textsuperscript{3}

The ASV technique utilizes a three electrode test method where a working electrode is used to monitor the oxidation-reduction reaction, a counter electrode is used to complete the circuit, and a reference electrode is used for comparison. Typically reference electrodes and counter electrodes are silver/silver chloride and platinum wire, respectively. However there are a number of different types of both electrodes.

The working electrode (test electrode) has been proven to strongly influence the performance of the electrochemical measurements. Historically, mercury electrodes worked very well due to a renewable, reproducible, and smooth surface.\textsuperscript{1,4} However because of the toxicity concerns with mercury, a suitable alternative needs to be incorporated in the working electrode design. Alternative metals have been utilized, such as gold or platinum, and results have been presented for both elements.\textsuperscript{3,6,8,9,11-14} Additionally many experiments have favorable outcomes utilizing gold working electrodes over other element choices.\textsuperscript{3,6,8,9,12,13}

1.2.2 Square Wave Anodic Stripping Voltammetry (SWASV) and Differential Pulse Anodic Stripping Voltammetry (DPASV)

As previously mentioned, the second step in stripping analysis involves a sweeping of the potential from an under potential to an over potential state. Sweeping techniques including linear, staircase, square wave, and pulse methods have been used.\textsuperscript{3,5,6,8,12-15} Higher sensitivities have been reported depending on the sweeping method and the environment the test is being performed with.\textsuperscript{6} Square wave voltammetry (SWV) and differential pulse voltammetry (DPV) are derivatives of linear sweep and staircase where current is monitored while the potential between a reference electrode (example Ag/AgCl) and a
working electrode is swept in a series of stair steps with a square wave or a series of regular voltages superimposed on stair steps. These advanced sweeping methods offer greater sensitivity than linear sweep or staircase sweep.6,8,13 When combined with the preconcentrating step in anodic stripping analysis these methods are named square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping voltammetry (DPASV). Furthermore, these methods have been proven with heavy metal ion detection in aqueous systems.1-4,6,8,10,12,13,15-21

1.2.3 Microelectrode and Nonlinear Diffusion

Electrochemical testing can further be improved by utilizing microelectrodes in place of traditional electrodes. Microelectrodes are defined to be electrodes that have micrometer (μm) dimension; in contrast, traditional electrodes are on the millimeter (mm) scale or larger. Miniaturization of electrodes offers many practical and fundamental advantages, namely, reduction of resistance (ohmic drop), reduction of sample consumption, ability to incorporate many electrodes in a small area, and greater ability to facilitate measurements in low-ionic-strength water samples.1 The foremost advantage to using this small sized electrode is in the mass transport uniqueness from the nonlinear diffusion properties accompanying it and this advantage is further amplified when multiple electrodes are utilized in an array. Nonlinear diffusion happens at the boundary of the electrode and from the increased perimeter-to-surface area ratio exhibited by microelectrodes, with respect to larger traditional electrodes, current amplification is accomplished.3,11,14,22-26 Extensive work has been done to show that microdisk design (circular disk shaped) have hemispherical diffusion patterns and microband design have hemispherical or a combination hemicylindrical-hemispherical diffusion pattern whether they are square or rectangular shaped, respectively.3,22,25,26 Diffusion layers are formed next
to the electrode surface and electroactive analytes must pass through this layer to reach the electrode. These diffusion patterns are established within seconds and are significant due to the radial component of the diffusion; greater amounts of electroactive analyte particles per surface area travel to the electrode within a set amount of time. Furthermore 3-D (hemispherical) diffusion associated with microdisk or micro-square electrodes have a steady state mass flux to the electrode surface resulting in a sigmoidal cyclic voltammograms instead of peak shaped voltammograms that would be observed with traditional or non-square microwand electrodes. With their small size, larger perimeter-to-surface area ratio, and nonlinear radial diffusion through the diffusion zones greater current density is possible. This leads to larger response changes during testing and improves signal-to-noise ratios, which is by definition is an increase in sensitivity.

By utilizing microelectrodes in an array fashion, one can capitalize on the enhanced properties the smaller microelectrode size contributes and also further diversity and flexibility by having a platform that can be utilized in multiple microelectrode combinations. One can simply use all microelectrodes, set at different potential ranges (assuming voltammetry electrochemical method is performed), use the microelectrodes as a census electrode with all electrodes performing as one capitalizing on their individual enhancements but allowing greater current flow which could be beneficial if the current monitoring instrumentation is not capable of small currents (1 – 1000 pA), or some situational unique combination of the two former scenarios. However, there is a fundamental criterion associated with microelectrodes in an array design. Namely, inter-electrode spacing must be such that diffusion zones from the individual microelectrodes don’t overlap and constructively interfere to produce planar diffusion zones much like those associated with larger electrodes. Extensive studies comparing inter-electrode spacing with
current responses reportedly use or suggest using an inter-electrode spacing of ten times the width or diameter of the electrode.\textsuperscript{2,3,26–28}

1.2.4 Combination of Voltammetry and Microelectrode

By utilizing an electrochemical testing method coupled to microelectrodes in an array design, trace levels of heavy metal ions can be detected. Advantages with preconcentrating, associated with stripping analysis, and increased current density characteristics from the microelectrodes should allow sensing in the low part-per-billion (ppb) range. Furthermore, due to the small size of microelectrode arrays and the small instrumentation requirements a portable, environmentally friendly, and simple sensing system can be designed.

1.3 Aims

This thesis is the summary of the work completed to develop a low cost reliable sensor that is sensitive and selective to the heavy metal ions, copper and lead, that act as contaminants in aqueous systems. The goals of this project are:

(i) Design and fabricate a new sensor platform to perform voltammetric measurements.

(ii) Design a microelectrode pattern (microdisk, microband, or micro-ring) that maximizes current density at the electrode surface and improves signal-to-noise ratio and sensitivity.

(iii) Incorporate multiple microelectrodes in an array design to allow detection of multiple measurable analytes in one aqueous solution and to allow comparison of same solution responses between multiple electrodes.
(iv) Prove function and characterize the microelectrode sensing system in $K_3$Fe(CN)$_6$ electrochemical standard.

(v) Demonstrate the feasibility of using the microelectrode sensing system to detect copper and lead ions in aqueous solutions.

(vi) Evaluate the potential of future coupling the microelectrode sensing system with a homemade square wave voltammetry device.

1.4 Outline of Technical Contents

The remainder of this thesis focuses on the fabrication, characterization, application, and future potential of a prototype platform microelectrode array sensing system for water quality monitoring. The information is organized into design, fabrication, proof, and characterization (chapter 2), application with ASV for copper and lead ion detection in aqueous solutions (chapter 3), and feasibility of future coupling with a homemade electrochemical-chip analyzer (chapter 4). Each technical chapter will include introductory and concluding sections pertinent to the information conveyed within the chapter. Following the technical chapters is a concluding chapter, discussing future applications and related work, and an engineering applications chapter further discussing simultaneous individual electrode experimentation, along with, advanced discussion of on-site environmental monitoring. Ending the thesis is an Appendix containing additional information on the fabrication and application of the sensor platforms.
CHAPTER 2
DESIGN AND CHARACTERIZATION

2.1 Voltammetric Criteria for Testing Utilizing Microelectrodes

When using Anodic Stripping Voltammetry (ASV) as the electrochemical testing method for heavy metal ion detection, sensitivity is greatly increased due to the preconcentrating step the method employs. Furthermore, sensitivity and testing versatility is further enhanced when the preconcentrating step is coupled with microelectrodes in an array fashion. However, great care needs to be taken in the design of the microelectrodes and microelectrode arrays to constructively enhance sensitivity and versatility.

Microelectrode array design is most complicated by criteria involved with the microelectrode parameters. The benefits and current amplification from microelectrodes needed to be realized and diversity with an array is desirable, but size, shape, composition, fabrication technique, and interelectrode spacing needs to be specified. These parameters were investigated and design rational for each is given in the following discussion.

Compact size, high sensitivity, low cost, and high repeatability are of great importance in sensor fabrication, especially when multiple electrodes comprise an array. The diversity of testing that can be performed is expanded with all of the electrodes having same shape, size, composition and characteristics. One can only expect comparable responses between electrodes to be correlated if the electrodes are identical. This makes the photolithography technique, utilized in silicon semiconductor industry, very appealing for microelectrode array fabrication. The process of photolithography involves constructing masks and utilizing ultraviolet light to photoactively change a resist polymer. Thus through development and etching (layer removal), microfabricated devices are made.
This fabrication technique is very repeatable and one can develop any electrode pattern desired by simply modifying the photomasks that pattern the microdevices. Final products, being on the low micron scale (limited to 1-5 μm), have reproducible and well defined geometries exhibiting near identical chemical and physical performance characteristics. Other methods of microelectrode construction have been reported, an example being conductive wire in a capillary tube that is heated to seal the glass around the wire, or epoxy in glass holding a conducting wire, and screen printed microdevices but these methods are not as repeatable or arrays are more difficult to construct than by lithography processes.

Size and shape of a microelectrode are also very important. Thormann stated in 1985 that microelectrodes fabricated with lithography techniques similar to the design we are attempting in this thesis are size limited to less than or equal to 10 μm width or diameter. Technological advancement has pushed the size limitations to much less than 10 μm for lithography fabrication. However, for literature comparison reasons we choose to match the 10 μm sized electrodes for the initial protocol sensor platform. Most microelectrodes have one of three different fundamental shapes: microdisk, microband, or microring shapes, shown in Figure 2.1.

![Figure 2.1 - Fundamental microelectrode geometries including microdisk (A), square microband (B), and microring (C).](image)

Literature review has indicated that nonlinear, 3-D, hemispherical diffusion is prevalent in microdisk, microring, and square microband electrode shapes.
Hemispherical 3-D diffusion has steady state sigmoidal cyclic voltammograms from the steady state mass flux of electroactive analytes to the sensor surface. This nonlinear diffusion mass transport enhancement, over traditional electrodes, leads to response amplification and greater sensitivity. Additionally, further literature evidence explains that current flow is a function of perimeter-to-area ratio (P/A) and indicates that the microring has the best response over long testing time. However, over short times, microband geometry will outperform microring geometries with square microband geometries maximizing performance. On an aside, when utilizing photolithography to micromachine a sensor platform, masks must be generated to photoactively react a resist polymer. Square mask geometries are much easier to make, compared to circular geometries, and greater precision is accomplished by using them.

The important parameter with utilizing microelectrodes in an array format is the interelectrode spacing. If the electrodes are close packed, the diffusion zones formed in the first few seconds of testing can interfere resulting in overlap which destroys the nonlinear diffusion enhancement from the microelectrodes. An array with closely packed electrodes will perform like one large traditional electrode (macroelectrode), while an array of loosely packed electrodes, will perform closely to an ideal state of multiple responses of a single microelectrode. It has been suggested that using an interelectrode spacing of 10x the width or diameter of the microelectrode is considered to be loosely packed.

Traditionally ASV is performed with a mercury based electrode, thin mercury film electrode and mercury hanging drop as examples, but due to the environmental and toxic concerns with mercury an alternative solid element electrode composition is desirable. Studies have shown platinum or gold to be candidates for electrodes and many argue that gold has better performance over platinum. Alternative compositions have been suggested including bismuth-film, carbon, and silver. Due to literature review suggesting
gold to be superior to platinum and silver for solid single element electrodes, it was deemed the best candidate for ASV testing of heavy metal ions.\(^8\)

Final parameters that need to be addressed are the composition of the mask layer that shields the electrode wiring and electrode position with respect to this mask layer. There are a variety of mask layers that can be utilized in this type of sensor platform including oxide coatings (silicon oxide), silicon nitride, or a simple resist coating.\(^{14,23,28}\) Due to the fabrication simplicity and 1981 work by AOKI, resist polymer coating was deemed advantageous over other coatings while silicon nitride would be less susceptible to corrosion.\(^{23,28}\) Furthermore, the most simplistic fabrication approach would be to open holes in the resist mask layer directly above the electrodes and then to utilize plasma etch to clean the electrode surface. This approach was performed on a traditional electrode (macroelectrode) but a literature search failed to show where it was done on a microelectrode array.\(^{14,23}\) Work has been done to model the transient current response through recessed microelectrodes. While there is not as much current that flows through recessed compared to raised or flat microelectrodes there still is nonlinear diffusion which amplifies the current density increasing sensitivity.\(^{22}\)

The result from the aforementioned advantages in stripping analysis and microelectrode array performance lead to the development of a simplistic prototype sensor platform utilizing square gold microelectrodes in an array with 10x the width for interelectrode spacing. This sensor platform is tested with cyclic voltammetry to demonstrate 3-D hemispherical steady state sigmoidal voltammograms, compared with a commercially purchased 10 \(\mu\)m microdisk electrode, and utilized with ASV in heavy metal ion analysis for aqueous environments. Figure 2.2 is the design schematic for microelectrode array platform that is used in this thesis work. Part A displays the electrodes, wiring, and electronic contact pads placement on the glass slide. Part B is an
expanded view of 1 test site showing electrodes, wiring, and electronic contact pads. Part C is an expanded view of 1 test site showing the electrodes and wiring connections. The large red bands seen in the top and bottom of part A are for glass slide alignment. Note Figure 2.2 shows the initial gold layer before a final layer of resist is applied and holes are opened up above the electrode contact pads, defining the true electrode, and the electronic contact pads.

Figure 2.2 - Microelectrode array design platform including entire glass slide array (A), 1 test site with 18 individual microelectrodes (B), and zoomed in view of the electrode pads for 1 test site (C).
2.2 Experimental

2.2.1 Photolithography Fabrication of MEA

Microelectrode arrays (MEA) sensors were constructed by implementing basic photolithography methodology utilized in integrated circuit fabrication. Glass slides were acquired and through electron beam deposition a thin layer of titanium, approximately 150 nm, was adhered to the exterior glass surface to act as a bonding agent intermediate between the glass elements and the much thicker gold layer, approximately 1 μm thick, part A-C in Figure 2.3. Layer thickness was monitored with a piezoelectric quartz crystal microbalance based thickness monitor. Entire gold-coated slides were stripped to exact geometries specified for 54 individually isolated electrodes with the photolithography technique; number of electrodes was convenient for prototype platform. Figure 2.3 shows the schematic process for the general photolithography technique utilized in sensor fabrication that is summarized as follows:

![Photolithography procedures for fabricating the MEA on glass slide.](image)

1. Fresh gold-coated glass slides were used as substrates, and Photoresist 1813 was applied to thickness by spinning 40 seconds at 2000 rpm on a spin coater, part D in
Figure 2.3. This was done directly after gold surface sputtering for clean surface assurance. The photoresist was heat set on the slide surface by heating to 95°C for 90 seconds on a general hot plate.

2. The slide is then exposed on a mask aligner to light from a mercury lamp at 365 nm wavelength for 8 seconds. Submerging in developer 352 for 1 minute develops and removes the exposed part of the photoresist. The slide is then cleaned with deionized water and dried with a nitrogen gun to stop development reaction on the photoresist.

3. The gold layer is removed from everywhere exposed to UV light with iodine based gold etch followed with a HF bath using buffered oxide etch (BOE) to remove titanium layer beneath, part E in Figure 2.3. These etch steps were completed quickly to avoid overexposure leading to sensor damage. The slide is then cleaned with consecutive rinses in acetone, ethanol, methanol, deionized water, and then dried with a nitrogen gun. This left all contact pads, circuitry, and electrode pads on the slides.

4. Further cleaning was completed with oxygen plasma etching (OPE) utilizing ignited oxygen plasma in an evacuated state for 1 minute.

5. A second layer of photoresist 1813 was spun and heat set at the same parameters as previously reported, part F in Figure 2.3. Followed with UV exposure in the mask aligner with a secondary mask; exposing only 10 μm × 10 μm holes over each 50 μm × 50 μm electrode pad, as well as, the electronic contact pads on the outer slide edge. Once more, development and rinsing were performed with developer 352 and deionized water with parameters as before, followed with drying with a nitrogen gun, part G in Figure 2.3.

6. Electrode surfaces were cleaned with OPE for 1 minute. Storage was done in a dessicator to avoid atmospheric contamination before testing.
The slides were completed with three arrays per slide giving a total of 54 individually isolated working electrodes per slide. The final step, in sensor construction, was an adhesion of the sterol plastic wells cut from a 96-welled plate. The sensor construction is designed for future application and coupling with a 96-welled plate. Herein we report experimental results from wells previously cut out of the plate and adhered to the sensor. The wells were attached with the use of a non-conductive epoxy, shown to have no effect on the photoresist mask or the individual circuitry that comprised the array electrodes.

2.2.2 MEA Sensor Fabrication and Construction

The microelectrode arrays were based on a planar design where 10 μm x 10 μm gold working electrodes are positioned (1 μm thick) on glass to form arrays. Adequate adherence to glass is accomplished by thin (150 nm) layer of titanium between gold surface and glass support base. Glass was chosen as the support base for its low electrical conductivity. The exact geometry of these electrodes and arrays are as follows: nine 50 μm × 50 μm base electrodes with 30 μm circuitry to connect the electrodes with an outer slide connection pad, utilized for connection to an external electrochemical analyzer, comprise half an array. Two half arrays work together to form an array with connection pads on each side of the glass slide. The three central electrodes in a nine electrode half array have short spans of 10 μm circuitry for ease in fabrication. A final layer of photoresist 1813 masks the entire slide with exception for the 10 μm × 10 μm holes allowed over each 50 μm × 50 μm pad and the connection pads on the glass slide edges. Figure 2.4 shows these half arrays both before and after the final photoresist mask is applied and treated. Figure 2.5 shows a completed array consisting of two, nine electrode, half arrays. Figure 2.6 show a finished
glass slide with all the individual electrodes comprising the three arrays as well as the numbering scheme developed to label each array.

Figure 2.4 - Half array pictures including: final half array comprising of 9 electrodes, wiring, and electronic contact pads (A), zoomed in views of the 9 electrode test site before and after the final layer of resist is applied and holes are opened up, (B) and (C), respectively.

Figure 2.5 - Complete array consisting of 18 electrodes, wiring, and electronic contact pads. Three arrays are located on each glass slide.
Figure 2.6 - MEA and numbering scheme for completed sensor platform. Numerical designation continued as across wells; Well #2 electrode designations are 10-18, Well #3 electrode designations are 19-27.

Additional optical characterization information for the sensor platform, as well as, additional conformation depictions can be found in the Appendix, Figures A.1 – A.9.

2.2.3 Electrochemical Measurements and Reagents

All electrochemical testing was done using CHI 1220 Electrochemical Analyzer (CH Instruments, TX, USA) and all experiments were done in the standard three electrode configuration. Gold electrodes of the MEA, fabricated as aforementioned, 2 mm gold electrode (termed as “macrobelectrode”), or a 10 μm gold wire working electrode (CH Instruments) were utilized as the working electrode with silver|silver chloride (Ag|AgCl) reference electrode and platinum wire counter electrode (both from CH Instruments). All potentials applied in the electrochemical testing are referred to this reference electrode. Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were done on varying concentrations of 0.05, 0.1, 0.3, 0.5, 0.8, and 1.0 0.05 mM K₃Fe(CN)₆ in 0.01 M PBS (both from Sigma-Aldrich) and recorded at the working electrode, Table 1 shows the CV and SWV
testing parameters. The $\text{K}_3\text{Fe(CN)}_6$ in 0.01 M PBS solutions were deoxygenated by nitrogen purge for at least 10 minutes prior to testing. Polishing of the 10 μm gold wire working electrode was done by successive polishing using 1 (bare borundum sanding paper only), 0.3, 0.1, and 0.05 alumina slurries, followed by thoroughly rinsing with distilled water. The MEA gold working electrodes were utilized “as is” after the oxygen plasma etch treatment described earlier. The electrochemical cell consisted of the sterol plastic well of approximately 400 μl volume, for the MEA working electrode tests, and a 25 ml glass beaker, for the 10 μm gold wire working electrode tests. The counter and reference electrodes were inserted through the top opening, Figure 2.7, for the MEA working electrode tests, and all three electrodes were inserted through the top opening of the glass beaker for the 10 μm gold wire working electrode tests.

Figure 2.7 - Electrochemical cell configuration during testing of the MEA sensor platform.
Table 2.1 - Input parameters for cyclic and square-wave voltammetry testing.

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<th>Parameter Type</th>
<th>CV Parameter</th>
<th>Parameter Type</th>
<th>SWV Parameter</th>
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<tr>
<td>Sensitivity (A/V)</td>
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<td></td>
<td>1*10⁻⁹</td>
</tr>
</tbody>
</table>

2.3 Results and Discussion

2.3.1 Comparison of CV Results of MEA Microelectrode and 2 mm Au Electrode

Initial tests to determine if the MEA electrodes were operational and to characterize the electrodes were done with CV measurements on the ferric/ferrocyanide redox couple. A solution of 0.1 mM K₃Fe(CN)₆ in 0.01 M PBS was tested on individual MEA electrode with potential range from 0.5 to -0.1 V with scan rate of 10 mV/s to prove operation. Figure 2.8 shows a typical response from the MEA electrode compared to that of a 2 mm macroelectrode. The voltammogram gives the sigmoidal shape indicative of nonlinear hemispherical 3-D diffusion as expected from a microelectrode tested on the ferric/ferrocyanide couple and is in agreement with CV curves from literature.³,¹⁰,¹⁴,²⁸

While the current is monitored, the CV testing begins at 0.6 V or 0.5 V potential for MEA or the macroelectrode, respectively, and proceeds in a sawtooth sweeping manner towards -0.1, causing the iron species of K₃Fe(CN)₆ in solution to be reduced on the MEA electrode.

\[ \text{K}_3\text{Fe(CN)}_6 + e^- \rightarrow \text{K}_4\text{Fe(CN)}_6 \]

The voltammogram from the macroelectrode shows the increasing current response typically seen in the reducing pass but there is a peak formation at approximately 0.25 V
due to the transient limiting diffusion in the diffusional zone formed over the electrode surface (red line in Figure 2.8). However, the MEA electrode does not have the transient diffusion limitation due to the increased nonlinear diffusion influence; thus, the voltammogram has the steady state sigmoidal appearance. Once the scanning potential reaches -0.1 V the scan direction reverses and the oxidative pass begins with scanning returning to initial potential, and K₃Fe(CN)₆ is oxidized.

\[ K₄Fe(CN)₆ - e^- \rightarrow K₃Fe(CN)₆ \]

Once more the macroelectrode shows the transient diffusion limited peak at approximately 0.25 V and the MEA electrode shows the steady state sigmoidal shape. The hysteresis is proportional to the width or diameter of the electrode and there is significantly less hysteresis observed in the MEA electrode voltammogram.

Figure 2.8 - Comparison of cyclic voltammograms of typical MEA electrode (R10 in this case) and that of a 2 mm macroelectrode on 0.3 mM K₃Fe(CN)₆ in 0.01 M PBS; MEA electrode: 0.5 to -0.1 V, scan rate of 10 mV/s; macroelectrode: 0.6 to -0.1 V, scan rate of 10 mV/s. Arrows indicate the potential scanning direction.
2.3.2 Repeatability of CV Results for Single MEA Electrode

Figures 2.9 and 2.10 show the results of the L9 electrode as it was tested in five successive runs with 0.1 mM K₃Fe(CN)₆ in 0.01 M PBS, 0.5 to -0.1 V with scan rate of 60 mV/s. This was done to gain a sense of the repeatability of the electrodes and to check for sensor drift. Clearly these electrodes have a high degree of repeatability as no significant drift is observed over the five runs tested. There was a slight difference with the initial portion of the reducing path observed on the first cycle tested but it is negligible because the maximum current response is monitored which lies at the end of the reducing path at -0.1 V. At this maximum current response there is almost no difference between the five cycles tested noted by the standard deviation laying atop the average, shown in Figure 2.10. Also from the cycles there is greater observed hysteresis at the 0.5 V to 0.2 V range. It is unclear what the cause of this influence was from, possibly the difference between using a scanning rate of 60 mV/s compared to the typical 10 mV/s utilized on all other CV testing.

Figure 2.9 - CV testing of electrode L9 in five successive runs on 0.1 mM K₃Fe(CN)₆ in 0.01 M PBS, 0.5 to -0.1 V with scan rate of 60 mV/s. Arrow indicates the potential scanning direction.
Figure 2.10 - Average and 1 standard deviation of L9 electrode tested in 0.01 M PBS, 0.5 to -0.1 V with scan rate of 60 mV/s. Arrow indicates the potential scanning direction.

2.3.3 Repeatability of 18 MEA Electrodes in 0.3 mM and 0.5 mM K$_3$Fe(CN)$_6$ Solutions

All of the electrodes comprising 1 test site were tested on 0.3 mM and 0.5 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS with potential from 0.5 to -0.1 V with scan rate of 10 mV/s, in order to gain a sense of the electrode variation when each is tested with the same solution independently. Results for 0.3 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS are shown in Figures 2.11-2.13, and results for 0.5 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS are shown in Figures 2.14-2.16. Figures 2.11-2.12 and 2.14-2.15 show the actual voltammograms for individual 18 electrodes, and the average and 1 standard deviation for each concentration is shown in Figures 2.13 and 2.16.

Firstly it is noted, that each individual MEA electrode has the steady state sigmoidal shape where no transient limited peaks appear. There is a small spike in the voltammogram of the L11 electrode at ~ 0.3 V that was caused by accidental bumping of the
electrochemical cell as the test was being performed. It is completely negligible because the maximum current reading is used as the response signal and this spike is far away from the -0.1 V potential where this reading is taken.

Secondly, there is a small amount of variation between electrodes of one test site with both 0.3 mM and 0.5 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS. Figure 2.17 compares the average and standard deviation of all 18 MEA electrodes at both concentrations. The responses show smaller variation at the lower 0.3 mM concentration than that of the higher 0.5 mM concentration. A possible reason for the variance may be saturation of the sensors ability to reduce and oxidize the K$_3$Fe(CN)$_6$ by excess analyte in solution, implicating the linear full span output or the linear testing range of the sensor has been surpassed and the response has become nonlinear as it approaches some asymptote current value it cannot surpass by adding more analyte. However, later it will be shown that this is not the case as the linear full span output is greater than 0.5 mM, and higher concentrations can be monitored in a linear fashion. As of now, the variation increase in 0.5 mM compared to that of 0.3 mM is believed to be a product of experimentation as these tests were performed only once for each electrode, and duplication of the experiment with triplicate testing on the electrodes could shed insight into the observed difference in variation.

There is a difference between responses at the tested concentrations. As expected, the higher 0.5 mM analyte concentration gave a response of approximately 530 pA, compared to that of approximately 350 pA for 0.3 mM analyte, as shown in Figure 2.17. Furthermore, the average responses of the 18 MEA electrodes, with respect to both concentrations, have non-overlapping 1 standard deviation difference; they are significant and different.
Figure 2.11 - CV voltammograms for individual 18 MEA electrodes comprising one test site with 0.3 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s.
Figure 2.12 - Overlaps of CV curves of all 18 MEA electrodes comprising one test site with 0.3 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s.

Figure 2.13 - Average CV voltammogram and 1 standard deviation for all 18 MEA electrodes comprising one test site with 0.3 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s.
Figure 2.14 - CV voltammograms for individual 18 MEA electrodes comprising one test site with 0.5 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s.
Figure 2.15 - Overlaps of CV curves of all 18 MEA electrodes comprising one test site with 0.5 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s.

Figure 2.16 - Average CV voltammogram and 1 standard deviation for 18 MEA electrodes comprising one test site with 0.5 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s.
After the MEAs were proven to be operational and responses between electrodes were evaluated, testing at different concentrations K₃Fe(CN)₆ in 0.01 M PBS was done to examine the linearity of MEA responses at different concentrations. Figure 2.18 shows CV testing performed with solutions of 0.05, 0.1, 0.3, 0.5, 0.8, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS from 0.5 V to -0.1 V with a scan rate of 10 mV/s; combined R5 and R10 responses to construct plot, 0.05 mM and 0.1 mM from R5 while remainder of concentrations from R10. The sigmoidal shape is observed on all the responses from concentrations tested with no transient limited peak formation. The 0.05 mM response sigmoidal shape is difficult to resolve in the plot due to small current change, with respect to the higher current changes.
from the larger concentration, when plotted together as is done in Figure 2.18. These responses represent testing that was done in single iteration fashion.

A calibration curve plot for MEA CV results in the varying K$_3$Fe(CN)$_6$ solutions is shown in Figure 2.19. Each data point presents the maximum responses for the concentrations tested. It is noted that the MEA electrode response was taken to be the maximum current which occurred at the -0.1 V potential. There is a strong linear fit to the concentration responses, shown by the black line in Figure 2.19, and the squared correlation coefficient ($R^2$) equals 0.981. The span output over the concentrations tested is approximately 1.3 nA and occurred with the highest concentration tested (1.0 mM).

For comparison purposes, a 10 μm electrode was purchased from CH Instruments and tested in triplicate with solutions of 0.05, 0.1, 0.3, 0.5, and 1.0 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS from 0.5 V to -0.1 V with a scan rate of 10 mV/s. Figure 2.20 presents the 10 μm electrode performance over the analyte concentrations tested. The sigmoidal steady state shape is present with concentrations greater and equal to 0.3 mM but the low concentrations 0.05 mM and 0.1 mM did not have a sigmoidal shape, but rather, solely increased to a maximum current at -0.1 V and then returned to the initial state and did not come to a resolving plateau. This indicates the solution was continuously reduced and oxidized throughout the entire reducing and oxidizing passes, respectively. In other words, there is implication the full extent of combined linear and nonlinear diffusion was not achieved by this commercial 10 μm electrode when tested in these low concentrations.

Similarly to the MEA electrode, a calibration curve was constructed for testing done with increasing concentration of K$_3$Fe(CN)$_6$, shown in Figure 2.21. Similarly, there is a strong linear fit to the concentration responses, shown by the black line in Figure 2.21, and the $R^2 = 0.996$. With the testing done in triplicate, error bars (black bars) are reported; however, the deviation between runs was small and they are difficult to deconvolute on
Figure 2.21. The squared correlation coefficient is closer to 1 for the 10 μm electrode, which indicates it has better linear fit, compared to the MEA electrode. The span output over the concentrations tested is approximately 1.0 nA and occurred with the highest concentration tested (1.0 mM) and is a lower span than that observed with the MEA electrode (approximately 1.3 nA at 1.0 mM K₃Fe(CN)₆). This indicates the MEA electrode is more sensitive to the same concentration of K₃Fe(CN)₆ within the solution ranges tested. Sensitivity is defined as the change in responses over the change in the concentrations; the slope of the calibration curves.

Due to both the early use of more than one MEA electrode to construct the calibration plot for K₃Fe(CN)₆ in 0.01 M PBS and the small variation between electrodes tested with same solutions, it was deemed necessary to repeat the testing of 1 MEA electrode on K₃Fe(CN)₆ in 0.01 M PBS. Figure 2.22 shows average CV testing responses, performed in triplicate, with solutions of 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS from 0.5 V to -0.1 V with a scan rate of 10 mV/s. Once more the sigmoidal steady state response was observed on with all concentrations; however the current change for both 0.05 mM and 0.1 mM was small and does not resolve on Figure 2.22. It is noted that fresh solutions of K₃Fe(CN)₆ in 0.01 M PBS were not mixed prior to this repeat experiment and degradation of the K₃Fe(CN)₆ may have occurred which would decrease the current change expected during the CV testing.

As was done before, a calibration curve was constructed for CV testing done in the varying K₃Fe(CN)₆ solutions, shown in Figure 2.23. Again, the MEA electrode response was taken to be the maximum current which occurred at the -0.1 V potential. The linear fit, $R^2 = 0.995$, was closer to that of the 10 μm electrode, $R^2 = 0.996$. Error bars (black bars) are reported on the figure but the deviation between runs was small so they are difficult to resolve. The span output over the concentrations tested is approximately 1.1 nA and
occurred with the highest concentration tested (1.0 mM). This is still slightly higher than the span that was observed with the commercial 10 μm electrode (approximately 1.0 nA at 1.0 mM K₃Fe(CN)₆), which indicates the MEA electrode is still slightly more sensitive to the K₃Fe(CN)₆ within the solution ranges tested.

Figure 2.18 - CV curves of an MEA electrode in 0.05, 0.1, 0.3, 0.5, 0.8, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=1

Figure 2.19 - CV calibration curve of MEA electrode in 0.05, 0.1, 0.3, 0.5, 0.8, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=1
Figure 2.20 - Average CV curves of 10 μm CH electrode tested with 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3

Figure 2.21 - CV calibration curve of 10 μm CH electrode in 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3
Figure 2.22 - Average CV curves of MEA electrode tested with 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3

Figure 2.23 - CV calibration curve for MEA electrode in 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3
2.3.5 Comparisons of SWV Results for MEA Electrode and 10 μm CH Electrode

Following CV testing, square-wave voltammetry (SWV) testing was investigated on the ferri/ferrocyanide redox couple. SWV testing combines staircase sweeping of the potential and superimposing a square-wave on it while monitoring the current change. Figure 2.24 shows average SWV testing responses, performed in triplicate with the L6 MEA electrode, with solutions of 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS from 0.5 V to -0.1 V with a scan rate of 10 mV/s. Results indicate a peak formation between 0.4 V to 0.2 V and there seems to be baseline shifting as the concentrations are increased. It is noted that fresh solutions of K₃Fe(CN)₆ in 0.01 M PBS were not mixed prior to this experiment and degradation of the K₃Fe(CN)₆ may have occurred which would decrease the current change expected during the SWV testing. It may also explain the small difference between the 0.05 mM and 0.1 mM responses as they did not follow the expected linear trend.

Figure 2.24 - Average SWV responses of MEA electrode L6 tested with 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3
The identical procedure was performed on the 10 μm CH electrode as a means of comparison. Figure 2.26 shows average SWV testing responses, performed in triplicate on the 10 μm CH electrode, with solutions of 0.05, 0.1, 0.3, 0.5, and 1.0 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS from 0.5 V to -0.1 V with a scan rate of 10 mV/s. These responses do not show the expected peak as clearly. The 1.0 mM solution showed a significant departure from the low concentration trend. This could be attributed to the electrode saturation or some other unknown effect causing the large deviation from expected response, as seen in Figure 2.26.

![SWV calibration curve for MEA electrode L6 tested in 0.05, 0.1, 0.3, 0.5, and 1.0 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3](image)

Calibration curves were constructed for the SWV testing done in the varying K$_3$Fe(CN)$_6$ solutions, shown in Figure 2.25 and 2.27, for the MEA electrode and the 10 μm CH electrode, respectively; it presents the maximum responses for the concentrations tested in the 0.4 V to 0.2 V range on the MEA and over the entire tested range for the 10 μm CH electrode. Linear fits were again performed on the average responses with concentration change. Correlation was measured by the correlation coefficient squared method and R$^2$ = 0.862 and R$^2$ = 0.988 for the MEA electrode and the 10 μm CH electrode,
respectively. The highest concentration (1.0 mM K₃Fe(CN)₆ solution) was not used for the linear fit for the SWV 10 μm CH electrode testing. Standard deviation bars (black bars) are reported on the figures and there is significantly more variance within the triplicate testing for the 10 μm CH electrode than the MEA electrode.

Figure 2.26 - Average SWV responses of 10 μm CH electrode tested with 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3

Figure 2.27 - SWV calibration curve for 10 μm CH electrode tested in 0.05, 0.1, 0.3, and 0.5 mM K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, scan rate of 10 mV/s. n=3 (response taken as maximum current observed)
2.4 Conclusions

Microelectrode array sensors were designed and fabricated, by lithographic means, to effectively increase the sensitivity and selectivity in electrochemical stripping analysis over that traditionally reported from macroelectrode sensors. These MEA sensors employed a resist layer as an insulating layer that protected the circuitry and wiring of the sensor and was convenient for finalizing the electrode size, as holes were made in the layer to exact electrode dimensions. These MEA sensors consisted of planar arrays of gold square microelectrodes with an interelectrode spacing of 100 μm, making the spacing 10x the width (10 μm x 10 μm square) of the electrode, effectively enhancing the mass transport properties of the electrochemical analyte by allowing nonlinear diffusion around the perimeter of the electrode. The enhancement of mass transport was checked by cyclic voltammetry on the ferri/ferrocyanide redox couple and exhibited the theoretical sigmoidal shaped curves on the voltammogram which signifies 3-D hemispherical diffusion of the electrochemical analytes.

The MEA sensor was proven and compared against a 10 μm CH electrode in both cyclic and square-wave voltammetry testing. Evidence suggests the MEA electrodes perform better than the 10 μm CH electrode with increases in sensitivity, selectivity, and repeatability.
CHAPTER 3

STRIPPING ANALYSIS FOR COPPER AND LEAD IONS

3.1 Stripping Analysis and Testing Criteria

As mentioned earlier, stripping analysis is a powerful electrochemical technique capable of detecting metals at trace concentrations\textsuperscript{1-4,6,8-13}. Also, there are strong advantages in utilizing micro-sized electrodes most importantly a micro-sized working electrode, as this is the electrode that testing potential or current is monitored from, with respect to a reference electrode and the counter electrode, needed to complete the circuit\textsuperscript{1-3,10,11,14,26}. Counter electrode size is somewhat arbitrary as long as it does not interfere with the diffusion zone that forms around the working electrode, as it is used simply for circuit completion. The reference electrode is for comparison or reference status and its size is somewhat arbitrary also, as long as, once more, it does not hinder, amplify, or in any way affect the diffusion zone around the working electrode.

Voltammetry is a class of electrochemical techniques where the current at a working electrode is monitored and measured as a function of the potential applied to electrode and changes with respect to the waveform of the potential\textsuperscript{4}. Due to lab instrumental availability and simplistic nature of voltammetry, stripping analysis is limited to anodic stripping voltammetry (ASV) in this thesis and stripping potentiometry is not explored. ASV is a very powerful analytical technique of stripping analysis with many citations indicating its usage\textsuperscript{2,3,6,8,10,12,13,26}. ASV is essentially a two phase testing technique. Phase one employs an underpotential held constant for a certain amount of time effectively reducing and electroplating the electrochemical analyte on the electrode surface. Phase two begins sweeping the potential towards overpotential and the plated analyte is oxidized and stripped off. Electrochemical analytes (e.g., heavy metals) have different oxidation-
reduction potentials specific to the analyte species of interest and the stripping oxidation from the electrode surface causes a significant change in current at this oxidation-reduction potential. Therefore, this testing technique can be utilized on individual or mixed analyte systems where analyte concentrations are correlated to the change in current registered at oxidation-reduction potentials; these will show as peaks on voltammograms recorded during the sweeping phase of ASV testing. Speciation is accomplished correlating oxidation potentials of analytes to peaks of the voltammogram.

Due to the inherent preconcentration step in ASV testing procedure, lower concentrations of heavy metal ions can be detected in this manner over other voltammetric techniques. However, preconcentration time can affect the test results by increasing the amount of reduced metal analytes electroplated to the electrode surface and thus registering an increase in current change once the analytes are stripped off during the sweeping step. At some point the preconcentrating time reaches a saturation level where the electrode surface is completely covered by reduced analytes, as they can only form monolayer coverage, and no more analyte will be electroplated. At this saturation time, further preconcentration leads to arbitrary increase in output signal during the sweeping testing. When microelectrodes are utilized there may be a decrease in the preconcentration time needed due to the mass transport enhancement. Preconcentration is recommended to be just long enough to form well defined peaks, and must be determined experimentally. Due to constraints of having a fast sensor platform capable of rapid return on results, and literature references to similar microelectrodes working in stripping analysis with their preconcentration times reported, and fundamental initial tests done in lab; a preconcentration time of 60 seconds was utilized in the experiments reported herein.
In a typical voltammetric test, the applied potential to the working electrode controls the oxidation-reduction of the electroactive analyte and is varied in some systematic way to control the experiment. Strong negative potentials cause the electrode to be more reductant and strong positive potentials will cause oxidation. By varying the applied potential in a sweeping manner the current will change as a applied potential becomes sufficient to oxidize or reduce the present analyte." It is unclear from the literature which type of sweeping voltammetry to utilize during the second phase of ASV testing in order to maximize the microelectrode sensor performance. Many authors have used both square-wave voltammetry (SWV) or differential pulse voltammetry (DPV) but there was limited references found where both methods were utilized and performance evaluated.\textsuperscript{2,3,6,8,10,12,13,26} Therefore, both DPV and SWV are evaluated with the microelectrode sensor to determine which method is more sensitive and selective in ASV testing. Typical nomenclature for ASV with DPV or SWV sweeping is differential pulse stripping voltammetry (DPASV) and square-wave anodic stripping voltammetry (SWASV), respectively, and will be used to describe the methods utilized herein.

Differential pulse may be the favored method of sweeping potential during stripping analysis due to its inherent design to compensate for charging background currents.\textsuperscript{4} DPV involves equal amplitude pulses superimposed on linear sweep or stair steps. Current is monitored twice, once before amplification and again prior to pulse termination. The first current is subtracted to the post amplification current and this difference is plotted verse the potential. Figure 3.1 (C) shows the potential-time sequence for differential pulse sweeping.\textsuperscript{4}

Another way of compensation for charging background current is by using square-wave potential sweeping, shown in Figure 3.1 (D). By superimposing a square-wave on a potential staircase sweep where the current is recorded on the end of each half wave,
background current is discriminated by different current decay rates following each potential step. By utilizing stripping analysis on the fabricated microelectrode array experiments were conducted to show the microelectrodes (i) are feasible for ASV testing of heavy metals and (ii) to explore sensitivity and selectivity of DPASV compared with SWASV to further prove future stripping methods used on the microelectrode platform.

Figure 3.1 - Potential-time sequence for linear (A), staircase (B), differential pulse (C), and square-wave (D) sweeping stripping modes.

3.2 Experimental

All electrochemical tests were done using CHI 1220 Electrochemical Analyzer (CH Instruments, TX, USA) in the standard three electrode configuration. Gold electrodes of the MEA, fabricated as aforementioned, or a 10 μm gold wire electrode (CH Instruments) were utilized as the working electrode with silver|silver chloride (Ag|AgCl) reference electrode and platinum wire counter electrode (both from CH Instruments). DPASV and SWASV was
done on varying concentrations of 1, 10, 20, 50, 70, 100, 200, 500, and 1000 ppb Cu, Pb, and mixed Cu and Pb solutions with HNO₃ as counter electrolyte, mixed from 1000 ppm with 2% HNO₃ copper and lead standards (Fisher Scientific) and recorded at the working electrode. All solutions were diluted to exact concentrations with 18 MΩ deionized water and deoxygenated by nitrogen purge for at least 10 minutes prior to testing. Polishing of the 10 μm gold wire working electrode was done by successive polishing using 1 (bare borundum sanding paper only), 0.3, 0.1, and 0.05 alumina slurries, followed by rinsing with double-stilled water. The MEA gold working electrodes were utilized “as is” after the oxygen plasma etch treatment described earlier. The electrochemical cell consisted of the sterol plastic well (approximately 400 μl volume), for the MEA working electrode tests, and a 25 ml glass beaker, for the 10 μm gold wire working electrode tests. The counter and reference electrodes were inserted through the top opening (Figure 2.7), for the MEA working electrode tests, and all three electrodes were inserted through the top opening for the 10 μm gold wire working electrode tests.

<table>
<thead>
<tr>
<th>Parameter Type</th>
<th>DPASV Parameter</th>
<th>Parameter Type</th>
<th>SWASV Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial E (V)</td>
<td>-0.1 (Cu)¹</td>
<td></td>
<td>-0.1 (Cu)</td>
</tr>
<tr>
<td></td>
<td>-0.6 (Pb)²</td>
<td></td>
<td>-0.6 (Pb)</td>
</tr>
<tr>
<td></td>
<td>-0.6 (Cu &amp; Pb)³</td>
<td></td>
<td>-0.6 (Cu &amp; Pb)</td>
</tr>
<tr>
<td>Final E (V)</td>
<td>0.3 (Cu)¹</td>
<td>0.3 (Cu)</td>
<td>0.4 (Cu &amp; Pb)³</td>
</tr>
<tr>
<td></td>
<td>0.0 (Pb)²</td>
<td>0.0 (Pb)</td>
<td>0.4 (Cu &amp; Pb)</td>
</tr>
<tr>
<td>Increment E (V)</td>
<td>0.004</td>
<td></td>
<td>0.004</td>
</tr>
<tr>
<td>Amplitude (V)</td>
<td>0.025</td>
<td></td>
<td>0.025</td>
</tr>
<tr>
<td>Pulse Width (s)</td>
<td>0.05</td>
<td></td>
<td>15.001</td>
</tr>
<tr>
<td>Sample Width (s)</td>
<td>0.0167</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulse Period (s)</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quiet Time (s)</td>
<td>60</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Sensitivity (A/V)</td>
<td>1*10⁻⁹</td>
<td></td>
<td>1*10⁻⁹</td>
</tr>
</tbody>
</table>

¹,²,³ different potential scanning ranges.
3.3 Results and Discussion

Concentrations of 1, 10, 20, 50, 70, 100, 200, 500, and 1000 ppb Cu, Pb, and mixed Cu and Pb solutions with HNO₃ as counter electrolyte, 1:1 molar ratio, were mixed from 1000 ppm copper and lead standards. DPASV and SWASV were performed by utilizing typical DPV and SWV methods in the CHI 1220 software and setting the quiet time parameter to the desired preconcentration time, after which, the potential was swept in a typical DPV or SWV method. Typically ASV technique requires stirring of the solution or rotation of the working electrode during the phase 1 preconcentration step, for convective transport of the metal ions. Due to the enhanced mass transport properties of the microelectrode preconcentrating was done in quiescent conditions, directly following deoxygenating purge with nitrogen. DPASV and SWASV tests were ran in triplicate, with preconcentration time of 60 seconds.

3.3.1 DPASV Detection of Cu Ion Solutions by MEA Electrode

Individual solutions, with Cu as the only target analyte, were tested with DPASV on a scanning range -0.1 to 0.3 V in an effort to observe the Cu peak on the voltammograms for each of the aforementioned concentrations, shown in Figures 3.2-3.10 (left). There is a well defined obvious Cu peak formation between 0.1 V and 0.25 V, which coincides with literature reports. The repeatability is good between the three tests for each concentration but there are some outlaying curves that deviate from the other runs. As an attempt to best represent the information averages were taken, generally of the three runs with limited cases where all three tests were not used; these are shown in Figures 3.2-3.10 (right). Specifically run 1 of 1 ppb and 20 ppb Cu, run 2 and 3 of 200 ppb Cu, and run 3 of 500 ppb Cu were excluded from the average calculations.
Figure 3.2 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Cu with HNO3; 60 s preconcentration, -0.1 to 0.3 V scan range. n=2

Figure 3.3 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Cu with HNO3; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure 3.4 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Cu with HNO3; 60 s preconcentration, -0.1 to 0.3 V scan range. n=2
Figure 3.5 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure 3.6 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure 3.7 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
Figure 3.8 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure 3.9 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure 3.10 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
The average current response was plotted with the potential range, shown in Figure 3.11, to analyze the Cu peak over all the concentrations tested. There is a very clear peak and all of the concentrations peaks lie within the overall peak. There is some slight shifting of the oxidation potential between concentrations of Cu. However, slight shifting is frequently seen in literature.\textsuperscript{3,4,10,12} In effort to further prove the Cu peak, Table 3.2 and Figure 3.12 were constructed which shows the concentrations 1 ppb to 100 ppb and 1 standard deviation error for each peak current response, within the peak range, for the individual concentrations. By analyzing peak by peak, there is no overlap of error, concluding significant difference between peak responses at the various concentrations. Furthermore, Figure 3.13 was constructed which shows Cu peak current (with error) vs. concentration for 1 ppb to 1000 ppb Cu concentrations. The peak currents exhibit good linear fit over the entire concentration range with correlation coefficient squared $R^2=0.994$. Furthermore, analysis of the error shows significant difference between responses by no overlap of the error bars.

![Figure 3.11 - MEA electrode L8 DPASV response on 1 - 1000 ppb Cu ions in HNO$_3$; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3](image)


In an attempt to compare the fabricated MEA electrodes with a standard commercially available electrode, identical testing was performed on a 10 μm CH electrode. Figure 3.14 shows the current responses recorded over the same -0.1 V to 0.3 V potential range, with 60 seconds quiescent preconcentration; individual runs are given in the Appendix (Figures A.10 – A.18). There is no Cu peak formation associated with the DPASV testing at any concentration and by comparison, the MEA electrode surpassed it in performance, peaks shown in Figure 3.11.

Table 3.2 - Cu peak analysis with DPASV testing and -0.1 to 0.3 V scan range.

<table>
<thead>
<tr>
<th>Cu Concentration (ppb)</th>
<th>Peak Current Response (A)</th>
<th>Peak Current Standard Deviation (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-3.23E-11</td>
<td>3.13E-12</td>
</tr>
<tr>
<td>10</td>
<td>-4.93E-11</td>
<td>8.13E-13</td>
</tr>
<tr>
<td>20</td>
<td>-5.93E-11</td>
<td>1.03E-12</td>
</tr>
<tr>
<td>50</td>
<td>-6.62E-11</td>
<td>5.92E-12</td>
</tr>
<tr>
<td>70</td>
<td>-8.33E-11</td>
<td>4.07E-12</td>
</tr>
<tr>
<td>100</td>
<td>-9.43E-11</td>
<td>1.36E-12</td>
</tr>
</tbody>
</table>

Figure 3.12 - Average MEA electrode L8 DPASV response, with 1 standard deviation, on 1 - 100 ppb Cu ions in HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
Figure 3.13 - Cu peak current vs. concentration for MEA electrode L8; DPASV, 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure 3.14 - Average 10 μm CH electrode DPASV response on 1 - 1000 ppb Cu ions in HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
3.3.2 SWASV Detection of Cu Ion Solutions by MEA Electrode

Individual solutions, with Cu as the only target analyte, were tested with SWASV on a scanning range -0.5 to 0.3 V in an effort to observe the Cu peak on the voltammograms for each of the aforementioned concentrations. The individual triplicate runs and averages with deviation are given in the Appendix (Figures A.19 – A.27), for continuity reasons. Figure 3.15 shows the average responses over the all concentrations tested. The same well defined peak is observed between 0.1 V and 0.25 V and is attributed to Cu ions, which matches DPASV and literature reports.3,12 There was some instability in the current flow with the 500 ppb and 1000 ppb Cu initially as the test was initiated, flat zone between -0.5 V to -0.4 V. However, this was resolved and tests were completed. This instability is an overflow of electrons at the sensitivity level at which the test is being performed. The instability in the 1000 ppb Cu after the oxidation stripping peak is negligible due to the peak current response being used as the response indicator. Figure 3.16 was constructed which shows Cu peak current (with error) vs. concentration for 1 ppb to 1000 ppb Cu concentrations. The peak currents exhibit good linear fit over the entire concentration range with correlation coefficient squared $R^2 = 0.949$ and error analysis shows significant difference between responses by no overlap of the error bars. Furthermore, by inspection of Figure 3.16, the linear dynamic range of performance is determined to be 10 ppb to 500 ppb Cu ion concentration. Comparison between DPASV and SWASV testing of the MEA electrode should not be compared at this time due to the difference in scanning range, -0.5 vs. -0.1, respectively.

SWASV was again performed with the same conditions and concentrations aforementioned on the 10 μm CH electrode and the results are shown in Figure 3.17; individual runs are given in the Appendix (Figures A.28 – A.36). Unlike the DPASV results
under similar conditions, there is a Cu peak formation but only with the relatively high concentrations of those tested, namely 200, 500, and 1000 ppb Cu. Despite the peak formation clearly the MEA electrode performed much better, as shown in Figure 3.15, compared to that of the 10 μm CH electrode.

Figure 3.15 - Average MEA electrode L8 SWASV response on 1 - 1000 ppb Cu ions in HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure 3.16 - Cu peak current vs. concentration for MEA electrode L8; SWASV, 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure 3.17 - Average 10 μm CH electrode SWASV response on 1 - 1000 ppb Cu ions in HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

3.3.3 DPASV Detection of Pb Ion Solutions by MEA
Electrode and 10 μm CH Electrode

Solutions with Pb ions as the only target analyte, were mixed as previously mentioned and tested with DPASV on the MEA electrode with a scanning range -0.6 to 0.0 V to observe the Pb peak. The individual triplicate runs and averages with deviation are given in the Appendix, Figures A.37 – A.45, for continuity reasons. Shown in Figure 3.18 is the average current responses of the MEA electrode for 1, 10, 20, 50, 70, 100, 500, and 1000 ppb Pb ions in HNO₃ (60 s quiescent preconcentration). There is a well defined and obvious peak formation between -0.4 V and -0.25 V for the lower 1 ppb to 100 ppb range while there is a potentially shifted peak between -0.25 V and -0.15 V for 500 ppb and 1000 ppb. 200 ppb was neglected completely due to extreme deviation from the expected voltammogram but is reported in the Appendix (Figure A.43). This peak is attributed to Pb ions and lies in the expected region based on similar literature reports.¹⁰,¹² The peak shifts at the higher
concentrations are not entirely understood or expected. However, the basic Pb ion peak formation is recorded and possible additional optimization of the counter electrolyte concentration should be explored as adjustment of counter ion concentration can resolve stripping peak formation.

![Graph showing current vs. potential for different Pb ion concentrations.](image)

**Figure 3.18** - Average MEA electrode L8 DPASV response on 1 - 1000 ppb Pb ions in HNO₃; 60 s preconcentration. -0.6 to 0.0 V scan range. n=3

The peak current response vs. concentration with 1 standard deviation error is shown in Figure 3.19. Once more it shows the expected linear trend with a correlation coefficient squared $R^2 = 0.982$. Furthermore, by inspection of Figure 3.19, the linear dynamic range of performance is determined to be 10 ppb to 1000 ppb Pb ion concentration. There is a greater amount of error at the extremes of concentration range tested compared to Cu working curves. However, there is little error overlap and the majority of the points are significant. This increase in error could be a product of more...
negative potential preconcentration or unoptimized parameters, such as counter ion concentration, and further optimization may increase the linear dynamic span.

Figure 3.19 - Pb peak current vs. concentration for MEA electrode L8; DPASV, 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Again, the MEA electrode response was compared with the 10 μm CH electrode by testing the same solutions at identical parameters with it. Figure 3.20 shows the 10 μm CH electrode response at 1, 10, 20, 50, 70, 100, 200, 500, and 1000 ppb Pb ions in HNO₃, with 60 s quiescent preconcentration; individual runs are given in the Appendix (Figures A.46 – A.54). There is a great deal of noisy peaks in the voltammograms but the expected Pb peak at -0.4 V to -0.25 V is not evident until high concentrations (200, 500, and 1000 ppb Pb) are tested much like the SWASV response on this electrode in Cu ion solutions. It is evident that the MEA electrode again outperformed the CH commercial electrode, shown with well defined peak formation on Figure 3.18.
3.3.4 SWASV Detection of Pb Ion Solution by MEA Electrode and 10 μm CH Electrode

SWASV was performed on the MEA electrode with the same Pb ion solutions in the scanning range of -0.6 to 0.0 V. The individual triplicate runs and averages with deviation are given in the Appendix (Figures A.55 – A.63), again for continuity reasons. Shown in Figure 3.21 is the average current responses for 1, 10, 20, 50, 70, 100, 500, and 1000 ppb Pb ions in HNO₃ (60 s quiescent preconcentration). The response is very similar to Figure 3.18, as expected, with only slight differences noted. The defined and obvious peak formation between -0.4 V and -0.25 V for the lower 1 ppb to 100 ppb range formed and the peak shifted between -0.25 V and -0.15 V for 500 ppb and 1000 ppb, 200 ppb was neglected again due to extreme deviation from the expected voltammogram but is reported in the Appendix. The lower concentration peaks were not linear and there was overlap so a working or calibration curve was not constructed. There is a small initial current change at -0.6 V that
is slightly larger than that observed in the Cu solutions; this is where the sweeping starts and is most likely attributed to background current effects the first square-wave has not discriminated apart from the analyte signal or corrected.

Figure 3.21 - Average MEA electrode L8 SWASV response on 1 - 1000 ppb Pb ions in HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

MEA electrode response is compared with the 10 µm CH electrode. Figure 3.22 shows the 10 µm CH electrode response at 1, 10, 20, 50, 70, 100, 200, 500, and 1000 ppb Pb ions in HNO₃; 60 s quiescent preconcentration; individual runs given in the Appendix (Figures A.64 – A.72). As was seen when this electrode was tested with DPASV, there is a great deal of noisy peaks in the voltammograms and the expected Pb peak at -0.4 V to -0.25 V is not evident until 500, and 1000 ppb Pb concentration is reached. The apparent trend is set that the MEA electrode is sufficient to resolve the individual ion (Cu and Pb) solution
peaks at low concentration, compared to the CH electrode which can only resolve the peaks at 2 orders of magnitude higher concentration.

![Graph showing SWASV response on Pb ions in HNO3](image)

**Figure 3.22 - Average 10 μm electrode SWASV response on 1 - 1000 ppb Pb ions in HNO3; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3**

Since DPASV and SWASV methods on Pb ion solutions were run with same parameters: scan range, increment, amplitude, preconcentration time, and sensitivity; they can be compared. DPASV showed linear response in Pb ionic solutions while the SWASV did not. However, additional optimization of the preconcentration time and supporting electrolyte concentration will probably give SWASV methods results as good as or better than DPASV. Counter ion concentration is related to peak definition and preconcentration time can increase sensitivity. With two different electrochemical test methods employed they should each be optimized for increased performance. SWASV is also a faster method and inherently performs ASV in less time the DPASV. This comparison will be further analyzed in mixed Cu and Pb ion results.
3.3.5 Effect of Reversing Potential Direction on Cu and Pb Stripping Analysis

There is a question of what will be the response if the potential is charged at a more positive potential during the preconcentration step and then swept toward the negative? One would expect minimal or no preconcentrating and reduction of the metal species as the potential is swept past the reduction potential for the analyte. The DPASV and SWASV was tested on 20, 50, 100, and 500 ppb Pb ions in HNO₃; 60 s preconcentration at 0.0 V and 0.0 V to -0.6 V scan range. The individual triplicate runs and averages with deviation are given in the Appendix, Figures A.73 – A.80, again for continuity reasons. Figure 3.23 and 3.25 shows the average responses for the DPASV and SWASV, respectively, for reverse potential sweeping as explained above. There is a lot of variation between each individual run comprising the average, as shown at the peak responses in Figure 3.24, but the reduction peak is present at the expected -0.4 V to -0.2 V range. The DPASV method averages do show an increase in response with increasing Pb concentration but it is not very linear, \( R^2 = 0.469 \), and the standard deviation overlaps in all concentrations tested arguing no significant difference between responses at the different concentrations. The 20 ppb Pb solution gave a greater response than that of both 50 ppb and 100 ppb Pb solutions in SWASV, so no working curve was constructed for this method. Analysis of the variance in the individual runs between concentrations, the Appendix, shows error overlap; arguing no significant difference in responses between concentrations. This information is taken as proof that ASV is not reliable if preconcentration is done at a more positive potential then the analytes reducing potential, during step 1, and then swept towards negative during the step 2 sweeping phase of the method.
Figure 3.23 - Average MEA electrode L8 DPASV response on 20 - 500 ppb Pb ions in HNO₃; 60 s preconcentration, 0.0 V to -0.6 V scan range (reverse potential sweep). n=3

Figure 3.24 - MEA electrode L8 DPASV response vs. concentration on 20 - 500 ppb Pb ions in HNO₃; 60 s preconcentration, 0.0 V to -0.6 V scan range (reverse potential sweep). n=3
Figure 3.25 - Average MEA electrode L8 SWASV response on 20 - 500 ppb Pb ions in HNO₃; 60 s preconcentration, 0.0 V to -0.6 V scan range (reverse potential sweep). n=3

Analysis was also done on 1, 10, 20, 50, 70, 100, 200, 500, and 1000 ppb mixed Cu & Pb solutions with HNO₃ with DPASV and SWASV. The individual triplicate runs for each method are given in the Appendix, Figures A.81 – A.89, again for continuity reasons and averages were not taken due to narrow peaks of Cu having great sensitivity on the average calculation. The narrow peaks are slightly offset from each other and one may average the peak of one response with the trough of another. This is not an accurate representation of the data, however. Therefore, triplicate runs were taken to show repeatability and one run was chosen for representation in plots containing all concentrations.

Figure 3.26 shows the DPASV responses of the mixed analyte solutions (both ion concentrations the same), with scanning range of -0.6 V to 0.3 V, 60 s quiescent preconcentration, and closer examination of the Cu peak, upper embedded plot. Both Pb
and Cu attributed peaks are present at the expected ranges, -0.4 V to -0.25 V and 0.2 V to 0.35 V, respectively. There is good speciation in the responses and it is easy to identify the current change associated with each analyte. The Cu peaks are narrow with respect to the Pb peaks and similar to the peaks observed when Cu was the only analyte species. This peak narrowing, could be due to difference in preconcentration effects on the stripping response, diffusion rate difference between Cu and Pb, or non-uniform electroplating of the Cu ions to the electrode surface. Further investigation into counter electrolyte concentration effect and preconcentration parameters may shed some light on the narrow peak effect. However, for the purpose of proving the sensor platform for application in heavy metal detection by stripping analysis these results suffice.

Furthermore the same solutions were tested with the SWASV method, with scanning range of -0.6 V to 0.3 V and 60 s quiescent preconcentration, shown in Figure 3.27, along with closer examination of the Cu peak, upper embedded plot. The results are consistent with those done with DPASV and show the Pb and Cu peaks in the expected ranges. Once more the Cu peak is narrow with respect to the Pb peak and Cu peaks acquired with SWASV when Cu was the only target analyte. This argues that the peak narrowing of Cu is not specific to the test method but is a factor of the environment within the electrochemical cell at the MEA electrode surface. Figures 3.28 – 3.29 and Figures 3.30 – 3.31 shows the effects observed at the Cu peak for 1, 10, 20, 50, 70, 100, 200, 500, and 1000 ppb Cu & Pb in HNO₃ tested with DPASV and SWASV, respectively. In both testing methods there were a saturation of the MEA electrode between 70 ppb and 100 ppb Cu in Cu & Pb mixed solutions. This is evident by small change in peak current response on Cu peak for 100 ppb to 1000 ppb Cu & Pb solution. In the 1 ppb to 100 ppb Cu & Pb (DPASV) and 1 ppb to 70 ppb Cu & Pb (SWASV) solution range both test methods exhibited very sensitive linear behavior, shown in the lower embedded plots of Figures 3.29 and 3.31,
with correlation squared coefficients equal to 0.920 and 0.940, respectively. There is also an increase in sensitivity for both methods on the response at the Cu peak, as shown in Table 3.3. For example, as for DPASV, Cu and Pb mixture solution gave almost one magnitude order better sensitivity than Cu only solution. The similar trend is also observed for SWASV. This could be due to complexation of analytes at the electrode surface, difference in preconcentrating potential (-0.6 V vs. -0.1 V), or the increase in counter electrolyte concentration from the mixing of Cu and Pb standards and then dilution to desired concentration with 18 MΩ deionized water. Further analysis would need to be performed to optimize the responses for application. However, the information collected here is sufficient to prove the feasibility in using the MEA sensor platform in stripping analysis for mixed analyte aqueous systems.

![Figure 3.26](image)

**Figure 3.26** - MEA electrode L16 DPASV on response on 1 - 200 ppb Cu & Pb ions in HNO₃, -0.4 V for Pb and 0.3 V for Cu; insert expands Cu responses; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3
Figure 3.27 - MEA electrode L16 SWASV on response on 1 - 100 ppb Cu & Pb ions in HNO₃, -0.4 V for Pb and 0.3 V for Cu; insert expands Cu responses; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3

Figure 3.28 - MEA electrode L16 DPASV on response on Cu peak in 1 - 1000 ppb Cu and Pb mixtures in HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3 (Expanded insert from Figure 3.26)
Figure 3.29 - MEA electrode L16 DPASV current response vs. concentration at the Cu peak for 1 - 1000 ppb Cu and Pb mixtures in HNO₃ at the Cu peak; 60 s preconcentration, -0.6 to 0.4 V scan range. R² = 0.920 (1-70 Pb).

Figure 3.30 - MEA electrode L16 SWASV on response on Cu peak in 1 - 1000 ppb Cu and Pb mixtures in HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range.
Figure 3.31 - MEA electrode L16 SWASV current response vs. concentration at the Cu peak for 1 - 1000 ppb Pb ions in HNO₃ at the Cu peak; 60 s preconcentration, -0.6 to 0.4 V scan range. $R^2 = 0.940$ (1-70 Pb).

Table 3.3 - DPASV vs. SWASV for Cu response in Cu and Cu & Pb mixed solutions.

<table>
<thead>
<tr>
<th>[Cu] (ppb)</th>
<th>DPASV Cu only Response (pA)¹</th>
<th>SWASV Cu only Response (pA)²</th>
<th>DPASV Cu &amp; Pb Mixed Response (pA)³</th>
<th>SWASV Cu &amp; Pb Mixed Response (pA)⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-32.3</td>
<td>-50.1</td>
<td>-575</td>
<td>-431</td>
</tr>
<tr>
<td>10</td>
<td>-49.3</td>
<td>-108</td>
<td>-691</td>
<td>-709</td>
</tr>
<tr>
<td>50</td>
<td>-66.2</td>
<td>-168</td>
<td>-760</td>
<td>-1020</td>
</tr>
<tr>
<td>70</td>
<td>-83.3</td>
<td>-206</td>
<td>-788</td>
<td>-1190</td>
</tr>
<tr>
<td>100</td>
<td>-94.3</td>
<td>-241</td>
<td>-942</td>
<td>-1180</td>
</tr>
</tbody>
</table>

¹from Figure 3.13; ²from Figure 3.16; ³from Figure 3.29; ⁴from Figure 3.31;

Table 3.3 gives insight into which method, DPASV or SWASV, is better for stripping analysis utilizing the MEA platform. When analyzing the Cu responses at the Cu peaks, for both Cu ion only solutions and mixed Cu and Pb ion solutions, SWASV consistently gives a stronger current at all concentrations signifying greater sensitivity. Both methods exhibited excellent selectivity of Cu and Pb ions by having well defined separate stripping peaks for both analytes. However, from Figure 3.21, SWASV did not exhibit linear correlation
between current response and concentration change. As previously eluded to, SWASV is a better test method than DPASV based on the higher sensitivity observed under same parameter examination and the faster speed of SWASV method. Wang discusses a rapid square-waveform that effectively shortens overall measurement times and list references where it was used. Decrease in overall testing time is very advantageous and allows users to conduct multiple tests in the same time one test would be conducted. Multiple tests allow greater confidence in experimentation results. Furthermore, optimizing preconcentration and supporting electrolyte concentration for SWASV is very feasible, and can be utilized with custom analyzers to increase portability and ease of testing. This will be discussed in the forthcoming chapter.

3.4 Conclusions

The MEA sensor platform was utilized in stripping analysis methods DPASV and SWASV on copper, lead, and mixed copper-lead aqueous solutions. Responses were acquired for concentrations varying between 1 ppb and 1000 ppb for all solutions analyzed. Both test methods exhibited well defined obvious peaks for Cu or Pb metal ions in solution and mixed Cu and Pb metal analytes in solution. When Cu or Pb was the only analyte in solution DPASV had a better defined peak associated to the analyte stripping compared to SWASV; however, SWASV was shown to be more sensitive than DPASV in all solutions tested. Both methods gave strong linear correlation over the concentration range tested with Cu solutions and DPASV gave strong linear correlation over the concentration range in Pb solutions; SWASV did not show a linear correlation. In the Cu and Pb mixed solutions both methods saturated the MEA electrode between 70 ppb and 100 ppb Cu and Pb in HNO₃. The low concentration range of 1 ppb to 100 ppb (DPASV) and 1 ppb to 70 ppb (SWASV) of Cu & Pb in HNO₃ exhibited strong linear correlation and analysis at the Cu peak
showed a significant sensitivity increase over solutions where only the Cu analyte was targeted.

Both Cu and Pb, individual target analyte, solutions were tested with DPASV and SWASV on commercially available CH 10 μm electrode. The CH working electrode did not respond in the Cu solutions using DPASV and only responded with high concentrations, compared to the concentration range tested, in Cu solutions, tested with SWASV, and Pb solutions tested with DPASV and SWASV. The MEA sensor platform was proven to outperform the commercially available electrode. Furthermore, the MEA sensor platform was proven to work well in stripping analysis and with some additional optimization of the preconcentration potential and supporting electrolyte concentration, this platform could be a very powerful method for heavy metal detection.
CHAPTER 4
COUPLING WITH ELECTROCHEMICAL CHIP ANALYZER

4.1 Feasibility in Coupling EC-Chip Analyzer with the MEA Platform

Electrochemical (EC) sensing consists of a transducer converting environmental (e.g. chemical, biological, mechanic) stimuli into electrical signal where an electrical devise (potentiostat analyzer) records, processes, and stores the information. Design, construction, and application of the microelectrode array (MEA) sensing platform were previously explored. However, further exploration of potentially coupling the MEA platform with a homemade EC analyzer has been done.

Colleagues within this lab have previously collaborated on the design and fabrication of a homemade microprocessor controlled mini-EC instrument, named EC-Chip, utilizing square wave voltammetry (SWV) as EC testing method. By using a direct digital frequency synthesizer to generate a low frequency waveform for SWV testing, along with, a high performance operational amplifier and multiple noise reduction methods a high sensitive, low cost, low power, portable analyzer was initially shown.

SWV is accomplished by superimposing a square-wave on a potential staircase sweep. The current is recorded on the end of each half wave, and as a result, background current is discriminated by different current decay rates following each potential step. SWV is a fast and versatile electrochemical testing method and has been shown to be very sensitive. Thus this homemade analyzer has strong potential to be coupled with the MEA sensor platform to generate a highly specific, sensitive, portable sensing system dedicated to heavy metal ion detection in aqueous systems.
4.2 Experimental

SWV Electrochemical testing was done using commercially available CHI 1220 Electrochemical Analyzer (CH Instruments, TX, USA) and homemade EC-Chip Electrochemical Analyzer, done in the standard three electrode configuration. Macroelectrode (2mm diameter gold) were utilized as the working electrode with silver|silver chloride (Ag|AgCl) reference electrode and platinum wire counter electrode (all from CH Instruments). MEA electrodes were utilized as working electrodes following fabrication and oxygen plasma etch treatment.

SWV was done on varying concentrations of 0.05, 0.1, 0.3, 0.5, and 1.0 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS (Sigma-Aldrich) and on varying concentrations of 100, 300, 500, 700, 1000 ppb, and 200 ppm Cu solutions, mixed from 1000 ppm copper standards with 2% HNO$_3$ (Fisher Scientific), diluted with 18 MΩ deionized water; recorded at the working electrode. Table 4.1 shows the SWV testing parameters for each electrochemical analyzer. All solutions were deoxygenated by nitrogen purge for at least 10 minutes prior to testing. Polishing of the 2mm diameter gold working electrode was done by successive polishing using 1 (bare borundum sanding paper only), 0.3, 0.1, and 0.05 alumina slurries, followed by thoroughly rinsing with distilled water. The electrochemical cell consisted of a 25 ml glass beaker, where the electrodes were inserted through the top opening for 2 mm diameter electrode configuration and the cell consisted of the sterol plastic well of approximately 400 µl volume, for the MEA working electrode tests, where only the reference and counter electrode were inserted in the top, as shown in Figure 2.7.
Table 4.1 - Input parameters for SWV testing.

<table>
<thead>
<tr>
<th>Parameter Type</th>
<th>EC-Chip SWV Parameters</th>
<th>CHI 1220 SWV Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial E (V)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Final E (V)</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>Increment E (V)</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Amplitude (V)</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>15.001</td>
<td>15.001</td>
</tr>
<tr>
<td>Quiet Time (s)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sensitivity (A/V)</td>
<td>1*10^{-5}</td>
<td>1*10^{-5}</td>
</tr>
</tbody>
</table>

4.3 Results and Discussion

4.3.1 Comparison of K₃Fe(CN)₆ SWV Results on 2 mm Au Electrode

Initial tests to compare the responses of the EC-Chip versus a commercially available EC analyzer were done with SWV measurements on the ferri/ferrocyanide reduction of K₃Fe(CN)₆ in 0.01 M PBS utilizing a 2 mm diameter gold working electrode. Solutions of 0.05, 0.1, 0.3, 0.5, and 1.0 mM K₃Fe(CN)₆ in 0.01 M PBS were prepared as described and tested, in triplicate, on 2 mm diameter gold working electrode with potential range of 0.5 to -0.1 V. As the potential is swept toward the negative -0.1 V, the iron species of K₃Fe(CN)₆ to be reduced on the working electrode surface and the current change is recorded.

K₃Fe(CN)₆ + e⁻ → K₄Fe(CN)₆

The voltammograms show a characteristic current peak shape at the reduction potential of the iron species as shown in Figures 4.1 and 4.2 for the EC-Chip and CHI 1220 analyzers, respectively. Both analyzers recorded similar peaks for all concentrations tested and they are significantly different indicated by the one standard deviation error bars included at each current recorded. The CHI 1220 analyzer samples at more data points within the potential range and thus the smoother curve shape associated with
voltammograms acquired with it. However, the EC-Chip performs much faster, with experimental time less than one half that of the CHI 1220 analyzer, and still collects well defined and significant voltammograms.

![Figure 4.1 - Average SWV responses of 2 mm gold working electrode tested in triplicate with 0.05, 0.1, 0.3, 0.5, and 1.0 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS; 0.5 to -0.1 V, recorded with the EC-Chip analyzer.](image1)

![Figure 4.2 - Average SWV responses of 2 mm gold working electrode tested in triplicate with 0.05, 0.1, 0.3, 0.5, and 1.0 mM K$_3$Fe(CN)$_6$ in 0.01 M PBS; 0.5 to -0.1 V, recorded with the CHI 1220 analyzer.](image2)
The peak current responses were analyzed with respect to concentration to obtain working curves for both the EC-Chip and CHI 1220 analyzer, as shown in Figures 4.3 and 4.4, respectively. Both analyzers show strong linear trends for the concentration range tested with correlation coefficients squared equaling 0.990 and 0.997, for the EC-Chip and CHI 1220, respectively. Error at the peak height is very comparable between the two instruments as both working curves have low error at every point analyzed, with slight exception to 1.0 mM for the EC-Chip and 0.3 mM for the CHI 1220 Analyzer. The CHI 1220 analyzer proved to be more sensitive than the EC-Chip analyzer with 1.0 mM current response of approximately 8 nA compared to approximately 5 nA for the EC-Chip. However, there most certainly must be a tradeoff between total experimentation time and sensitivity and, while the CHI 1220 analyzer is more sensitive, the EC-Chip analyzer is still proven to be sensitive and significant with a greatly reduced experimentation time.

![Graph of peak current vs. concentration for 2mm gold working electrode SWV testing of K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, recorded with the EC-Chip analyzer.](image)

**Figure 4.3 -** Peak current vs. concentration for 2mm gold working electrode SWV testing of K₃Fe(CN)₆ in 0.01 M PBS; 0.5 to -0.1 V, recorded with the EC-Chip analyzer.
4.3.2 Comparison of SWV Results on Cu Ions Using 2 mm Au Electrode

To further compare the responses of the EC-Chip versus a commercially available EC analyzer, SWV measurements were done on the reduction of copper ions, as reduction potential for copper falls in 0.5 to -0.1 V potential range. Solutions of 100, 300, 500, 700, 1000 ppb, and 20 ppm Cu solutions with HNO₃ as counter electrolyte were prepared as described and tested, in triplicate, on 2 mm diameter gold working electrode with potential range of 0.5 to -0.1 V. Once more, as the potential is swept toward the negative -0.1 V, the Cu ions will be reduced on the working electrode surface and current change is recorded. Previous analysis done with anodic stripping voltammetry (chapter 3) on lead ions where the preconcentrating and sweep were done in a reverse direction (positive toward negative), showed reduction peaks but results had much variance. We expect similar results on reduction of copper ions with SWV testing.
Figures 4.5 and 4.6 show SWV triplicate testing on 2 mm gold working electrode in 100, 300, 500, 700, and 1000 ppb Cu solutions with HNO₃ on the potential range of 0.5 to -0.1 V; for EC-Chip and CHI 1220 analyzers, respectively. There is a pseudo peak formation around 0.5 to 0.3 V but it is not very well defined. Additionally the 100, 500, and 700 ppb Cu concentrations tested with the EC-Chip recorded as noise and were deemed unsuccessful, Figure 4.5. Closer examination of 300 and 1000 ppb Cu concentrations tested with both EC-Chip and CHI 1220 analyzer is shown in Figure 4.7. These concentrations were deemed successful with the EC-Chip testing and they appear as similar compared to the same solutions tested with the CHI 1220 analyzer; the latter appears to be more sensitive. Question was raised as to whether the solutions were too dilute to record at the 2
mm gold electrode surface. Therefore, the concentration was increased to 20 ppm Cu in HNO₃ and tested on the same potential range of 0.5 to -0.1 V. Figure 4.8 shows the results for both EC-Chip and CHI 1220 analyzer and the voltammograms are near identical shape but once more, the CHI 1220 analyzer was more sensitive.

![Graph showing voltammograms for different concentrations of Cu in HNO₃](image)

**Figure 4.6 - Average SWV responses of 2 mm gold working electrode tested in triplicate with 100, 300, 500, 700, and 1000 ppb Cu in HNO₃; 0.5 to -0.1 V, recorded with the CHI 1220 analyzer.**

Copper appears to be difficult to reduce in solution with SWV test as given by the pseudo shaped peaks in the voltammograms recorded at the 2mm electrode surface. Perhaps further analysis with increased HNO₃ counter electrolyte could resolve the peaks. Otherwise it could be concluded that the redox couple of copper is favored in an oxidation direction only.
Figure 4.7 - Comparison of Average SWV responses of 2 mm gold working electrode tested in triplicate with 300 and 1000 ppb Cu in HNO₃; 0.5 to -0.1 V, recorded with the CHI 1220 and EC-Chip analyzers.

Figure 4.8 - Comparison of Average SWV responses of 2 mm gold working electrode tested in triplicate with 20 ppm Cu in HNO₃; 0.5 to -0.1 V, recorded with the CHI 1220 and EC-Chip analyzers.
4.3.3 SWV Results on Cu Ions Using the MEA Sensor Platform

Figure 4.9 - Average SWV responses of MEA electrode L8 tested in triplicate with 100, 300, 500, 700, and 1000 ppb Cu in HNO₃; 0.5 to -0.1 V, recorded with the CHI 1220 analyzer.

To compare the responses of SWV measurements on the reduction of copper ions between the 2 mm diameter working electrode and the MEA electrode solutions of 100, 300, 500, 700, and 1000 ppb Cu with HNO₃ as counter electrolyte were prepared as described and tested, in triplicate, with potential range of 0.5 to -0.1 V. Figure 4.9 shows the results of SWV testing utilizing MEA electrode L8 with the CHI 1220 analyzer. The peak formation is more dominant when the MEA electrode is utilized which is evident when compared against Figure 4.6. This is expected due to the enhanced mass transport associated with microelectrodes. Also the monitored current is two orders of magnitude
lower with the MEA electrode, which is expected, than that observed with the larger 2 mm macroelectrode. The same solutions were tested with MEA electrode L8 with the EC-Chip analyzer but due to the lower current registered, results were unable to be collected. Further modification, by reprogramming the microprocessor and adjusting the circuitry to increase sensitivity for lower current measurements, of the EC-Chip should enable the devise to be coupled with the MEA electrodes.

4.3 Conclusions

The homemade EC-Chip analyzer was compared against the commercially available CHI 1220 Electrochemical Analyzer to evaluate feasibility of potentially coupling with the MEA sensor platform. SWV measurements on the ferri/ferrocyanide reduction of K₃Fe(CN)₆ in 0.01 M PBS utilizing a 2 mm diameter gold working electrode were performed with both instruments and showed the expected current peak formation on the acquired voltammograms of every concentration tested. While the voltammograms collected with the CHI 1220 analyzer displayed greater resolution and higher sensitivity to the reduction of K₃Fe(CN)₆, the EC-Chip performed the experiments quicker and maintained resolution when far fewer data points were collected. Furthermore, SWV measurements on the reduction of copper ions utilizing a 2 mm diameter gold working electrode was performed on both instruments and results indicate similarity and likeness of the voltammograms obtained when Cu ions are present in the higher ppb and low ppm concentrations. Due to previous exploration of positive to negative potential sweeping done with ASV testing there is expected greater variance in heavy metal current peaks obtained when SWV testing is done in this manner, and indeed, larger variance was observed in triplicate testing of Cu ions.
The CHI 1220 analyzer and the EC-Chip analyzer was utilized in testing the MEA electrode L8 in SWV testing and results we obtained with the CHI 1220 analyzer but not with the EC-Chip analyzer. This was due to the decrease in current associated with microelectrode electrochemical testing. However, results from the CHI 1220 analyzer coupled with the microelectrode showed, as expected, resolution of the reduction peak of Cu ions from the acquired voltammograms.

Overall feasibility analysis of the EC-Chip versus the CHI 1220 analyzer indicates, reprogramming the microprocessor of the EC-Chip and some additional optimization of the instrument to maximize sensitivity at the low current required for microelectrode electrochemical analysis testing; could lead to a highly sensitive instrument dedicated to heavy metal testing of aqueous systems. This system would have portability, low power, low cost, and increased ease of operation compared with a commercially available electrochemical instrumentation.
CHAPTER 5
PROJECT CONCLUSION

5.1 Problem Elucidation

Charged species identification is of particular interest in academic, industrial, and municipal systems. Generally samples are taken in the field or at the locale of interest, stored, transported, and then analyzed in a traditional lab utilizing electrochemical, chromatography, and spectroscopic methods. This traditional quantification method has disadvantages in slow speed of conveying results, possible contamination in transport, and the possibility of sample loss and/or transformation between sampling and testing. This thesis reported on the design, characterization, application, and future coupling potential of a reliable low cost sensor platform capable of in situ environmental monitoring of the heavy metal ions, copper and lead, in aqueous systems.

Microelectrode array sensor platform, showing strong advantages in conveying system information in a timely manner without adversely affecting the system environment, was optimized for maximum performance by evaluation of size, shape, composition, interelectrode spacing, and functionality based on literature review. Furthermore, electrochemical methods were reviewed and cyclic voltammetry, square wave voltammetry, square wave anodic stripping voltammetry, and differential pulse anodic stripping voltammetry were utilized to characterize and demonstrate the operation of the sensor platform.

5.2 Attainment of Project Aims

The overall project goals were listed as:

1) Design and fabricate a new sensor platform to perform voltammetric measurements.
2) Design a microelectrode pattern (microdisk, microband, or micro-ring) that maximizes current density at the electrode surface and improves signal-to-noise ratio and sensitivity.

3) Incorporate multiple microelectrodes in an array design to allow detection of multiple measurable analytes in one aqueous solution and to allow comparison of same solution responses between multiple electrodes.

4) Prove and characterize the microelectrode sensing system in K₃Fe(CN)₆ electrochemical standard.

5) Demonstrate the feasibility of using the microelectrode sensing system to detect copper and lead ions in aqueous solutions.

6) Evaluate and prove potential of future coupling the microelectrode sensing system with homemade square wave voltammetry device.

5.2.1 Voltammetric Criterion Design

The voltammetric method requires a three electrode configuration where potential is adjusted at the working electrode surface and referenced to a reference electrode. This requires a conductive working electrode isolated from the sensor platform and other electrodes in the array if solitary electrode functionality is desired. This was accomplished by utilizing lithography techniques to microfabricate individually isolated gold electrodes, in a planar array formation, on a nonconductive glass substrate. The lithography method was chosen as the fabrication technique due to its repeatability and low cost for production. Furthermore gold was utilized as the electrode composition as it outperforms platinum and has ability to be used with biological interfaces; this platform may have potential use with immobilized DNA, enzymes, or antibodies.¹³,⁶,⁸-¹⁴

5.2.2 Microelectrode Pattern Design Criterion
Exact electrode test area size and shape was fabricated by opening a hole in a resist insulating mask layer above an electrode base pad, thereby, insulating the array wiring and exactly defining the electrode. Each electrode was constructed to 10 μm x 10 μm square shape to amplify the current density due to mass transport enhancement from nonlinear (3-D) hemispherical diffusion around the perimeter of the microelectrode. This enhanced mass transport gave rise to steady state sigmoidal cyclic voltammograms obtained when the electrodes were demonstrated and characterized. Micro-square band electrode shape was incorporated due to its ease in fabrication, and it outperforms microring, microdisk, and rectangular microband shapes in short experimentation times.2,3,14,22,24-26

5.2.3 Array Design Criterion

Individual electrodes were incorporated in a planar design to house 18 electrodes on one test platform. This allows diversity in testing from electrode utilization in solitary, group census, or some combination thereof to perform electrochemical testing. This gives greater diversity and flexibility in testing than that of traditional macroelectrode systems. The electrodes were spaced at ten times the width of the electrodes to ensure diffusion zones, formed over each microelectrode, did not overlap to constructively form a large diffusion zone over the entire array (similar to macroelectrode) and eliminate the current enhancement from nonlinear hemispherical diffusion of the microelectrodes.2,3,26

5.2.4 Demonstration and Characterization of the MEA Electrodes

The MEA microelectrodes were demonstrated and characterized by monitoring the current changes associated with the ferri/ferrocyanide redox couple using cyclic voltammetry. The attained voltammograms gave a sigmoid shape characteristic of steady state (3-D) diffusion of the electroactive K₃Fe(CN)₆ electrochemical standard over the 0.05
mM to 1.0 mM K₃Fe(CN)₆ concentration range. Repeatability was shown by monitoring the current while cycling the potential through five CV tests and analyzing the deviation and drift over the cycles. Only a slight departure in the current response was observed on the first cycle as it initiated. However, this was insignificant and the remainder results showed no drift and exact repeatability. Interelectrode variance was checked at 0.3 mM and 0.5 mM K₃Fe(CN)₆ solutions by testing all 18 individual electrodes comprising one test site with CV. There was variance between electrode responses at both concentrations but the average response was significant at both concentrations with non-overlapping one standard deviation.

Furthermore, the MEA electrodes were compared against a commercially available 10 μm diameter Au working electrode with CV testing on a 0.05 mM to 1.0 mM K₃Fe(CN)₆ concentration range. It was found that the 10 μm diameter Au electrode resulted in a slightly stronger linear fit. However, the MEA electrode’s voltammogram had a better sigmoidal shape, less hysteresis, and was more sensitive to the K₃Fe(CN)₆ electrochemical standard. Due to the increased sensitivity and better defined voltammograms obtained with the MEA electrodes, it was deemed to outperform the commercially available 10 μm diameter Au working electrode.

5.2.5 Application of the MEA Platform to Stripping Analysis

Feasibility for using the MEA sensor platform in stripping analysis for copper and lead ions in aqueous solutions was proven by performing SWASV and DPASV on solutions containing copper ions, lead ions, and mixed copper with lead ions. In copper ion solutions both DPASV and SWASV gave distinct peaks in their respective voltammograms at the reduction potential of copper on Au electrodes. Both methods had strong linear correlation over 1 ppb to 1000 ppb Cu concentration range tested. DPASV, however, was slightly more
linear then SWASV, while SWASV demonstrated greater sensitivity. The commercially
available 10 μm diameter Au working electrode was tested in the same solutions as the MEA
electrode as a method of comparison and its response was deemed unsuccessful with no
peak formation and no clear trend in the signals under our experimental conditions.

DPASV and SWASV were performed on lead ion solutions utilizing the MEA
electrode and both voltammetric methods proved successful with peak formation
approximately at the reduction potential for Pb on Au electrodes. The DPASV gave a strong
linear correlation while SWASV did not show linearity when response was taken from the
peak response in the lead reduction potential range. The concentration testing range was 1
ppb to 1000 ppb Pb. Again the commercially available 10 μm diameter Au working
electrode was tested in the same solutions and there was peak formation but only
accompanying the relatively higher concentrations tested, namely 500 ppb and 1000 ppb.
The low ppb concentrations were deemed unsuccessful with this commercial electrode.

Mixed Cu and Pb ion solutions were tested with DPASV and SWASV utilizing the
MEA electrode system and well defined peak formations were observed in both the
reduction potential ranges for Cu and Pb on Au electrodes. By analyzing the Cu peak
formation it was determined that the sensor electrode was saturating somewhere between
70 ppb to 100 ppb Cu and Pb in Cu and Pb mixed ion solutions with both voltammetric
methods. Peak verses concentration responses were constructed for both methods and
sensitivity enhancement was observed in the unsaturated concentration region of the 1 ppb
to 100 ppb Cu and Pb tested, compared to that of the individual ions in their respective
solutions. Once more the SWASV test proved to be more sensitive than the DPASV and
combined with the ability to perform the experiments faster it is deemed the better
sweeping method for performing stripping analysis for copper and lead ions in aqueous
solutions.
5.2.6 Feasibility for Future Coupling of the MEA Platform with EC-Chip Analyzer

In order to prove the feasibility for future coupling of the MEA sensor platform with a homemade SWV electrochemical instrument, the MEA platform and the EC instrument would be combined to form a highly sensitive specific dedicated sensing system for heavy metal ion detection. A piecewise proving method was employed because the prototype homemade EC-Chip was not designed for use with microelectrodes. This was done by confirming the system with comparison to a commercially available electrochemical analyzer (CHI 1220 analyzer) on reduction of K$_3$Fe(CN)$_6$ around the ferri/ferrocyanide redox couple using a 2 mm Au working macroelectrode. Then by utilizing this 2 mm Au working macroelectrode SWV reduction of Cu was performed using both instruments. Finally the commercially available analyzer was utilized to explore SWV reduction of Cu using the MEA platform.

In exploration of the 2 mm Au working macroelectrode SWV reduction of K$_3$Fe(CN)$_6$ around the ferri/ferrocyanide redox couple the homemade EC-Chip and the CHI 1220 analyzer proved to be successful. While the CHI 1220 analyzer was more sensitive to the K$_3$Fe(CN)$_6$ electrochemical standard and had a slightly stronger linear correlation over the 0.05 mM to 1.0 mM concentration range tested, the EC-Chip demonstrated well defined reduction peaks with strong linear correlation, and performed the experiments much faster. It was deemed successful in its ability to reduce K$_3$Fe(CN)$_6$ with the 2 mm Au working macroelectrode.

When SWV testing with the 2 mm Au working macroelectrode in attempt to reduce Cu ions, performed with both instruments, large variance was expected due to similar exploration of the MEA electrode with DPASV and SWASV operated in a reverse potential direction. This indeed was the case with slight peaks observed at a slightly shifted
reduction potential than that for Cu on Au electrodes. The concentration range tested was 100 ppb to 1000 ppb and 20,000 ppb Cu solutions with successful results shown at the higher ppb concentrations that correlated the EC-Chip analyzer and the CHI 1220 analyzer. Voltammogram similarity and slight peak formation were the basis of correlation between the two EC analyzers.

Cu solutions ranging from 100 ppb to 1000 ppb concentration were tested with both instruments utilizing the MEA electrode as the working electrode and results were unsuccessful for the EC-Chip. This was due to the cutoff current limit of the prototype EC-Chip. Further modification would be needed to utilize the EC-Chip with microelectrodes; this was hypothesized before the experiment and results confirm the hypothesis. In contrast, the CHI 1220 results with the MEA electrode showed slightly better defined reduction peaks than those shown when the same solutions were tested with the 2 mm Au working macroelectrode; the large amount of variance was noted and in either case results are not significant shown by overlapping one standard deviation error.

By performing the piecewise proving method described above it was shown that with further modification of the EC-Chip analyzer, successful coupling with the MEA sensor platform is expected. This coupling would be very advantageous due to ability to fabricate low cost accurate analyzers dedicated to heavy metal ion analysis in aqueous systems.

5.3 Further Development Suggestions

A prototype MEA sensor platform has been constructed and proven with the results presented in this thesis. Further development needs to occur on two fronts. First, further application of this sensor to heavy metal ion detection using stripping analysis would require optimization of testing parameters, such as, preconcentration time and potential in SWASV or DPASV testing, and counter electrolyte concentration. The correlation of
response verses concentrations should be explored by correlating the area under the peak in the acquired voltammograms with the concentration being tested as opposed to peak current response correlated with concentration. Furthermore, some method for deoxygenating samples when testing is performed *in situ* would need to be designed, or some method for compensating for the oxygen signal would need to be employed. Additionally, the EC-Chip analyzer needs further development to be coupled with the MEA sensor platform. This would include reprogramming the microprocessor to allow lower current processing, redesign of the software to manipulate testing parameters (as it stands now the parameters are fixed), and design of a more efficient connection with the electronic contact pads of the MEA platform.

Secondly, this was a prototype sensor platform and further development could be beneficial. Suggested further development would include incorporating counter and reference electrodes on the glass sensor platform to eliminate their insertion through the top of the electrochemical cell epoxied over the test sites, incorporating additional elemental compositions making up the electrodes (e.g. platinum electrodes with the gold electrodes comprising an array), utilizing silicon nitride as the insulating mask layer as opposed to resist, and changing the size of the electrodes in additional arrays. Each one of these suggestions has the potential to further improve the sensor platform.

5.4 Additional Applications of the MEA Sensor Platform

During the literature review, design evaluation, fabrication, and testing of this MEA sensing platform, alternative applications beyond heavy metal ion analysis have been realized identified. First, there is great potential in utilizing gold microelectrodes coupled with immobilized enzymes to analyze biological and chemical environments. Such enzymatic sensors would have applications for pesticides, ethanol, oxalate, and other
analytes.\textsuperscript{30} Due to the characteristics of gold's affinity toward sulfur, immobilizing enzymes with Cysteine amino acid units is possible. Alternatively proteins have been evaluated utilizing gold microelectrode arrays.\textsuperscript{28} DNA is also a plausible candidate for immobilization and then single strand mutations could be evaluated.
6.1 Simultaneous Multi-electrode Detection

As previously examined electrochemical testing can be improved by utilizing microelectrodes in place of traditional electrodes. Miniaturization of electrodes offers advantages of: reduction of resistance (ohmic drop), reduction of sample consumption, ability to incorporate many electrodes in a small area, and greater ability to facilitate measurements in low-ionic-strength water samples. Furthermore, nonlinear diffusion at the boundary of the electrode yields current amplification. Finally, by utilizing microelectrodes in an array fashion, diversity and flexibility are improved by having a platform that can be utilized in multiple microelectrode combinations, where the enhanced properties attributed to the smaller microelectrode are maintained. The platform has the flexibility of using all microelectrodes set at different potential ranges, using the microelectrodes as a global electrode with all electrodes performing as one capitalizing on their individual enhancements but allowing greater current flow, or some situational unique combination of the two former scenarios.

Utilizing individual electrodes, at different potential ranges, is primarily done in one of two fashions: utilizing a multichannel potentiostat (multipotentiostat), or adding a multiplexer in-line between the potentiostat and the electrochemical cell. The primary difference between the two experimental approaches is that a multipotentiostat allows parallel, simultaneous, electrode individual potential-time regimes to each working electrode on the array platform, while the multiplexer will switch between electrodes sequentially after each electrode’s individual potential-time regime has been completed. Thus, the foremost advantage to the multipotentiostat resides in the decreased total
experimentation time, compared to that from the sequential multiplexed experimentation time.

Both experimental setups have the ability to utilize a ‘potential window’ approach to selective determination of heavy metal ions; where individual electrodes scan different potential ranges to discriminate signals from different metal ions in mixed analyte systems. This ‘potential window’ approach further decreases measurement time, simplifies result analysis, and minimizes errors from ion interaction during the electroplating preconcentration phase of electrochemical stripping analysis. Partial selective deposition of metals in mixed analyte systems is accomplished by preconcentrating different electrodes at different potentials where each potential is attributed to a different metal ion of interest and stripping analysis is done over short range of potential, specific for each metal of interest. In this fashion, simultaneous stripping, with shortened stripping time, is realized. As a hypothetical example, imagine utilizing three electrodes to simultaneously detect copper and lead, as shown in Figure 6.1. Electrode 1 utilizes the deposition potential of 0.0 and strips during the potential range of 0.0 V to 0.4 V, thus producing a stripping peak attributed to copper ions. Electrode 2 utilizes the deposition potential of -0.6 V and strips during the potential scan of -0.6 V to 0.0 V, thus producing a stripping peak attributed to lead ions. Finally, Electrode 3 utilizes a deposition potential of -0.6 V and strips during the potential range of -0.6 V to 0.4 V, thus producing two stripping peaks attributed to lead and copper, respectively. Electrodes 1 and 2 have avoided error from ion interaction during the deposition phase, whereas, Electrode 3 will show affects from ion interactions however, this information is useful in determination of the magnitude of ion interaction effects.
In order to utilize this microelectrode array sensor platform to provide the data quality required for environmental and public health monitoring, intelligent experimental design must further be optimized and demonstrated. Within this thesis, heavy metal ion results and conclusions have been made from calibration standards constructed from standard reference materials and ultra pure water. In addition to these calibration standards, accurate sensor response information needs to be derived from, or as close as possible from, field blanks, spiked field blanks, spiked laboratory blanks, working standards, and field samples, as well.\textsuperscript{31} The importance of utilizing as many of these samples as possible is in validating the measurement process. The order and frequency blanks, field samples, and standards needs to be tested is dependent on each measurement situation or protocol.\textsuperscript{31} Therefore, the following discussion outlines theoretically how the sensor platform would be deployed to a specific area to be utilized in on-site testing.
The following discussion assumes there is a particular lake or stream that the sensor platform would be utilized in. Due to the difference in the field blank composition, compared to that of the calibration standards, numerous initial samples should be acquired and removed to a traditional lab setting. The amount of samples to be obtained should be calculated by statistical design which takes into account certainty levels and overall objective goals. Furthermore, sample collection needs to be done as carefully as possible to avoid contamination. Once the samples are acquired, each should be split up so field samples and spiked (e.g. copper and lead) field samples can be made. The reason for spiked field samples is to ensure stripping peaks for the copper and lead heavy metal ions are acquired with the sensor platform. However, we cannot simply use the calibration working curves acquired with the lab prepared calibration standards. Therefore, simultaneous testing should be done, as a comparison, with a traditional analytical chemistry method such as inductively coupled plasma – mass spectrometry (ICP-MS). The traditional method, tested with the same samples as the sensor platform, allows concentrations of copper and lead ions to be known in the initially acquired samples. Utilizing these initial concentrations and the spiked field samples, new working curves can be constructed for the specific lake or stream to be tested.

Once field specific working curves are constructed, limit of detection, limit of quantitation, and the linear dynamic range of testing should be determined so the sensing platform can be utilized to monitor real samples. Additional information may be derived if the field samples are modified to extract the copper and lead ions, giving field blanks for background influence information. As stated above, the importance of utilizing as many samples as possible is in validating the measurement process.

With the aforementioned testing complete and accurate signal responses are checked with a traditional testing method, the sensor platform is ready to be deployed for
field measurements. However, until a statistical number of field trials are performed to gain a large degree of certainty utilizing the sensor platform, samples should be taken in the same location, as the platform test samples, and transported to the lab for traditional method verification. Additionally, all logistics of testing must be adhered to in the field to match those performed in the lab, namely, deoxygenation of the samples and any pretreatment.
REFERENCES


A.1 Additional Microfabrication and Sensor Characterization

Figure A.1 - Complete fabricated MEA sensor (left) and partially completed sensor (right).

Figure A.2 - Nine-electrode array constituting half of one test site on the MEA sensor platform; before resist layer (left) and after resist layer is applied (right).
Figure A.3 - Nine-electrode array constituting half of one test site on the MEA sensor platform after resist layer is applied (left) and with approximate dimensions (right).

Figure A.4 - Nine-electrode array (before resist mask layer) with approximate dimensions of base sensor pads and wireing.
Figure A.5 - Electrode after resist mask layer is applied (left) and with approximate dimensions (right).

Figure A.6 - Wiring junction above electronic contact pads (left) and with wire dimensions (right).

Figure A.7 - Nine-electrode array composing half of one test site on the MEA sensor platform.
Figure A.8 - One test site on the MEA sensing platform consisting of 18 individual microelectrodes in the array.

Figure A.9 - Complete MEA sensing platform with 96 well plate future prototypes will be designed for.
A.2 Additional Stripping Analysis Results for Copper and Lead Ions

A.2.1 DPASV on Cu Ion Solutions Utilizing 10 μm Au CH Electrode

Figure A.10 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure A.11 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
Figure A.12 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure A.13 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure A.14 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
Figure A.15 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure A.16 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

Figure A.17 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3
Figure A.18 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Cu with HNO₃; 60 s preconcentration, -0.1 to 0.3 V scan range. n=3

A.2.2 SWASV on Cu Ion Solutions Utilizing MEA Electrode

Figure A.19 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure A.20 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.21 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.22 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure A.23 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.24 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=2

Figure A.25 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure A.26 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.27 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
A.2.3 SWASV on Cu Ion Solutions Utilizing 10 μm Au CH Electrode

Figure A.28 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.29 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure A.30 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.31 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.32 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure A.33 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.34 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

Figure A.35 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3
Figure A.36 - 10 μm CH electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Cu with HNO₃; 60 s preconcentration, -0.5 to 0.3 V scan range. n=3

A.2.4 DPASV on Pb Ion Solutions Utilizing MEA Electrode

Figure A.37 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=6
Figure A.38 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.39 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.40 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.41 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=2

Figure A.42 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.43 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3 (unsuccessful)
Figure A.44 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=2

Figure A.45 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=2
A.2.5 DPASV on Pb Ion Solutions Utilizing 10 μm Au CH Electrode

Figure A.46 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.47 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.48 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.49 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.50 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.51 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.52 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.53 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.54 - 10 μm CH electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

A.2.6 SWASV on Pb Ion Solutions Utilizing MEA Electrode

Figure A.55 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.56 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.57 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.58 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.59 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.60 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.61 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3 (unsuccessful)
Figure A.62 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.63 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=2
**A.2.7 SWASV on Pb Ion Solutions Utilizing 10 μm Au CH Electrode**

Figure A.64 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.65 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 10 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.66 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.67 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.68 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 70 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.69 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

Figure A.70 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 200 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=2

Figure A.71 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3
Figure A.72 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 1000 ppb Pb with HNO₃; 60 s preconcentration, -0.6 to 0.0 V scan range. n=3

A.2.8 DPASV on Pb Ion Solutions Utilizing MEA Electrode (Reverse Direction)

Figure A.73 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)
Figure A.74 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)

Figure A.75 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)

Figure A.76 - MEA electrode L8 DPASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)
A.2.9 SWASV on Pb Ion Solutions Utilizing MEA Electrode (Reverse Direction)

Figure A.77 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 20 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)

Figure A.78 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 50 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)
Figure A.79 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 100 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)

Figure A.80 - MEA electrode L8 SWASV testing (left) and average results with 1 standard deviation (right) on 500 ppb Pb with HNO₃; 60 s preconcentration, 0.0 to -0.6 V scan range. n=3 (reverse direction)
A2.10 DPASV and SWASV on Mixed Cu & Pb Ion Solutions Utilizing MEA Electrode

Figure A.81 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 1 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3

Figure A.82 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 10 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3
Figure A.83 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 20 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3

Figure A.84 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 50 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3

Figure A.85 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 70 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3
Figure A.86 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 100 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3

Figure A.87 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 200 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3

Figure A.88 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 500 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3
Figure A.89 - MEA electrode L8 DPASV testing (left) and SWASV testing (right) on 1000 ppb Cu & Pb with HNO₃; 60 s preconcentration, -0.6 to 0.4 V scan range. n=3