

# Photo-Induced Charge Movement (PICM) Sensors: Using Bathocuproine to Detect $\text{MgCl}_2$ , $\text{FeCl}_2$ , $\text{CuCl}_2$ , and $\text{CuCl}$

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## Introduction

### *Purpose*

PICM research deals with the development of sensor arrays for determining the presence and concentration of specific analytes (chemical to be sensed) in solution. The studies described here are preliminary investigations using one analyte per sensor to develop a database of information (i.e. photo-voltages at specified concentrations, selectivity, and other patterns that could follow from the experimental data). The purpose of using one sensor at a time to test one analyte at a time is to develop the database and thus the knowledge to produce successful sensor arrays or even a small, portable sensor in the future. The goal of the studies described here is to do preliminary studies on PICM sensor responses and selectivity. A future application of this research would be for selective sensor arrays to detect metal ions, other elements and compounds from water and soil samples. Detecting toxins in the environment, or even detecting toxins possibly used in terrorism can also be direct applications of future PICM research.

### *PICM*

When concentrated light strikes a surface, electric charges from the reactions between the sensor-solution interface are displaced when the photons from the light beam are absorbed by the sensor surface. This charge movement occurs when a surface is in a solution that facilitates charge movement. The charge movement is proportional to the resulting photo-voltage<sup>1</sup>.

PICM (Photo-Induced Charge Movement) sensors consist of two 3 mm platinum dots epoxied to both sides of a printed circuit board electrode. See Fig. 1. The sensors are plugged into an electrometer, or signal amplifier, in the experimental setup, and their resulting photo-voltages can then be detected. Different photo-voltages result when different analytes in solution and different concentrations of them modify their photo-voltages.

For this work, the analytes are metal ions in solution. There is 2 mL of a 1 mM concentration of a constant, overall neutral electrolyte (solute that produces ions in solution), which is NaCl, inside the holder for the electrodes (cuvette) at all times. This NaCl facilitates the electric charge movement on the sensor surface<sup>6</sup>. The cuvette is a 1 x 1 x 4 cm plastic holder for the solution and lets ultra-violet and visible light through. Analyte solutions containing  $\text{MgCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{CuCl}_2$ , (all divalent) and  $\text{CuCl}$  (monovalent) have been studied.

The charge movement in the aqueous solution of ions across the two platinum dots of the sensor is analogous to that of the parallel plates of a capacitor. A photo-

voltage across the two dots could be measured due to the movement of these charges<sup>2</sup>. See Fig. 1. The plastic circuit board is the positively charged dielectric in this model and the ions in the solution are negatively charged. The dot opposite of the one facing the light is plugged into the electrometer lead that is grounded. Once the light is triggered, PICM occurs on the platinum dot which faces the light. The resulting photo-voltage (PV) is then displayed on an oscilloscope, or a digitizer that displays how the signal voltage changes in time<sup>1</sup>. See. Fig. 2 for experimental details.

Fig 1. A Sensor in a Cuvette. Left: The opposite side of the sensor is comparable to the side shown. The sensor is plugged into an electrometer via the two leads at the top. Right: The side view of a PICM sensor as a capacitor model. The dot which the light strikes is the site of PICM since it is surrounded by ions in the solution. The side away from the light functions as a neutrally charged ground. The plastic circuit is a dielectric, which is positively charged when the charges migrate.

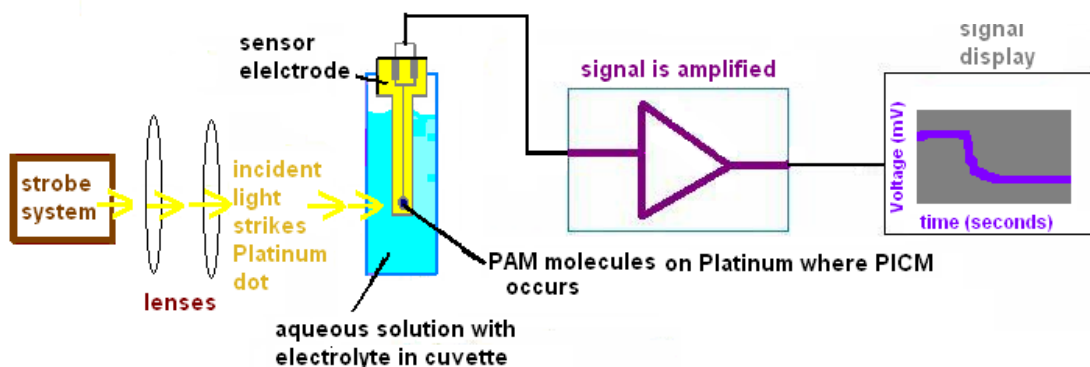
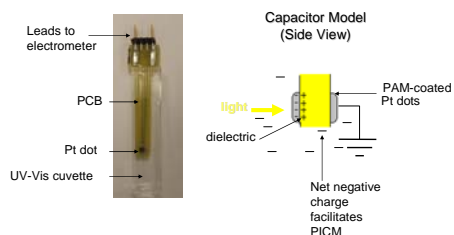


Fig. 2. Experimental Setup. The PICM sensor (patent pending) fits in 1 cm by 1 cm cuvettes. Light from a bulb filled with xenon is focused through two lenses on the platinum dot of the sensor that faces the light, where the PICM occurs. The sensor plugs into a buffer amplifier, or electrometer. The electrometer amplifies the voltage signal from the PICM activity on the platinum dot. This signal is then digitally displayed on an oscilloscope and recorded on a computer running LabView, a data acquisition and storage program. The sensor, cuvette, and electrometer are mounted inside a faraday cage (not shown) which reduces electric noise interference from the strobe and external sources<sup>3</sup>.

### PAMs

Materials that absorb light and displace electric charge are required to make PICM sensors work. These are called Photo-voltage Active Materials, or PAMS. To make a successful sensor, the photo-voltages must be modified by an analyte under investigation. The sensors are currently used to investigate one PAM per sensor. The PAM must be water-*insoluble* since it is on a sensor which is placed into solution.

A chemical PAM that could bond to the analyte in the solution is placed on the sensor, so that the bonding of the two substances could produce charge movement and thus a modified photo-voltage.

The purpose of this research with Bathocuproine as a PAM is to see how the photo-voltage is modified by the metal analytes (ions from  $\text{MgCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{CuCl}$ ) and if it is modified differently with increasing concentrations of them. This was accomplished by finding analyte-PAM pairs that change the sensor's photo-voltage from an original reading (with no analyte in the solution or PAM on the sensor).

There are two stages of photo-voltage change that occur. The first is the difference measured after the PAM has been placed on the sensor. The difference in photo-voltage in this case would signify that the PAM is functioning as a photo-voltage active material. Then, the photo-voltage is measured with varying concentrations of analyte in the cuvette. If this change in the value of the photo-voltage reading shows a statistically significant difference with the PAM and analyte present than the photo-voltage of the sensor with PAM only, it would signify that the photo-voltage of that sensor has been modified. The change in original photo-voltages depends on the concentration of metal ions present in the solution<sup>3</sup>. Photo-voltages scales also vary from sensor to sensor because of their hand-made nature.

### *Bonding*

Molecules that bond to metal ions are called ligands. When ligands are bonded to larger molecules, metal complexes are formed. Metal complexes that are part of other compounds are called coordination compounds<sup>6</sup>.

Bathocuproine contains a bidentate ligand called phenanthroline. Bidentate ligands are ligands that can occupy two coordination complex sites because each of the nitrogen atoms in the phenanthroline ligand has two valence electrons to donate. Divalent metal ions have two deficient electrons than a neutral atom. Both holes do not necessarily get filled. Only one divalent metal ion could bond to a Bathocuproine molecule because of the large size of the ion. These kinds of ligands are chelating agents, (from the Greek word *chele*, or claw) since they “grab” metal ions<sup>6</sup>.

The PAM chosen for this experimentation is called Bathocuproine, which is illustrated in Fig.3. Bathocuproine was chosen since it is known to form complex compounds with the metals in this experimentation,  $\text{FeCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{MgCl}_2$  (see for example, Bernhard, et. al and Tammiku, et. al)<sup>9,14</sup>.

Previous work by the PICM sensor group has shown that there are a variety of PAMs that have their photo-voltages significantly modified by selected analytes, while other PAMs seem to be unresponsive to all analytes tested. PAMs form chelates and have modified photo-voltages when metal ions are present in solution around the sensors give off varying photo-voltages. The extent of the modifications to the original photo-voltages depends on the concentration of chelating metal ions present. The presence and concentration of particular metal ion can theoretically be determined from variations in the photo-voltage amplitudes.

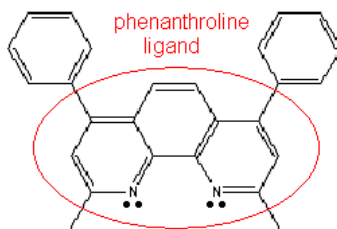


Fig. 3. The Structure of 2,9-Dimethyl-4,7-diphenyl-1,10 phenanthroline, or Bathocuproine. The phenanthroline ligand on the molecule has the two nitrogen atoms. Each has two electrons to donate, which are the binding sites for divalent ions<sup>6</sup>.

## Experimental Details

PICM sensors were used to determine the presence of metal ions in an indifferent aqueous solution, NaCl. A separate experiment was performed on each of the four metals to determine whether any of the analytes would change the photo-voltages of the sensors by chelating with the Bathocuproine.

First, the sensors needed to be custom made in the PICM laboratory. The circuit board were ordered with the correct alignment and spacing of electric leads.

Each sensor was then cut out from the board, sanded, insulated with epoxy, and coated with a protective plastic called parylene. It has been found that UV light from the strobe in the experimental setup degrades the parylene. This would cause the photo-voltage readings of the sensor to be unstable. To remedy this, before each sensor was used in an experiment, it was placed for 5 minutes into a cuvette with 2 mL of a 1 mM NaCl solution and in between two UV lamps. This solution was used because that is the same volume and concentration of NaCl as was used in the experiments. After this exposure, sensors previously used by PICM group researchers were determined to give stable photo-voltages. At this point, if the readings changed, were theoretically due to the interactions of the solution in the cuvette and the PAM on the sensor, and not the parylene degradation.

For experimentation, a sensor was cleaned by being rinsed in filtered water and air dried. It was then placed into a cuvette of 2 mL of 1 mM NaCl and hooked up to the electrometer. Light from the strobe was manually focused on the center of the platinum dot of the sensor.

Control readings with no PAM or analyte were first taken for each sensor before an experiment. Various long pass optical filters with cutoff wavelengths were used to control the portion of the spectrum of light struck the sensor (to measure in which wavelength of radiation coming from the strobe the photo-voltage changes occur). The wavelengths of the filters used included those greater than 585 nm (red filter), those greater than 387 nm (Plexiglas filter), those greater than 301 nm (Pyrex filter), and those greater than 230 nm (no filter). The no-filter readings were the most indicative of amplitude variation since those readings allowed the most UV light through and Bathocuproine is clear in solution. This suggests that it does not absorb light in the visible part of the spectrum but does absorb in the UV part. This is why no-filter readings, which let the most UV light through, are used in the all data analysis described here.

The sensor was then dipped in a 1 mM solution of Bathocuproine in the solvent acetone. This would create a thin layer of the Bathocuproine on the sensor once the

acetone evaporated. This methodology has been previously utilized by PICM researchers. A thin layer of PAM on the surface is desirable because with more layers, limited chelation would occur mostly the top layers and would not be transmitted through to the actual surface of the sensor, reducing PICM and thus the photo-voltage of the sensor<sup>4</sup>. The photo-voltages were taken again after the Bathocuproine application with the same cuvette and solution of NaCl.

For each separate metal analyte, a stock container of that metal in the solid, powder form was obtained. All metals were obtained in their salt form, i.e., bonded to  $\text{Cl}_2$  in the case of the divalent metals, and to Cl in the case of CuCl. Different concentrations of that analyte in filtered water were made up. The concentrations were 0, 20, 50, 100, 300, 600, and 900  $\mu\text{M}$ .

Readings with each successive concentration of analyte in the cuvette were taken. The photo-voltages before and after the addition of the analyte-PAM pair were compared for photo-voltage differences for that specific sensor.

For every reading taken, two consecutive readings were also taken with the same electrode at fifteen second intervals. The average value and standard deviation of the no-filter photo-voltage is readings plotted in Figs.6-10. The readings of the original control photo-voltages of the pristine sensor were subtracted from each reading so that each sensor's experimental photo-voltage values could all start at the same 0 mV reference point.

Also, in Figs. 6 – 10, a line was fit to connect the data points to make the relationship between increasing concentrations and photo-voltages clearer. See Appendix for standard deviation calculations and average photo-voltage values for each experiment.

This methodology was repeated in all experiments described in this project for each separate sensor. All experimental data were recorded using a Tektronix model TDS 2014 digitizing 1 GHz oscilloscope. An example of traces produced by the oscilloscope can be seen in Fig. 4.

#### Oscilloscope Traces of Photo-Voltage versus Time Readings for $\text{CuCl}_2$ Run on Electrode 238

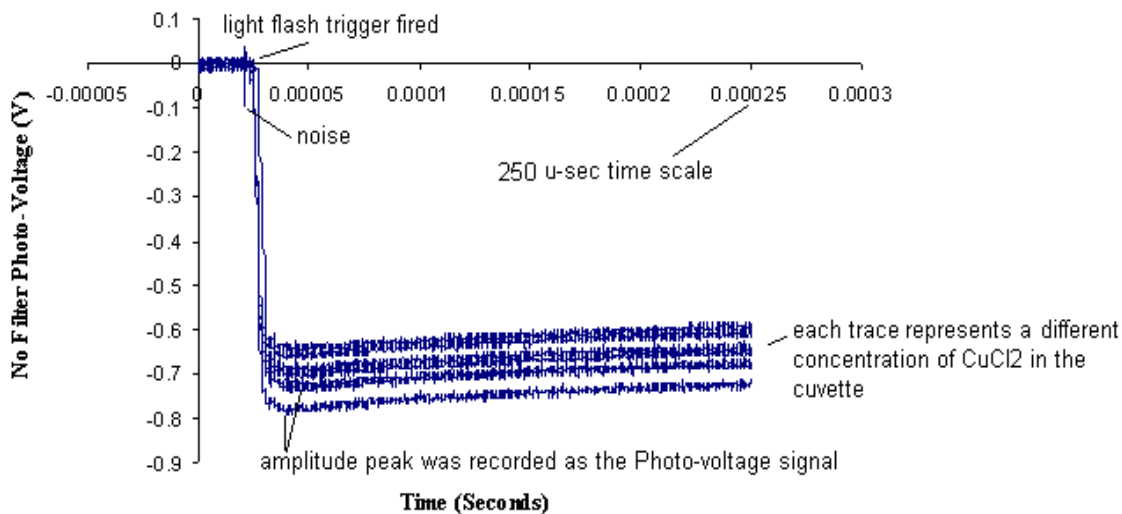


Fig. 4. Oscilloscope Traces of Photo-Voltage versus Time Readings for  $\text{CuCl}_2$  Run on Electrode 238. Most other traces look similar to this one, with the time scales and curve shapes, but with varying photo-voltage amplitudes. The flat part is before the strobe fires, at 0 volts. Minor “noise”, or radiofrequency

interference from flashing the trigger, occurs when the strobe trigger is fired. The rest of the signal is the photo-voltage of the sensor. This maximum amplitude peak is what was recorded in the experimental data as the Photo-voltage signal. NOTE: these are the readings for electrode 240 BEFORE the differences from the pristine sensor signal (-138 mV) were subtracted out from all of the readings.

For all of the data discussed, the maximum photo-voltage peaks off of the oscilloscope readings were recorded and plotted in Figs. 6 through 10 according to the description in Fig. 4. The data were transferred to a computer running Microsoft Excel and captured and stored using LabView software. In each experiment, the amplitudes of the waveforms after the light was triggered were recorded as the photo-voltage data points. The control readings and each concentration corresponds to a separate waveform. The oscilloscope was in AC coupling mode for all experiments performed, so the waveforms seen would have naturally decreased back to baseline. A long enough time period (15 seconds) elapsed between each experimental run to allow waveforms to reach zero. However, more analysis needs to be done with rise times and waveform images.

It should be noted that the waveforms seen here are fairly flat past the peak. Most waveforms go back to the 0 mV line, but at differing times. This is because the induced charges on the platinum dot move back and the induced voltage decreases back to 0 mV.

In order to determine if one can detect  $\text{MgCl}_2$  or  $\text{FeCl}_2$  in the presence of other divalent ions, experiments were conducted by adding 100  $\mu\text{M}$   $\text{CuCl}_2$  as an interferer in both experiments. In these experiments, 100  $\mu\text{L}$  of  $\text{CuCl}_2$  solution was added to the cuvette before  $\text{MgCl}_2$  or  $\text{FeCl}_2$  were added in increasing concentrations as described above. This way, there would be a constant concentration of  $\text{CuCl}_2$  in the cuvette. The purpose of these interferer experiments was to see if  $\text{CuCl}_2$  interfered with the bonding of  $\text{MgCl}_2$  or  $\text{FeCl}_2$  to the Bathocuproine, thus testing whether the  $\text{MgCl}_2$  or  $\text{FeCl}_2$  could be specifically sensed, or whether  $\text{CuCl}_2$  would interfere with the sensing of the two distinct divalent metals.

(It should be noted that the interferer graphs are plotted on a different scale than the other graphs. The interferer photo-voltage reading graphs introduce a 100  $\mu\text{M}$   $\text{CuCl}_2$  reading, and thus cannot be plotted versus increasing concentration metal analyte due to the introduction of  $\text{CuCl}_2$ . Thus, those graphs are plotted with series titles along the x-axis rather than scaled concentration readings like the other graphs. The only difference in scaling is caused by the individual sensor's photo-voltage output.)

The stability of the light intensity with each flash striking the dot was investigated by PICM researchers. See Fig. 5 for a graph of intensity as a function of wavelength on the spectrometer probe which illustrates this saturation of light. To produce Fig. 5, the probe tip was positioned where the light would strike the platinum dot. The input diameter of the spectrometer probe is 4mm, while the area of the platinum on the electrode is 3mm. The light measured by the spectrometer probe that actually does not illuminate the platinum/parylene coated circle on the electrode is negligible. The integration time for this run was 1 second, but shorter times were also used, all giving the same saturation effect with this instrument and procedure. These measurements were not taken through a cuvette, or through the water through which the light travels when performing actual experiments (which would cause a reduction in light intensity through a cuvette and solution). A neutral density 50% UV-Visible filter was then used in a second trial to obtain a clearer graph, but the same saturated pattern was seen. Spectrophotometer investigation with shorter integration times comparable to the sweep

time of the flash trigger for the experiments needs to be investigated. Other filters were not used since they would have cut off the UV range wavelengths. More investigation needs to be done to determine whether light of a consistent intensity is striking the sensors.

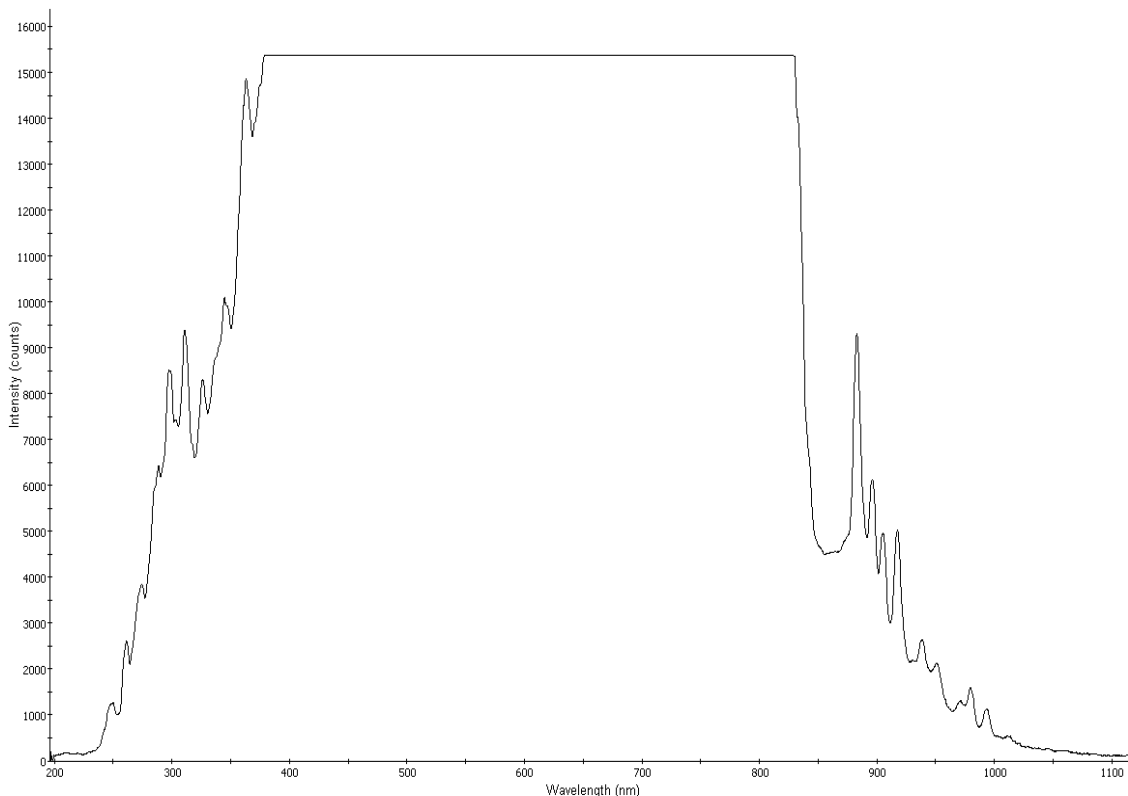


Fig. 5. A Graph of Light Intensity Versus Wavelength for the Light Intensity on the Strobe Light. In the PICM experimental setup, this is as it would appear on the platinum dot of an electrode. This data was taken by Brian Stradelmaier of the PICM group with an Ocean Optics spectrometer system.

## Experimental Results and Discussion

The results of the  $\text{MgCl}_2$ ,  $\text{FeCl}_2$ , and  $\text{CuCl}_2$  experiments are given in Figs. 6, 7, and 8, respectively. It can be noted that in both the  $\text{MgCl}_2$  experiment (Fig. 6) and in the  $\text{FeCl}_2$  (Fig. 7) experiment, the photo-voltage amplitude values increased with analyte concentration. This data suggests that  $\text{MgCl}_2$  and  $\text{FeCl}_2$  complexes with Bathocuproine because they give significant changes (i.e., greater than a 300 mV change from no analyte to 900  $\mu\text{M}$  analyte) in the photo-voltage amplitudes with increasing concentration of analyte in the cuvette.

The sensitivity of the concentrations in the  $\text{MgCl}_2$  and  $\text{FeCl}_2$  experiments may be inferred from the curves seen in Figs. 6 and 7. For instance, if one wanted to infer the response of electrode 234 at a 500  $\mu\text{M}$  concentration of  $\text{FeCl}_2$ , Fig. 7 implies that it would be close to -100 mV. If saturation of bonds occurs in the electrode, concentration cannot

be determined past that point. Saturation may have occurred if the concentrations of both analytes in these two experiments continued to be increased past 900  $\mu\text{M}$  concentration.

In both cases, the analyte concentration decrease fits a third degree polynomial curve for the concentrations of analyte tested, even though for the  $\text{MgCl}_2$  experiment, the trendline increases more rapidly and levels off faster in the  $\text{FeCl}_2$  experiment. The  $R^2$  value for a third degree polynomial in the data plotted for the  $\text{FeCl}_2$  experiment in Fig. 6 was 0.7499 and for the  $\text{MgCl}_2$  experiment in Fig. 7 it was 0.9732. Although for the  $\text{MgCl}_2$  experiment, many of the data points are within one standard deviation of each other, which implies statistically insignificant differences in the values, there is still a clear trend visible in the photo-voltages with increasing  $\text{MgCl}_2$  concentration. For the  $\text{FeCl}_2$  experiment, only the last three points are within one standard deviation of each other. This implies that the photo-voltage changes are caused by either some PICM mechanism or by a variety of experimental inconsistencies. Possibly, the last three data points also could suggest that the  $\text{FeCl}_2$  on the electrode saturated and so no further statistically significant changes in the photo-voltage were seen. There is also a noticeably larger fractional decrease in signal in the  $\text{FeCl}_2$  experiment. The interpretation of these results remains unclear.

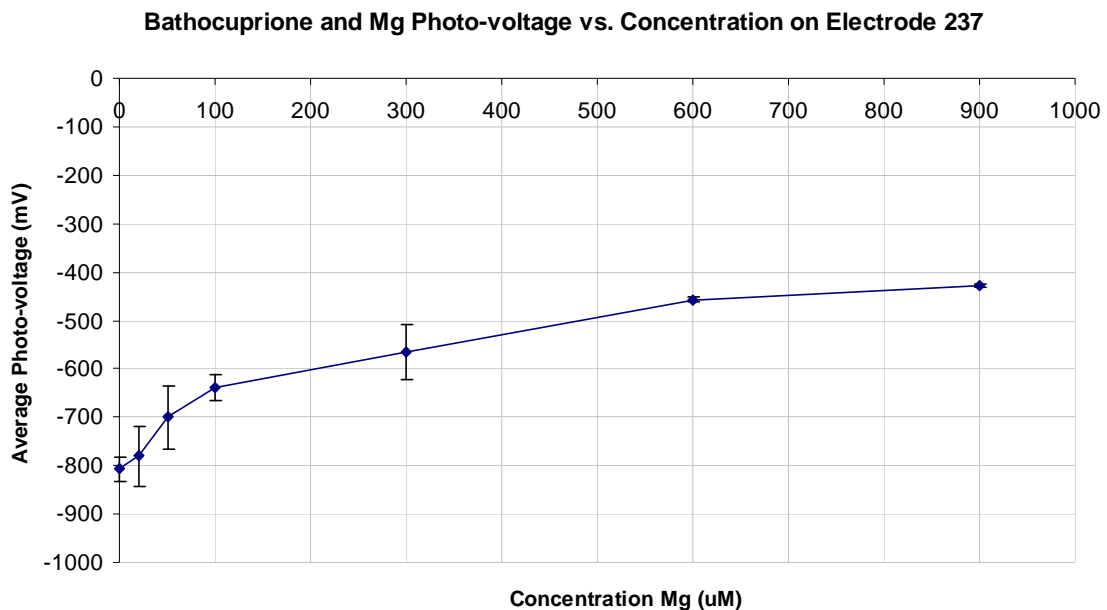


Fig. 6. Bathocuproine and Increasing  $\text{MgCl}_2$  Experiments on Sensor 237.

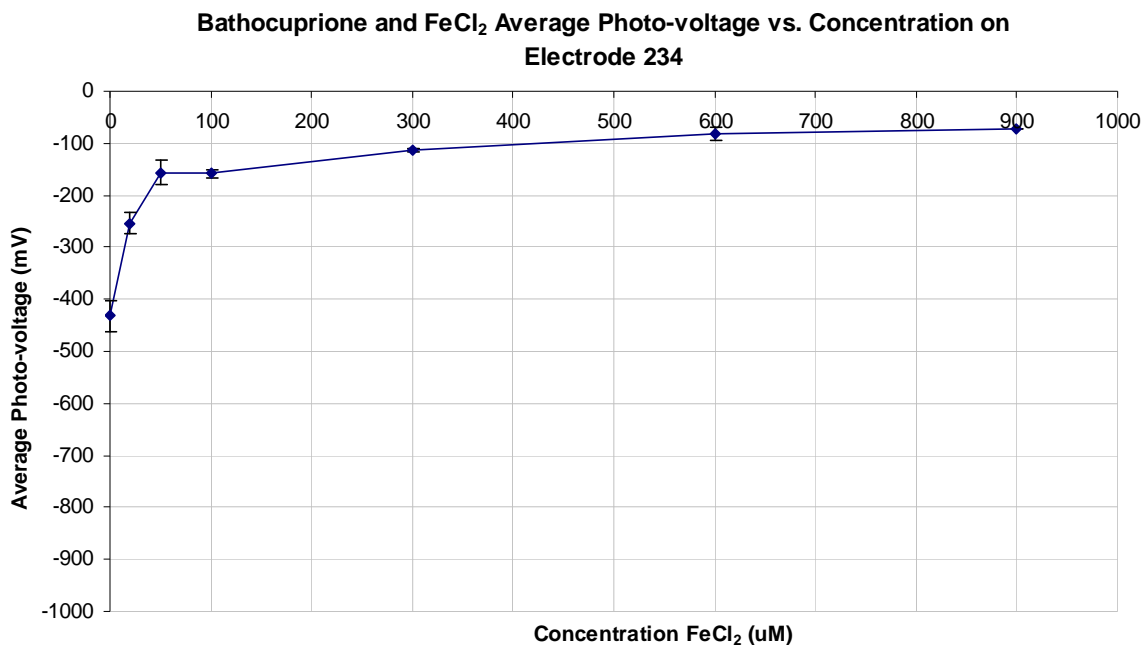


Fig. 7. Bathocuproine and Increasing FeCl<sub>2</sub> Experiment on Sensor 234.

The CuCl and CuCl<sub>2</sub> experiments turned out differently. Both the CuCl and CuCl<sub>2</sub> photo-voltage experiment curves (Fig. 8) remained almost flat (i.e., less than 100 mV change for all values and within one standard deviation of each other for most of the values). The almost flat curve for both the CuCl<sub>2</sub> and CuCl<sub>2</sub> experiments suggests that either a similar mechanism is causing the bonding of the different species or that both chelate strongly enough to Phenanthroline and saturate all of the available bonds on the sensor at or below 20 μM (the smallest concentration of both ions introduced into the cuvette). A possible reason for the similarity between the results with both copper ion species may be that CuCl<sub>2</sub> is reduced to CuCl in the solution, an effect studied independently by both Perreira et. al. and Matsushita et. al.<sup>12,13</sup>.

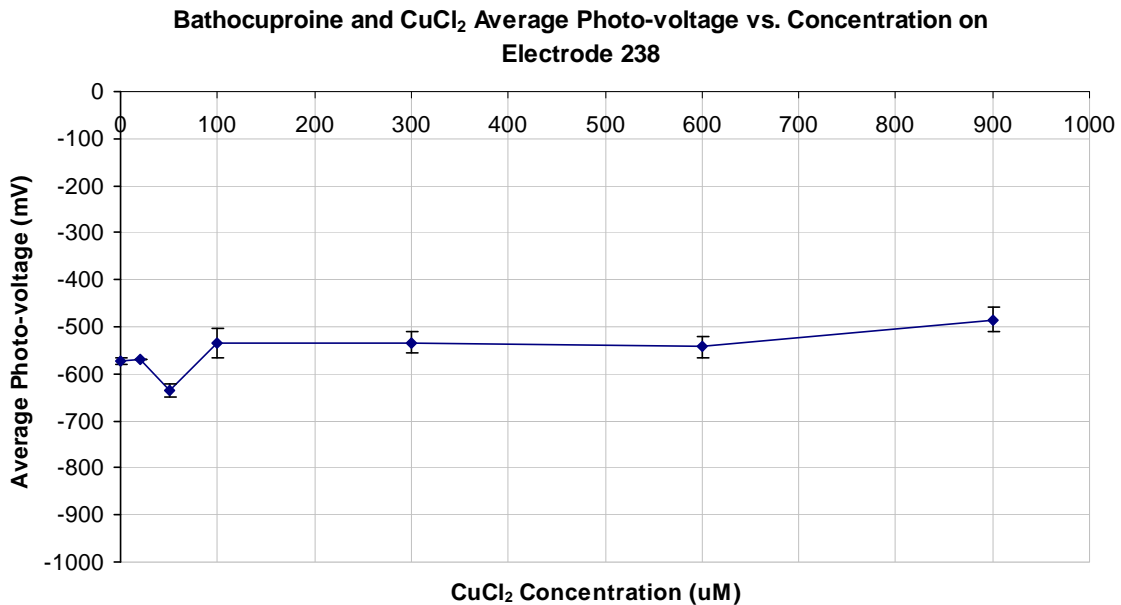
The photo-voltages for the CuCl and CuCl<sub>2</sub> experiments did not change by more than 100 mV over the course of the experiment. This pattern has been established by testing other sensors using the same methodology in the cases of both CuCl and CuCl<sub>2</sub> and Bathocuproine. The CuCl and CuCl<sub>2</sub> experiments suggest that copper may not complex with Bathocuproine since the photo-voltages did not change with increasing concentration of either type of copper. Or, it is possible that the chelated complexes do not modify the photo-voltages. On the other hand, it is possible that the copper bonds so strongly to the Bathocuproine and thus saturated the phenanthroline bonds at 20 μM of either CuCl or CuCl<sub>2</sub>. This may have prevented the increased concentrations to affect the photo-voltages.

Also, the fact that the standard deviation bars overlap if the CuCl and CuCl<sub>2</sub> experiments were superimposed on top of each other further implies that the reduction theory studied by both Perreira et. al. and also Matsushita et. al. may be true. See Fig. 8 for this data.

Both the CuCl and CuCl<sub>2</sub> experiments show an inconsistency. In both cases, from the first value, which is the value with no metal analyte, to the value with 20 uM analyte,

there is no statistically significant change in photo-voltage. This is true since in both copper experiments, these two points are within a standard deviation of each other. This pattern is not seen in any of the other experiments described. In all other cases, even in the interferer experiment data, a significant increase in photo-voltage was seen since in all but the  $\text{MgCl}_2$  experiments. This increase is a statistically significant one from no analyte concentration to 20  $\mu\text{M}$  concentration.

This inconsistency was investigated by repeating both  $\text{CuCl}$  and  $\text{CuCl}_2$  experiments on different sensors. It was found that in all other repeated experiments, the photo-voltages did in fact significantly increase from no analyte readings to 20  $\mu\text{M}$  analyte concentration readings. That data is not displayed because some of the data was biphasic, i.e., the waveform did not level off at a maximum amplitude, but increased to a positive photo-voltage. The interpretation of these biphasic results is unclear, even though the maximum amplitudes of all of the data and the first two points of the data fit the patterns described here. Also, the electrodes seemed to display a similar pattern of reaching a point of no significant photo-voltage changes with increasing concentration. This point was reached at different concentrations of copper in each experiment. The consistency of the statistically insignificant change pattern in all repeated experiments with both  $\text{CuCl}$  and  $\text{CuCl}_2$  is notable, still. The no-change pattern in the copper experiments suggests that PICM results are reproducible, even if it is currently unclear why these copper experiments seem inconsistent. Experimental error may have caused these results. It is possible that a circuit issue occurred in the setup, or that perhaps copper settled to the bottom of the cuvette and was therefore not bonded and sensed.



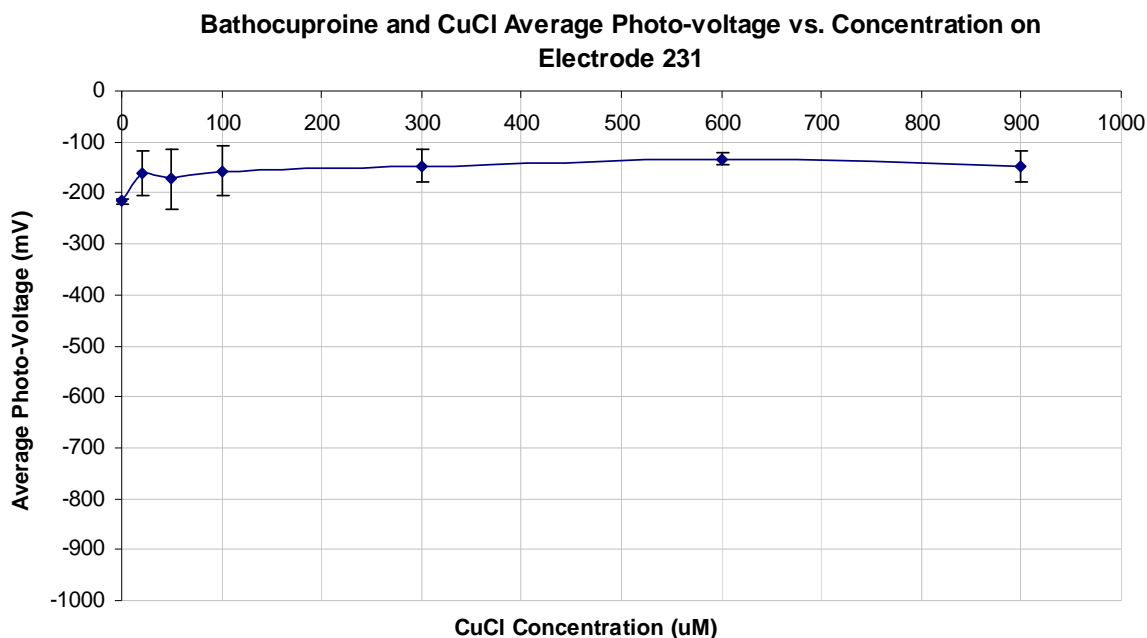


Fig. 8. A comparison of Bathocuproine and Increasing  $\text{CuCl}_2$  Experiment on Sensor 238 (top) and Bathocuproine and Increasing CuCl (monovalent copper) Experiment on Sensor 231 (bottom).

The interferer data for the experiment with  $\text{MgCl}_2$  and  $\text{CuCl}_2$  as the interferer can be seen in Fig. 9 and the experiment with  $\text{FeCl}_2$  and  $\text{CuCl}_2$  as the interferer can be seen in Fig 10. It is possible that  $\text{CuCl}_2$  (and thus possibly CuCl, if  $\text{CuCl}_2$  is reduced to CuCl) chelates more strongly than the  $\text{MgCl}_2$  or  $\text{FeCl}_2$ . This may be true since neither the  $\text{MgCl}_2$  nor the  $\text{FeCl}_2$  interferer experiments showed much of a photo-voltage change when  $\text{CuCl}_2$  was used as an interferer for both.

A possible explanation for the interferer results with the  $\text{CuCl}_2$  is that whichever metal ion first reaches the phenanthroline, it bonds strongly enough and saturates the bonds so that there are none left for any other ions introduced afterwards, even in increased concentrations.

The interferer experiments may also suggest that probably the  $\text{Cu}^{+1}$  ions, since  $\text{Cu}^{+2}$  likely reduces to  $\text{Cu}^{+1}$ , inhibit  $\text{MgCl}_2$  and  $\text{FeCl}_2$  from complexing with Bathocuproine. It could also be that the copper bonds may bond more strongly than other metal ions in general, because  $\text{Cu}^{+1}$  is smaller in size and takes up more available bonds<sup>7</sup>. Therefore, they saturated on the sensors at or below 20  $\mu\text{M}$ , and thus no further photo-voltage changes were seen. Further experimentation with other metals as interferers needs to be performed to certify this theory that copper bonds more strongly than other ions.

The overall trend in both experiments is that of a fairly constant (less than 50 mV) Photo-voltage curve versus increasing concentrations analyte. The same  $\text{MgCl}_2$  experiment was reproduced with electrode 77 (see Fig. 9), but the data was questionable because the original photo-voltage of the sensor used was positive, unlike all of the others. It is possible that electrode 77 gave the positive photo-voltage originally and after being coated with Bathocuproine because it was not pristine like the others, but used, cleaned, and recoated with parylene. The flat curve for interferer experiments, and the

questionable experiment, suggests that they are reproducible, given the inconsistencies.

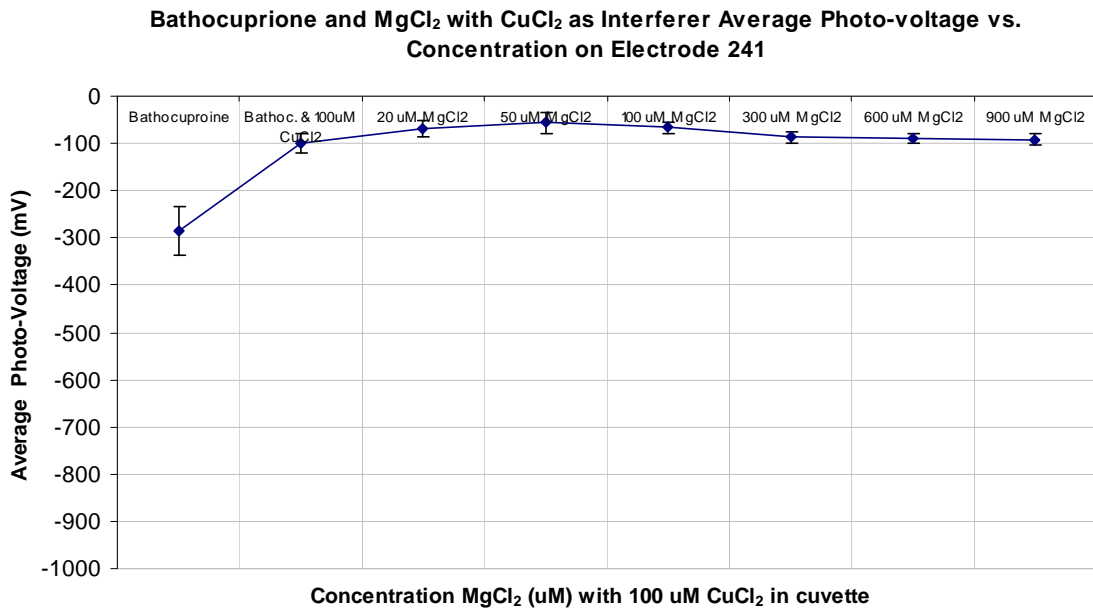
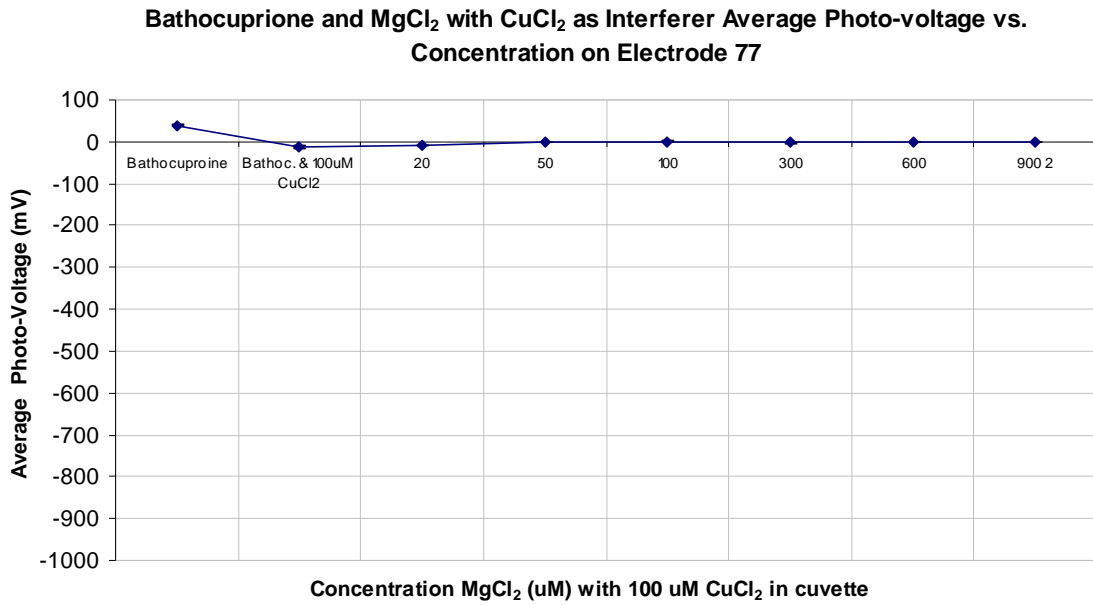


Fig 9. Bathocuproine with MgCl<sub>2</sub> and CuCl<sub>2</sub> as an Interferer Experiments on Sensors 77 (top) and 241 (bottom), respectively.

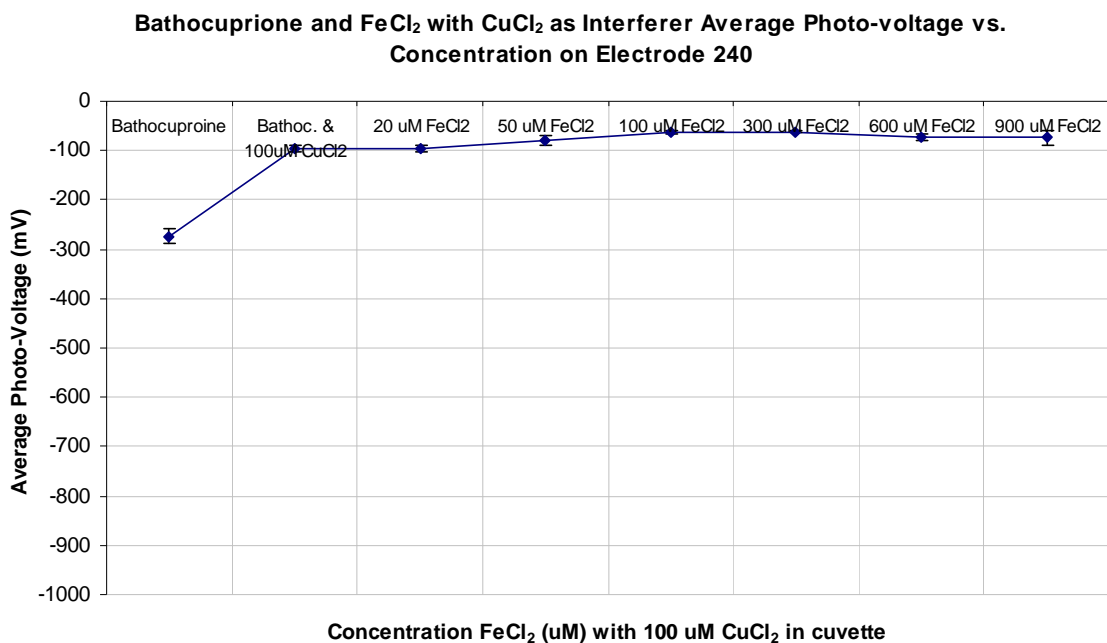


Fig. 10. Bathocuproine with FeCl<sub>2</sub> and CuCl<sub>2</sub> as an Interferer Experiment on Sensor 240.

## Conclusions

The experimental data in general suggests that all of the metal analytes tested chelate (or at least react with) with Bathocuproine. There seems to be a varying degree of chelation. Bonding chemistry needs to be studied to further interpret these results.

The CuCl<sub>2</sub> did interfere with the detection of distinct metals, as seen in the interferer data with both MgCl<sub>2</sub> and FeCl<sub>2</sub>, implying that Bathocuproine does not successfully detect particular divalent metals when interferer copper ions are present. This may also be true for other interferer ion and target analyte combination experiments; further interferer experiments need to be performed.

Even though this research has not yet successfully produced selective sensors, detection of the analytes studied has been achieved. There are reasons why the Bathocuproine and analyte pairs studied cannot be considered successful PICM detectors, even though Bathocuproine is a PAM with the analytes tested and has its photo-voltages modified by them. The interferer results show that the sensors respond non-selectively to the analytes in solution, producing no photo-voltage changes for increasing concentrations of the analyte under investigation when a second analyte was constantly present in the solution. Also, custom-made nature of each sensor introduces variability in each experiment which makes definite conclusions in the data difficult to find.

Lastly, the experimental setup introduces variability, as well. It is uncertain that the same intensity of light hits the platinum dot each time, making the actual photo-voltage readings of the sensors uncertain. This is because with each different sensor and experiment, the light may not be focused directly on the center of the platinum dot, and because the intensity each time may not be the same. Different methods of testing the intensity need to be investigated. Also, the dipping method for getting the Bathocuproine on the sensor surface may not be the best way to ensure that a thin enough layer of

Bathocuproine molecules covers the platinum dot. This causes uncertainty as to whether the chelation is detected as it should be.

Another issue with the UV light in the setup is that it may degrade the PAM on the sensor with multiple no-filter flashes, so the photo-voltages may not be accurate. Even though the sensors were exposed to a UV lamp for 5 minutes to prevent parylene degradation, there currently is no standardized way of preventing the PAM degradation.

Also, when sensors are dipped into the same Bathocuproine solution many times, a small amount of acetone evaporates from its container each time. This makes the concentration of Bathocuproine molecules on the dot variable, and thus causes inconsistent methodology.

Also, the dipping method causes Bathocuproine molecules to stick to not only the dot, but the plastic surrounding it. This causes chelation to take place on the plastic surrounding the dot, but these processes cannot be measured or studied because there is no way to detect the PICM activity on any part of the sensor other than the platinum dot. A method of using a pipette to place PAMs only on the dot only has been previously investigated by PICM researchers. This method does not allow a thin enough layer of molecules to be placed on the surface.

We are unsure about another procedure. It is uncertain whether analytes placed in the cuvette at various times respond differently. Also, it is unclear if the PAMs can become less reactive after a certain time, both on the sensor or in solution.

Although there is variability from sensor to sensor, the repeated  $MgCl_2$  interferer experiments showed a similar flat photo-voltage curve. Also, reproduced experiments were performed numerous times with  $CuCl_2$  and different sensors. Those results showed a similar flat photo-voltage curve trend to the  $CuCl_2$  experiment trend discussed. Each photo-voltage reading with increasing concentration either type of copper ion was within one standard deviation of the others. These and  $MgCl_2$  interferer results imply that reproducibility is at least possible with the given inconsistencies of the setup and sensors. Still, further reproducible results need to be performed with different sensors but more standardized procedures.

Another uncertainty remains in this data. Since many of the results suggest that at some concentration, the phenanthroline bonds may or may not be saturated, then increasing concentration of metal analyte after that point does not change photo-voltage. This way, one cannot accurately determine the concentration of metal analyte present.

There are many overall challenges in this PICM work for determining whether PICM sensors with Bathocuproine on their surface are indeed detectors of the metals tested. Overall, experimental inconsistencies, uninvestigated questions, and ambiguities of the data all suggest that a conclusion as to how Bathocuproine and  $MgCl_2$ ,  $FeCl_2$ ,  $CuCl$ , and  $CuCl_2$  function as successful PICM sensors cannot be currently made without further research.

This is true even though this work does further the overall goal of PICM. Still, progress could be made in the future toward developing sensor arrays in which one sensing element among other distinct ones would be Bathocuproine.

## **Further Studies**

Further experimentation needs to be performed with different concentrations of all the analytes used in order to determine whether the photo-voltage could go to zero, or if it would stop increasing at a certain concentration when chelation would saturate. Different divalent metals need further experimentation, such as  $ZnCl_2$ . Also, interference from other divalent metal ions could be investigated, using different combinations of interferers and analytes. For example, the interference of  $100 \mu M$  (or another concentration) of  $FeCl_2$  could be investigated in an experiment of increasing  $MgCl_2$  analyte concentration.

The mechanisms other than chelation could also be further investigated by analyzing the time duration of the photo-voltage signals, rise times of the signals, and the properties of the molecule bonding. Further investigation of the chemistry needs to be performed.

EDAX (Energy Dispersive X-ray analysis) and Environmental Scanning Electron Microscope (ESEM) analysis may be performed on the sensors to study how much of which metals are bound to the PAMs. The EDAX feature determines the abundance of specific elements on a sample surface. Preliminary analysis has been performed with the EDAX, but it was inconclusive.

### Appendix

The following tables correspond to each experiment done, in the same order they appear in the Results and Discussion section (Figs. 6 through 10). The standard deviation,  $\sigma$ , for the photo-voltage for each concentration of analyte was determined by obtaining three experimental values of each no-filter reading for each concentration of analyte and calculating the deviation using the following formula:

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{(n-1)}} \quad (1)$$

where  $n$  is the number of samples,  $x_i$  is each photo-voltage reading, and  $\bar{x}$  is the average of the three readings. The data is as follows:

MgCl <sub>2</sub> Concentration ( $\mu M$ )	Photo-voltage (mV) Flash 1	Photo-voltage (mV) Flash 2	Photo-voltage (mV) Flash 3	Average Photo-Voltage	Standard Deviation
0	-810	-830	-780	-806.6666667	25.16611478
20	-800	-830	-710	-780	62.44997998
50	-690	-770	-640	-700	65.57438524
100	-650	-660	-610	-640	26.45751311
300	-550	-630	-520	-566.6666667	56.86240703
600	-450	-460	-460	-456.6666667	5.773502692
900	-425	-430	-430	-428.3333333	2.886751346

Chart 1. Data for Bathocuproine and increasing  $MgCl_2$  experiments on Sensor 237.

FeCl <sub>2</sub>	Photo-voltage	Photo-voltage	Photo-voltage	Average	Standard
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concentration ( $\mu\text{M}$ )	(mV) Flash 1	(mV) Flash 2	(mV) Flash 3	Photo-Voltage	Deviation
0	-465	-425	-405	-431.6666667	30.55050463
20	-275	-250	-235	-253.3333333	20.20725942
50	-175	-165	-130	-156.6666667	23.62907813
100	-150	-165	-160	-158.3333333	7.637626158
300	-115	-115	-110	-113.3333333	2.886751346
600	-68	-90	-90	-82.66666667	12.70170592
900	-72	-72	-73	-72.33333333	0.577350269

Chart 2. Data for Bathocuproine and increasing  $\text{FeCl}_2$  experiment on Sensor 234.

$\text{CuCl}_2$ Concentration ( $\mu\text{M}$ )	Photo-voltage (mV) Flash 1	Photo-voltage (mV) Flash 2	Photo-voltage (mV) Flash 3	Average Photo-Voltage	Standard Deviation
0	-570	-570	-580	-573.3333333	5.77
20	-570	-570	-570	-570	0.00
50	-650	-630	-625	-635	13.23
100	-570	-520	-515	-535	30.41
300	-560	-520	-520	-533.3333333	23.09
600	-570	-530	-530	-543.3333333	23.09
900	-515	-470	-470	-485	25.98

Chart 3. Data for Bathocuproine and increasing  $\text{CuCl}_2$  experiment on Sensor 238.

$\text{CuCl}$ Concentration ( $\mu\text{M}$ )	Photo-voltage (mV) Flash 1	Photo-voltage (mV) Flash 2	Photo-voltage (mV) Flash 3	Average Photo-voltage	Standard Deviation
0	-220	-220	-210	-216.6666667	5.77
20	-210	-150	-125	-161.6666667	43.68
50	-240	-150	-130	-173.3333333	58.59
100	-210	-140	-120	-156.6666667	47.26
300	-180	-140	-120	-146.6666667	30.55
600	-140	-140	-120	-133.3333333	11.55
900	-180	-145	-120	-148.3333333	30.14

Chart 4. Data for Bathocuproine and increasing  $\text{CuCl}$  experiment on Sensor 231.

$\text{FeCl}_2$ Concentration ( $\mu\text{M}$ )	Photo-voltage (mV) Flash 1	Photo-voltage (mV) Flash 2	Photo-voltage (mV) Flash 3	Average Photo-Voltage	Standard Deviation
0	-290	-270	-260	-273.3333333	15.28
Bathoc. & 100 $\mu\text{M}$ $\text{CuCl}_2$	-100	-100	-90	-96.66666667	5.77
20	-100	-100	-90	-96.66666667	5.77
50	-90	-73	-73	-78.66666667	9.81
100	-67	-62	-62	-63.66666667	2.89
300	-65	-60	-60	-61.66666667	2.89
600	-80	-70	-70	-73.33333333	5.77
900	-88	-75	-60	-74.33333333	14.01

Chart 5. Data for Bathocuproine with  $\text{FeCl}_2$  and  $\text{CuCl}_2$  as an Interferer Experiment on Sensor 240.

$\text{MgCl}_2$ Concentration	Photo-voltage (mV) Flash 1	Photo-voltage (mV) Flash 2	Photo-voltage (mV) Flash 3	Average Photo-Voltage	Standard Deviation
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( $\mu\text{M}$ )					
0	-330	-230	-300	-286.6666667	51.32
Bathoc. & 100 $\mu\text{M}$ CuCl <sub>2</sub>	-120	-80	-100	-100	20.00
20	-90	-60	-60	-70	17.32
50	-80	-40	-50	-56.66666667	20.82
100	-80	-60	-60	-66.66666667	11.55
300	-100	-80	-80	-86.66666667	11.55
600	-100	-80	-90	-90	10.00
900	-105	-80	-90	-91.66666667	12.58

Chart 6. Data for Bathocuproine with MgCl<sub>2</sub> and CuCl<sub>2</sub> as an Interferer Experiment on Sensor 241.

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