


AN ABSTRACT OF THE THESIS OF

Brian P. Armstrong for the Master of Science in chemistry presented on 12/15/97

Title: CYCLIC VOLTAMMETRY OF HETEROPOLYTUNGSTATE
COMPLEXES WITH COMPUTERIZED DATA COLLECTION.

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The results of the construction and testing of a data collection system for use with a voltammetric analysis instrument is presented. A solution of copper(II) was studied with the instrument. A miniature electrode with a 0.5mm diameter graphite probe made from commercially available mechanical pencil refills was devised. Also, two heteropolytungstates, $([\text{H}_2\text{OBCo(III)W}_{11}\text{O}_{39}]\cdot\text{XH}_2\text{O})^{-6}$ and $([\text{pyrSiCo(III)W}_{11}\text{O}_{39}]\cdot\text{XH}_2\text{O})^{-6}$ were examined in the presence of 2-propanol. The 2-propanol was found to have little effect on the tungstates in the presence of the graphite electrode.

CYCLIC VOLTAMMETRY OF HETEROPOLYTUNGSTATE
COMPLEXES WITH COMPUTERIZED DATA COLLECTION

A Thesis

Presented to

the Division of Physical Sciences

EMPORIA STATE UNIVERSITY

In Partial Fulfillment

of the Requirements for the Degree

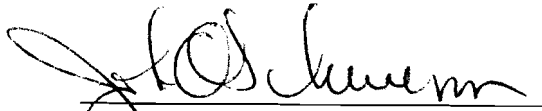
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by

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Approved for the Graduate Council

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I would like to thank Dr. Arthur Landis and the Emporia State University Physical Science Department, for their patience and support in the completion of this thesis

“Computers allow one to collect a great deal of very rapidly. They also help to make sense of the embarrassingly large amount of data collected.”

W.G.D.

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Chapter 1. Introduction

Objectives

The primary goal of this research was to develop a data collection system to enable the collection and analysis of cyclic voltammetry data without the use of an X-Y plotter. Collection of the data by a computer allows a greater variety of analysis options. For example, peak positions could easily be determined through numerical differentiation of the data and noisy data could be improved through the use of any number of smoothing algorithms. Also, as most X-Y plotters are limited to sweep rates slower than 500 mV/s, while acquisition of the data through the use of a computer affords access to sweep rates in the thousands of mV/s.

The computer interface hardware available in the department consisted of a low cost analog to digital conversion card purchased from Computer Boards Inc. of Boston, MA. This part of the research project required the installation of the card and verification of its proper operation.

Also, this research project was to determine if it was possible to make electrodes from commercially available graphite in the form of refills for mechanical pencils. The refills are readily available and inexpensive. Another part of the research project was to examine an aqueous copper solution and salts of two heteropolytungstate anions in the presence of simple organic ligands using the apparatus constructed above to verify that the interface was collecting data properly.

Background on Heteropolytungstates

In general, polytungstates are molecules containing more than one tungstate group, $(\text{WO}_4)^{-2}$. Tungstate groups share oxygen atoms in large complexes. Heteropolytungstates contain in addition to the tungsten and oxygen atoms, at least one other non-hydrogen atom in the anion. The crystals generally contain several waters of hydration, such as $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$ and $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 13\text{H}_2\text{O}$. A good background is given in the master thesis of Lou [1] and the references therein.

Chapter 2. Materials and Methods

Instruments

IBM Voltammetric Analyzer

The primary chemical analysis instrument used was an IBM EC225 Voltammetric Analyzer in the three electrode mode. The three electrodes in the cell were a 1.00 molar calomel electrode(NCE), a platinum auxiliary electrode, and a 0.5 mm diameter graphite working electrode. The graphite electrode was made by supporting the graphite core from a commercially available mechanical pencil refill (0.5 mm diameter) in a Fisher Pasteur pipette. The pencil leads were Pentel brand. The entire graphite electrode, except for the end surface, was coated with paraffin to ensure that the conductive area of the electrode remained a constant 0.79 mm^2 . The instrument has an output of 1 volt when the instrument displays a full scale reading.

The instrument itself allows the analyst to control the sweep rate, endpoint potentials, and the sensitivity of the detector. Potential sweeps are controlled by the instrument and can vary from a simple linear increase, to an increase to a maximum and back to the starting potential.

Computer Boards DAS08/Jr

The voltammetric analyzer was interfaced to a 386 personal computer with 8MB of memory through a data acquisition card manufactured by Computer

Boards Inc. of Boston, MA. The interface card performed the conversion of the analog output of the voltammetric analyzer to a digital signal which could be stored and interpreted by the computer. The data were collected with 8 digits of precision, and an accuracy of 1% of the least significant figure. The card itself had a data buffer with 2048 bytes of memory to prevent the loss of data in case the input changed more rapidly than the data could be saved to disk.

The analog to digital(A/D) conversion was achieved through the successive approximation method. The successive approximation method in general is efficient, accurate, and very common in today's instrumentation[2]. The method allows rapid conversion of input voltages over a wide range of values, with equal speed for all values. The method uses an internal voltage reference for comparison purposes. When an incoming signal is detected, the input is compared to half the maximum value of the internal reference. If the input is greater than the present value of the internal reference, half of the present value of the reference is added to the internal reference and a second comparison is made. If the input is less than the reference, half of the present reference value is subtracted and a second comparison is made. This process continues until the two values are equal within the accuracy of the measurement devices. The acquisition card has an accuracy of 0.1% of the lowest significant figure, this means that a value of 0.005 would be accurate to ± 0.0005 . Figure 3 has an indicator of the relative size of the error in this experiment.

Personal Computer and Software

The software supplied with the interface card, DataLab Solution[®], represents data manipulation procedures through the use of square symbols called blocks. These blocks allowed simultaneous collection of both voltage and current in the electrochemical cell and estimation of the first and second derivatives of the incoming data. The blocks can take on a variety of functions from simple analog collection, to mathematical functions. One of the block types allows the user to save data to a file. A description of DataLab Solution[®] is found in Appendix 1.

The data were saved to the hard drive as delimited text files. The text files were in ASCII format and comma delimited. In addition to the raw data, the files included a header portion which could be edited by the operator and could contain up to a maximum of four lines of text. The files were named with the date of collection and a number corresponding to the number of the scan. For example, in this study the first scan of the day was named with the date of collection, the number zero, and the MSDOS[®] file extension PRN. The text files were loaded into Microsoft Excel[®] for further analysis.

To aid in the determination of peak parameters, the data were also analyzed with PeakFit[®], a curve fitting program from Jandel Scientific. The voltammograms were split into the forward and reverse halves of the sweep and loaded into PeakFit[®] for analysis. PeakFit[®] facilitated fitting the data to a set of double sigmoidal functions. Since the peaks have the same form as sigmoidal polarographic curves, symmetric double sigmoidal functions were used to model

the data during the analysis. A sample deconvolution of a reverse sweep is shown in Figure 12. Any data set which had peaks towards negative current had to be inverted by multiplication by negative one. This ensured that the program would fit the peaks and not try to fit valleys between peaks to a positive peak. Quality of fit was judged by the square of the correlation coefficient and the distribution of the residuals.

Temperature Control

The cell was placed in a custom-fitted thermal jacket which was connected to a circulating water bath maintained at 25° C. The thermal jacket consisted of a copper coil fitted around the cell and held in place with a solder with a low melting point. This device was made by Mr. Roger Ferguson of ESU, Division of Physical Sciences.

Oscilloscope

A BK Precision 30MHz dual channel oscilloscope was used to aid in the selection of the voltage range and rate of the scan. An aliquot of sample was placed in the cell and scanned continuously while the scan rates and initial and final voltages were varied until a typical analyte response was obtained.

Chemicals

Heteropolytungstate Solutions

The samples of the various heteropolytungstates were synthesized by previous researchers, and provided by Dr. Landis. The samples were dissolved in a potassium acetate/acetic acid buffer with a pH of 5.11 and 1.0 mol/L of sodium sulfate to serve as an electrolyte. The total acetate/acetic acid concentration was 1.0 mol/L, and the pH was measured with a Checker pH pen calibrated pH 7.0 and 4.0 buffers from the Fisher Chemical Company. Potassium salts of $([\text{H}_2\text{OBCo(III)W}_{11}\text{O}_{39}] \cdot \text{XH}_2\text{O})^{-6}$ and $([\text{pyrSiCo(III)W}_{11}\text{O}_{39}] \cdot \text{XH}_2\text{O})^{-6}$ were used in 1.886×10^{-4} and 1.75×10^{-3} molar solutions respectively. Hereafter these two anions will be called the boron and silicon species respectively. The samples were both green crystalline solids. The heteropoly containing boron was a darker, uniform green while the heteropoly containing silicon had a more variegated, light green appearance.

The copper solution was prepared using a 1000 ppm copper standard with a density of 1.0080 g/mL, obtained from the Fisher Chemical Company. The standard was measured by mass into a volumetric flask and the mass of the standard was converted to a volume through the use of the density value. The standard was diluted to a final concentration of 9.373×10^{-5} mol/L by placing 1.489 mL of the standard in a class A 250 mL volumetric flask and diluted with de-ionized water to the final volume.

The isopropyl alcohol (IPA) used was HPLC grade 2-propanol purchased from the Fisher Chemical Company. In order to ensure consistency, a 25.0 mL class A volumetric flask was cleaned, dried, weighed and filled to the mark with IPA. The IPA in the flask had a density of 0.7820 g/mL and was the source for all of the IPA used in this research. This density value was used to convert masses to volumes in this work.

Oxygen Removal System

Nitrogen gas was bubbled through the sample solutions prior to voltammetric analysis to remove any oxygen interferences. The N₂ gas was first passed through an oxygen removal cartridge, a vanadium(II) solution, and finally distilled water. The cartridge and vanadium solution removed any oxygen present in the N₂, and the distilled water added moisture to the N₂ to prevent changes in sample concentration due to evaporation of the buffer in the sample.

The vanadium solution was prepared with vanadium(IV) sulfate dissolved in distilled water. Amalgamated zinc metal, pure zinc metal, and 6M sulfuric acid were added to effect the reduction of the V(IV) to the V(II) species. Early in the research, concentrated sulfuric acid was used in the reduction of the vanadium ion, but this practice was discontinued due to the formation of colorless crystals of what was assumed to be zinc sulfate. The amalgamated zinc provided a source of zinc that was consumed more slowly than the bare zinc metal.

Data Collection Procedure

Sample Analysis

Samples of the two salts were dissolved in Class A, 250.0 mL volumetric flasks with the pH 5.11 buffer. Samples of the heteropolytungstate solutions were placed in the reaction cell and purged for approximately two minutes with the N₂ gas. Scans were performed by setting the initial and final potentials and allowing the residual current to stabilize. Once the current had stabilized, the voltage was changed at a specific rate towards more negative potentials until the final potential. After the final potential had been reached, the voltage was swept at the same rate towards more positive potentials. Before the scan was initiated, the scan parameters were entered in the collection file header. After the instrument settings were set, the collection program was started and the scan was initiated. If any IPA needed to be introduced into the cell, it was added before the N₂ purge and the volume added was recorded in the collection file header.

Circuit Layout and Data Path

The voltammetric analyzer has four output lines to an X-Y plotter, lines for each of the axes, and two lines for controlling the up or down status of plotter pens. When a voltage sweep is initiated, the wires for the two axes send the voltage and current values in the cell to the plotter and the voltage of the two pen control lines goes from zero to approximately 1.3 volts. Connections were made between the interface card and the instrument through the two data lines and one

of the pen control lines. The pen control line was used as the trigger for starting collection of the data.

The collection setup in DataLab Solution[®] numbers and processes the blocks contained in the layout in the order in which they are added to the layout. To optimize the collection, the first block in the layout was configured to be an analog input block which was taking data from the junction to which the pen control line was attached. When the voltage at the pen control input went above 0.5 volts the rest of the blocks in the layout were activated and the results were saved to disk. Diagrams of the block layout and the circuit connections are in Appendix 1 as Figures 14 and 15.

Chapter 3. Results

Overall

In general, the voltammograms were resolved or deconvoluted by Peakfit[®] into four low, broad peaks in the reverse sweeps and three to four low and broad peaks in the forward sweeps. A plot of the silicate heteropolytungstate with 300mL of 2-propanol and swept at a rate of 300mV/s is shown in Figure 1 as a representative sample of the data collected. The raw data are archived on floppy disks given to Dr. Landis.

Effect of Scan Rate

More rapid scan rates seemed to increase the distance between the forward and reverse scans over the entire range of alcohol concentrations, as shown in Figure 2. The scan rate did not seem to influence the position of the peaks.

Heteropolytungstate Solutions

The plotted heteropolytungstate data appeared to have very few differences over the range of IPA concentrations. All of the scans had shallow peaks and showed almost no shifts in position with increasing IPA concentrations. Figures 3 through 6 display the variation of peak centers and heights for a fixed added volume of 2-propanol at varied sweep rates.

The data also displayed few differences in peak heights and positions over the range of added 2-propanol volumes at a fixed scan rate. Plots of peak height

against the added volume of 2-propanol showed lines of almost zero slope.

Figures 7 through 10 show the variation of peak parameters at a fixed sweep rate

over a range of 2-propanol volumes. The peak parameters over the range of

alcohol volumes are given in Tables I and II.

Table I: Peak Centers in mV

mL IPA	Forward Sweep				Reverse Sweep			
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4
0	-1.540	-0.337	0.837	1.330	-1.106	-0.473	0.190	1.147
100	-1.538	-0.321	0.843	1.318	-1.098	-0.461	0.213	0.930
200	-1.542	-0.353	0.832	1.342	-1.113	-0.485	0.167	1.363
300	-1.519	-0.274	0.920	1.327	-1.100	-0.479	0.144	0.949
400	-1.614	-0.305	0.937	1.341	-1.161	-0.622	0.018	0.851
500	-1.547	-0.296	0.799	1.299	-1.059	-0.507	0.059	0.958
600	-1.542	-0.299	0.806	1.330	-1.116	-0.561	0.089	0.947
700	-1.610	-0.524	0.729	1.336	-1.056	-0.549	0.043	0.954
800	-1.451	-0.367	0.764	1.207	-1.095	-0.478	0.157	0.778
900	-1.604	-0.349	0.815	1.288	-1.082	-0.517	0.146	0.964
1000	-1.571	-0.364	0.801	1.305	-1.134	-0.514	0.254	0.952

Table II: Peak Heights in mA

mL IPA	Forward Sweep				Reverse Sweep			
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4
0	-1.364	-0.022	1.289	1.839	-1.454	-0.483	0.535	1.671
100	-1.366	-0.005	1.296	1.828	-1.443	-0.464	0.570	1.671
200	-1.362	-0.038	1.282	1.850	-1.464	-0.501	0.500	2.334
300	-1.336	-0.282	1.375	1.827	-1.380	-0.444	0.498	1.714
400	-1.446	-0.283	1.387	1.836	-1.498	-0.676	0.299	1.571
500	-1.371	-0.275	1.236	1.792	-1.376	-0.526	0.343	1.727
600	-1.010	0.254	1.379	1.912	-1.475	-0.617	0.387	1.713
700	-1.442	-0.234	1.160	1.834	-1.272	-0.514	0.373	1.736
800	-1.228	-0.042	1.196	1.680	-1.392	-0.449	0.520	1.468
900	-1.406	-0.025	1.258	1.778	-1.376	-0.504	0.518	1.780
1000	-1.372	-0.041	1.244	1.800	-1.455	-0.499	0.685	1.761

Copper(II) Solution

The voltammograms of the copper solution had a single very strong peak

in the reverse sweep, and a very low peak in the forward sweep. The peak in the

reverse sweep occurred at 0.702 mV with a height of 2.88 mA. The forward peak was at 0.938 mV with a height of -0.946 mA. The half-wave potential from the data is 118 mV. A plot of the copper reference swept at the rate of 100 mV/s is shown in Figure 11.

Chapter 4. Discussion

Equipment Performance

The voltammetric analyzer and interface card functioned well together. One difficulty that arose was the fact that regardless of initial input voltage, the software that was collecting the data read the initial input as zero. For example, if a sweep was started at 2.0 mV, the collected data indicated that the sweep had started at 0.0 mV. However, the software provided for scaling of the incoming data, which means that the input could be linearly modified by selecting a slope and intercept to add to the incoming data. By setting the scale intercept to the value of the initial potential of the sweep, the data collected reflected the actual input to the card.

A second drawback was that this computerized data collection system made it very difficult to collect a series of sweeps as is traditional with cyclic voltammetry. With the computer, sweeps had to be collected one at a time because if the rate of the sweep changed during collection, the resolution of the data would have changed. This is because the rate of collection cannot be changed during collection. This discontinuous collection of sweeps made at different rates made it difficult to determine if the analyte was diffusing away from the electrode or absorbed on the surface in some non-electrostatic manner.

The setting up of the actual collection routine was slightly impeded by the fact that the software permitted the assignment of several parameters for each

incoming data signal. These parameters include the rate of collection, which of the eight possible input channels from which the data are to be collected, what signal will start the collection, and how to stop the collection of data. The program used icons or blocks to represent a data manipulation function. Thus if analog data are coming in through channel 1, there is an analog input block to represent channel 1. The block parameters had to be assigned individually, since it does not seem possible to assign a parameter to more than one block at a time. Also, the limitation of requiring at least two blocks to stop data collection, while not a significant impediment to this project could have an effect upon the collection rate. This difficulty would probably arise in cases where high speed data are being collected and manipulated on a slower system.

Interpretation of Results

The slight shifts in peak parameters in Figures 3 through 10 are considered to be insignificant and most likely due to variation in the fit of the data to the double sigmoidal functions. An example of the deconvoluted data is shown in Figure 12. Even though the fitted data had R^2 values of 0.90 or better, the remaining 10% of the error in the fit could have noticeable effects on the plot of the peak parameters. The double sigmoidal functions were considered to be the most appropriate model available because the ideal data should behave the same as a standard polarogram, which follows an increasing sigmoidal function.

The copper reference solution demonstrates that the data collected are in agreement with the literature which indicates that the half-wave potential can be

used as an approximation of the standard potential [6] for a reversible couple. The standard potential for a 1.0 M calomel electrode is +0.282 V and the standard potential for the reaction of copper(II) going to copper(I) is +0.153 V, which yields a calculated cell potential of -0.129 V.

Conclusion

A data collection system which allows the collection of cyclic voltammetry data in the absence of an X-Y plotter was successfully constructed. In addition, an inexpensive miniature graphite electrode was constructed and used to obtain cyclic voltammograms of aqueous copper(II) and heteropolytungstate solutions.

In conclusion, the data acquisition hardware performed as expected and collected data at a variety of rates without losing data. The software, though slightly cumbersome to use, did greatly facilitate the collection of the cyclic voltammetry data and would be useful in the collection of data in general.

The data analysis software, Peak Fit[®], was easily understood and easy to use. The portion of the analysis which took the most time, was the reformatting of the raw data into a form that allow analysis with Peak Fit[®]. The variety of functions available in the program allow the fitting of most instrumental data to known functions and provides values for most parameters of interest.

The conclusion that simple organic ligands added to the heteropolytungstates had little effect on the redox potential seems to indicate that the graphite electrode does not respond in the same manner as the dropping

mercury electrode in the presence of heteropolytungstates. Other researchers[7] have shown that the half-wave potentials of heteropolytungstates in the presence of simple ligands are altered when measured using a mercury electrode.

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Appendix 1: DataLab Solution[®]

General Layout

Construction Portion

The part of the program where the actual setup of the acquisition parameters takes place has two areas. A relatively large central area is boxed in by a set of controls on the left and a collection of boxes located along the bottom of the screen.

The boxes at the bottom are what the program call blocks. The blocks consist of a square icon which represents the collection of computer code that actually processes the input and output signals. A variety of settings are available for each block, depending on what type of signal processing functions the block is intended to perform. The program's help file has a portion devoted to the individual block types.

The Run control, located along the left side of the screen, places control of the computer in the hands of the acquisition setup in the central portion of the screen. When the Run control is clicked with the mouse the acquisition process is initiated. Depending on the block layout, some additional windows may appear during the run. If no "Vision" blocks are present in the layout, a window displaying the values of the incoming data will appear and will be continuously updated to display the incoming data. If a "Vision" block is present in the layout, a graph of the incoming data will be displayed in addition to the window with the

incoming data. With high speed incoming data on a relatively slow system care should be taken not to display too many graphs as this could overload the processor resulting in lost data.

The Icon Shelf control allows the user to temporarily take one or more blocks out of the layout without completely deleting the block. This allows the user to test individual portions of a layout without having to execute the entire layout. Blocks are placed on the shelf by dragging them there with the mouse.

The last control along the side is for removing blocks completely. Blocks that are dragged to this control are deleted along with their configurations.

Building an Acquisition Control Layout

Selecting Block Functions

The first step in constructing a layout is to determine the type of data to be collected, how fast the incoming data will be changing, and what will happen to the data after acquisition.

Most instrumental output will be in an analog form so analog input will be used the most. Check all available documentation for the instrument to verify the correct input settings are used.

Information regarding the optimal acquisition rate for a given data change rate can be found in the on-line help and in literature covering general data collection and conversion. In general, one wants to collect enough data to describe any changes in the data without being excessively redundant. For example,

collecting data at 500 points per second would be excessively redundant for data that only changes at a rate of a few units per second.

Data are usually only printed or stored. Results which are printed must be analyzed manually whereas stored data can be analyzed by a computer and printed. In general, it is usually better to store the data for later analysis because data storage devices can store the data more rapidly than most printers can print it out. This allows for a faster collection rate and a faster turnover from one sample to the next.

Figure 1: Current vs. Potential

$([\text{pyrSiCo(III)W}_{11}\text{O}_{39}])^{-6}$, 300uL IPA, 300mV/s

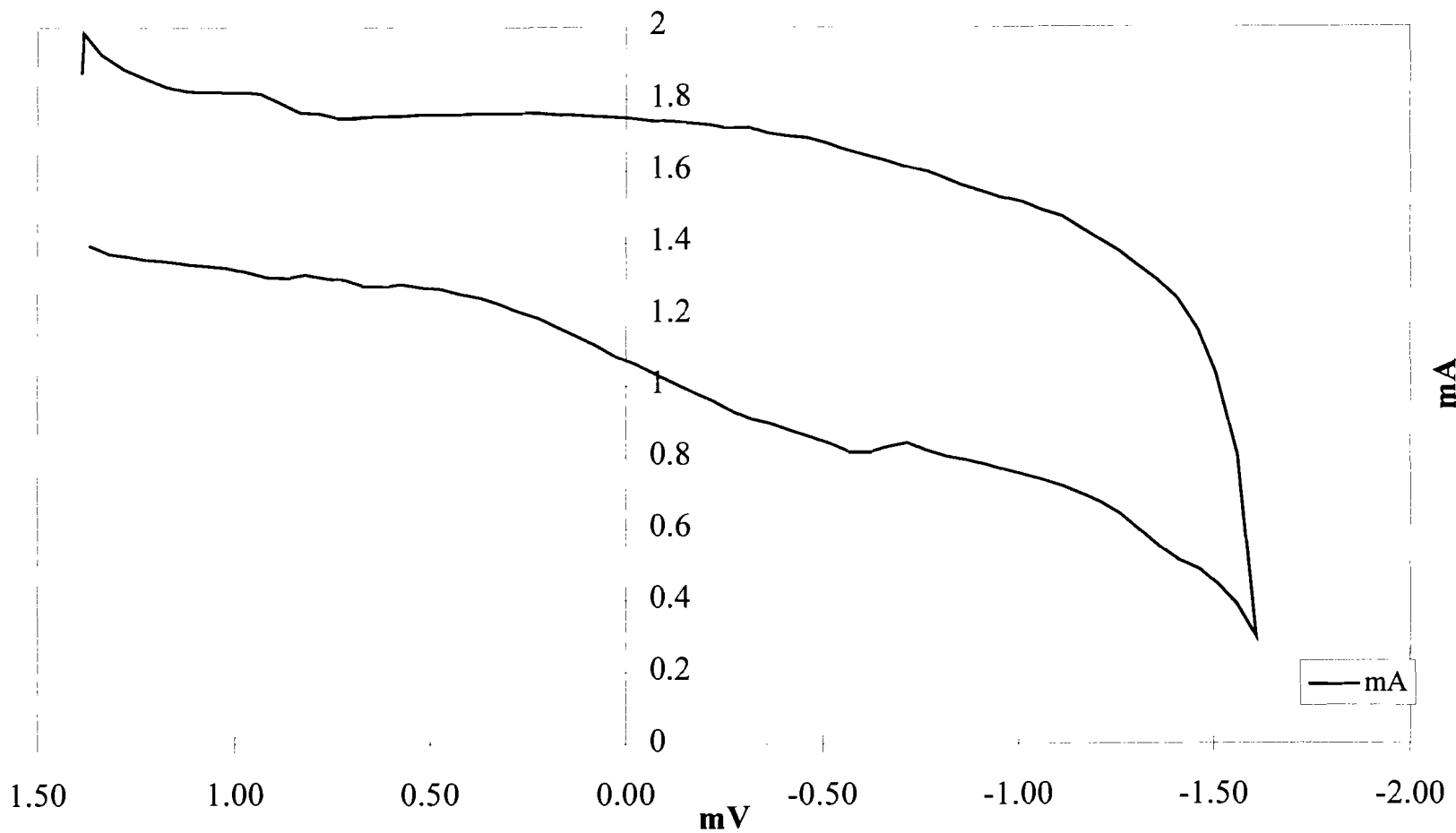


Figure 2: Current vs. Potential
([pyrSiCo(III)W₁₁O₃₉])⁻⁶, 200μL IPA

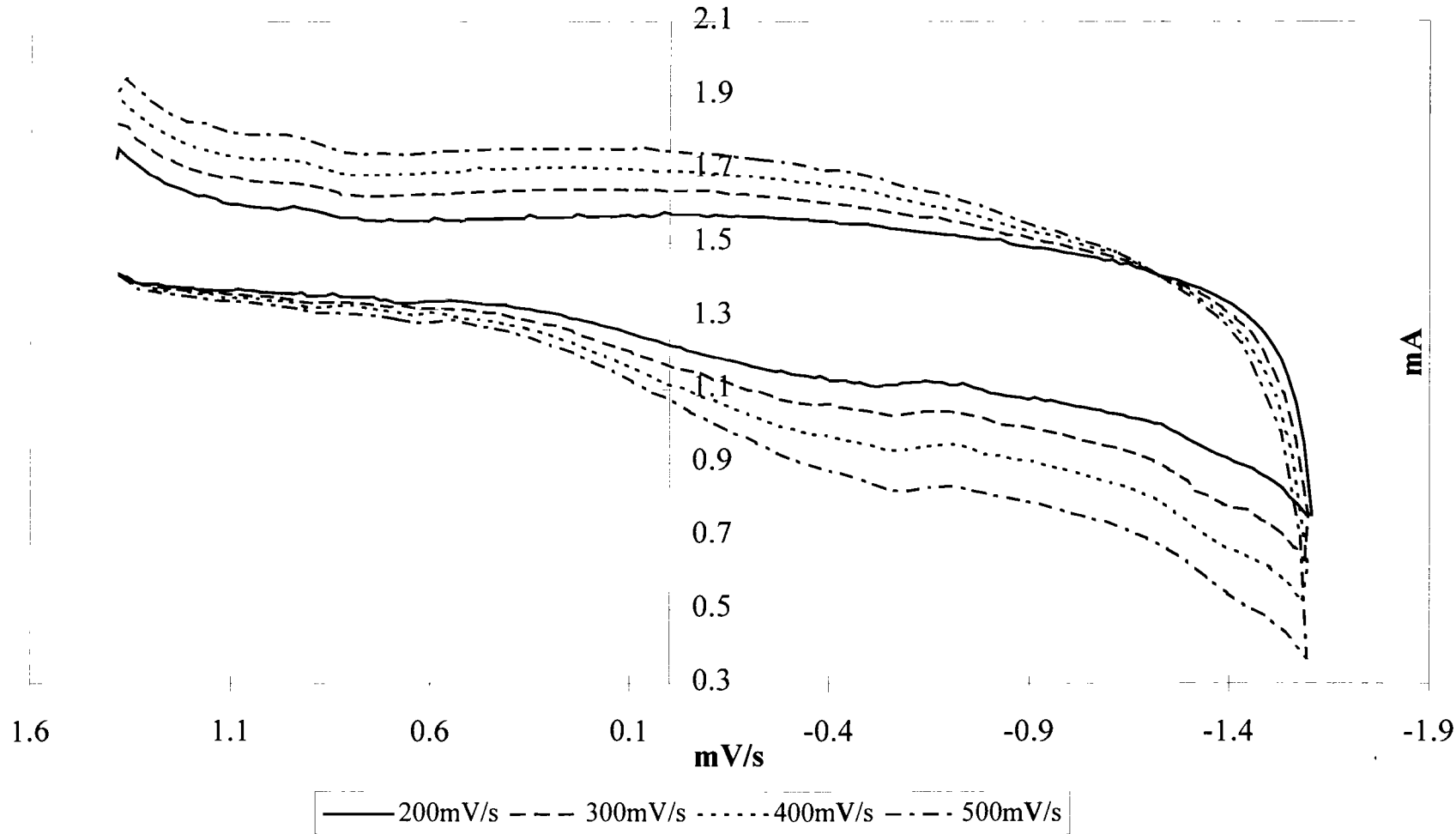


Figure 3: Peak Center vs. Sweep Rate
500 μ L 2-Propanol, Forward Sweep

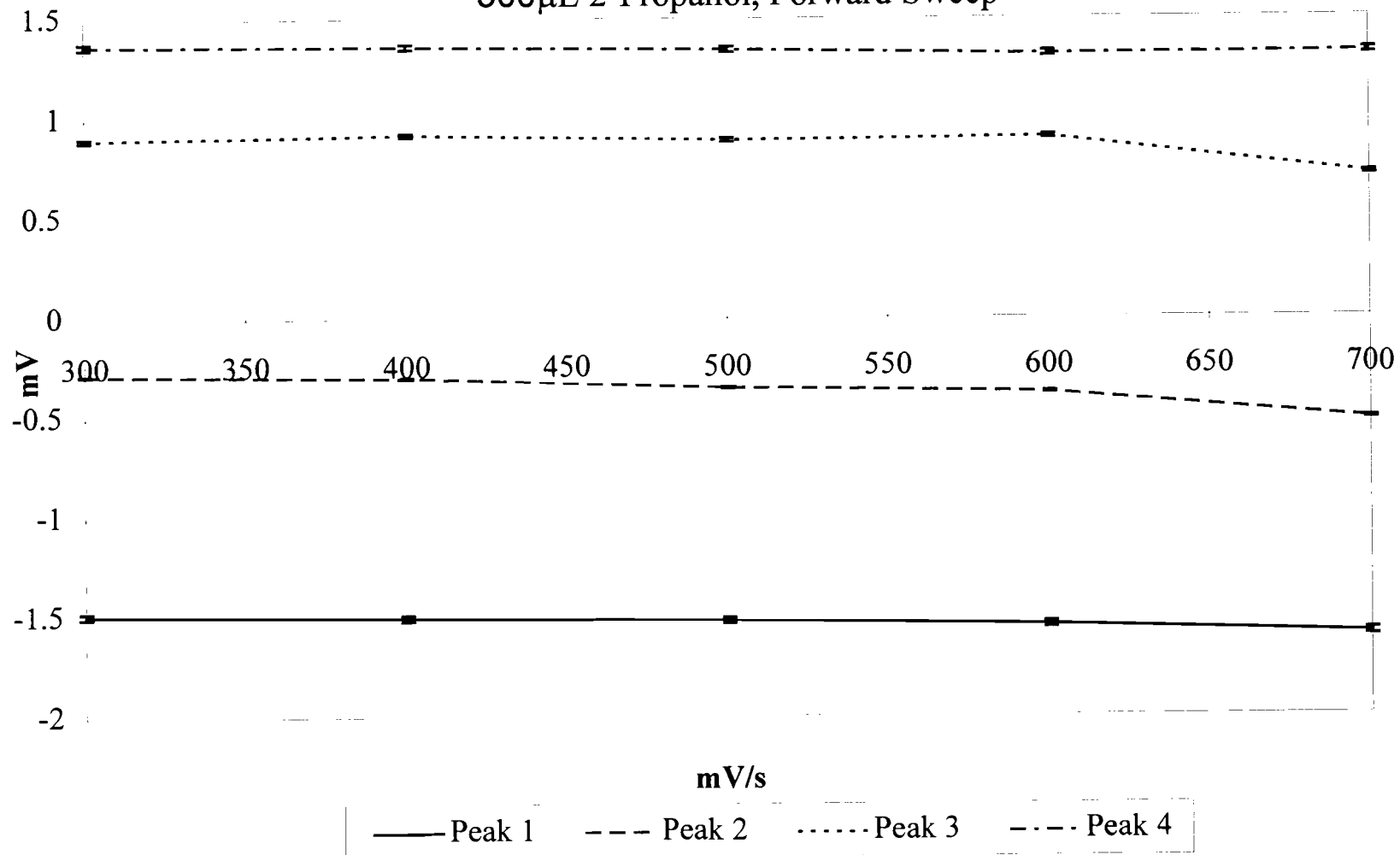


Figure 4: Peak Center vs. Sweep Rate

500 μ L 2-Propanol, Reverse Sweep

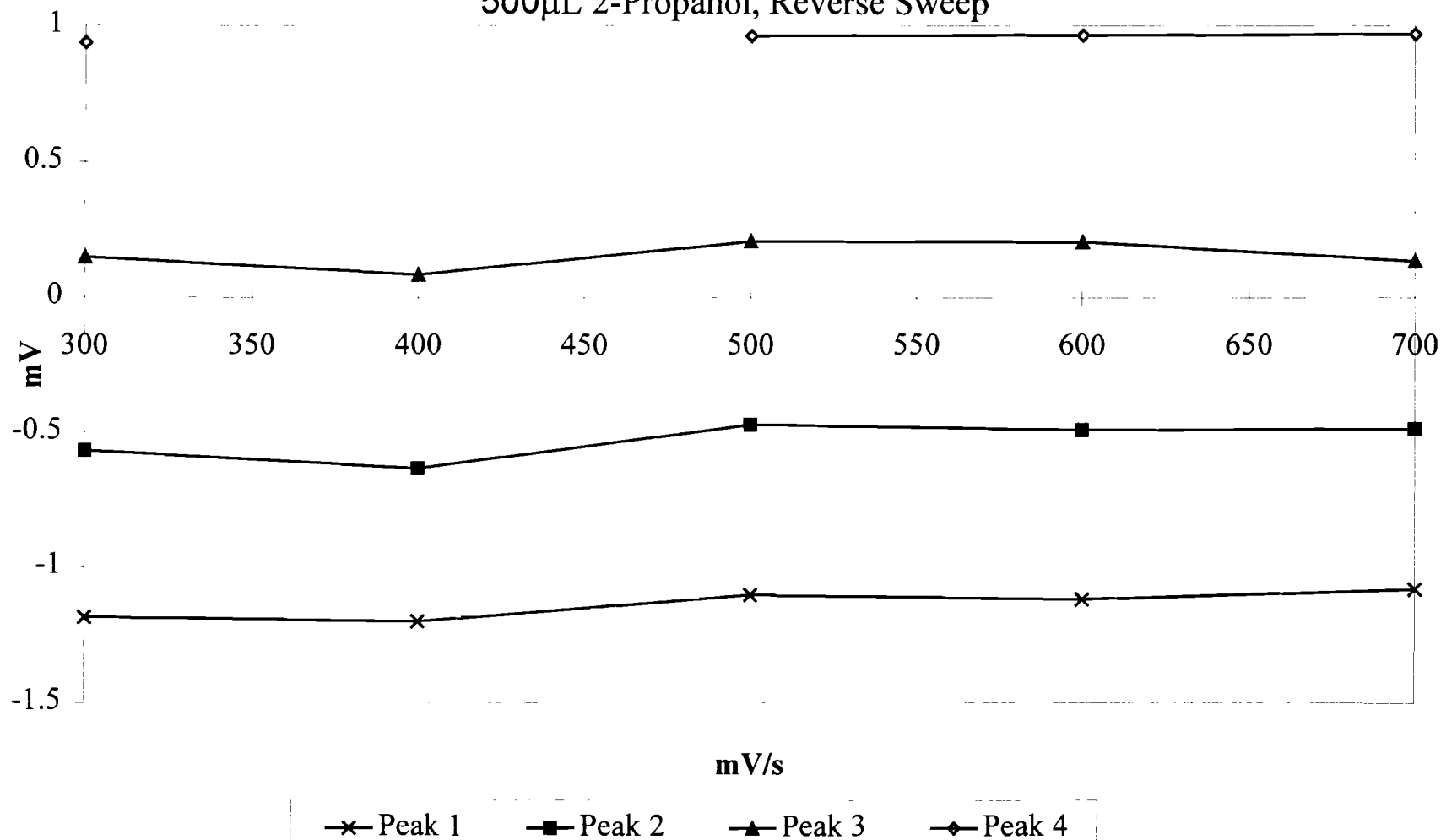


Figure 5: Peak Height vs Sweep Rate

500 μ L 2-Propanol, Forward Sweep

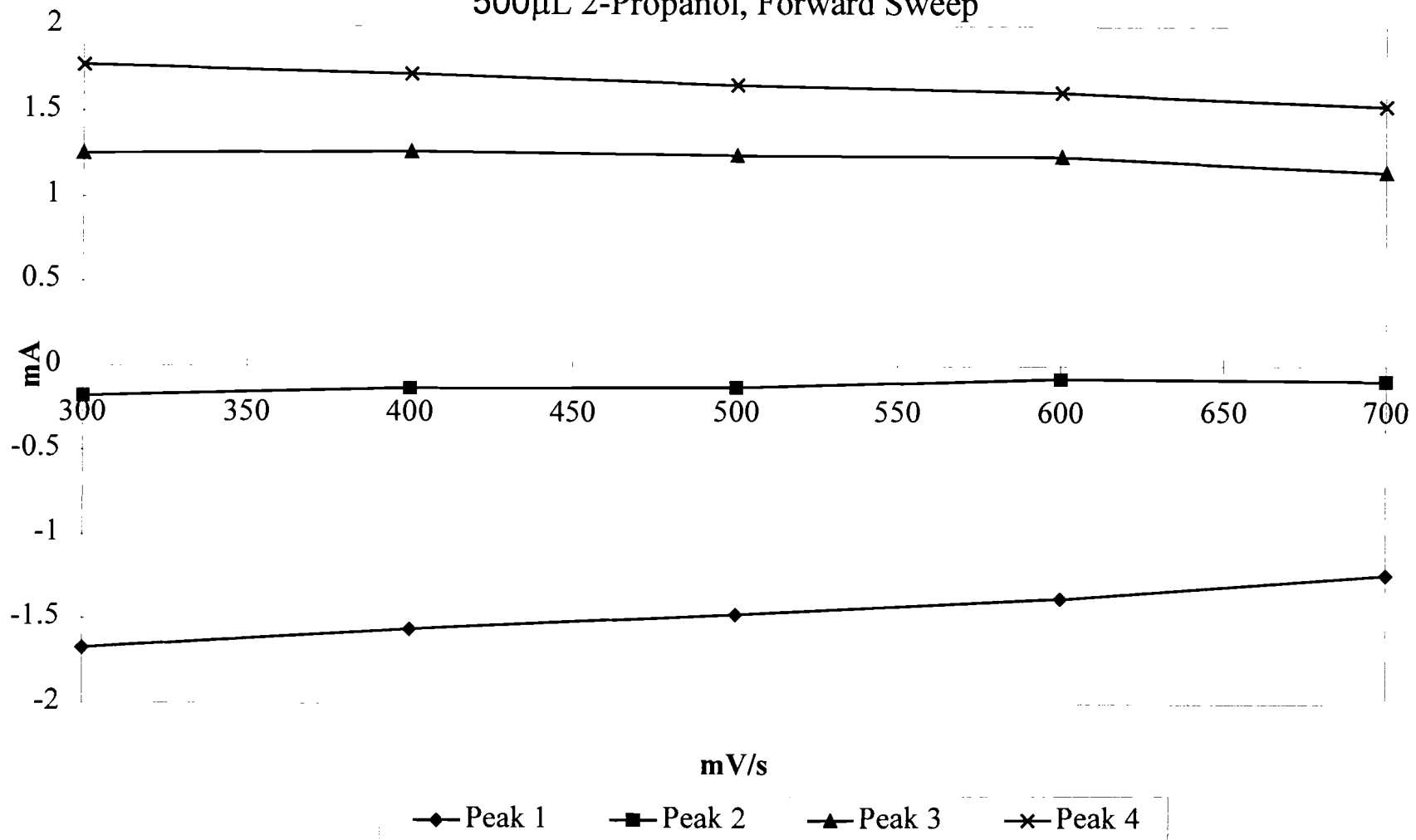


Figure 6: Peak Height vs Sweep Rate
500mL 2-Propanol, Reverse Sweep

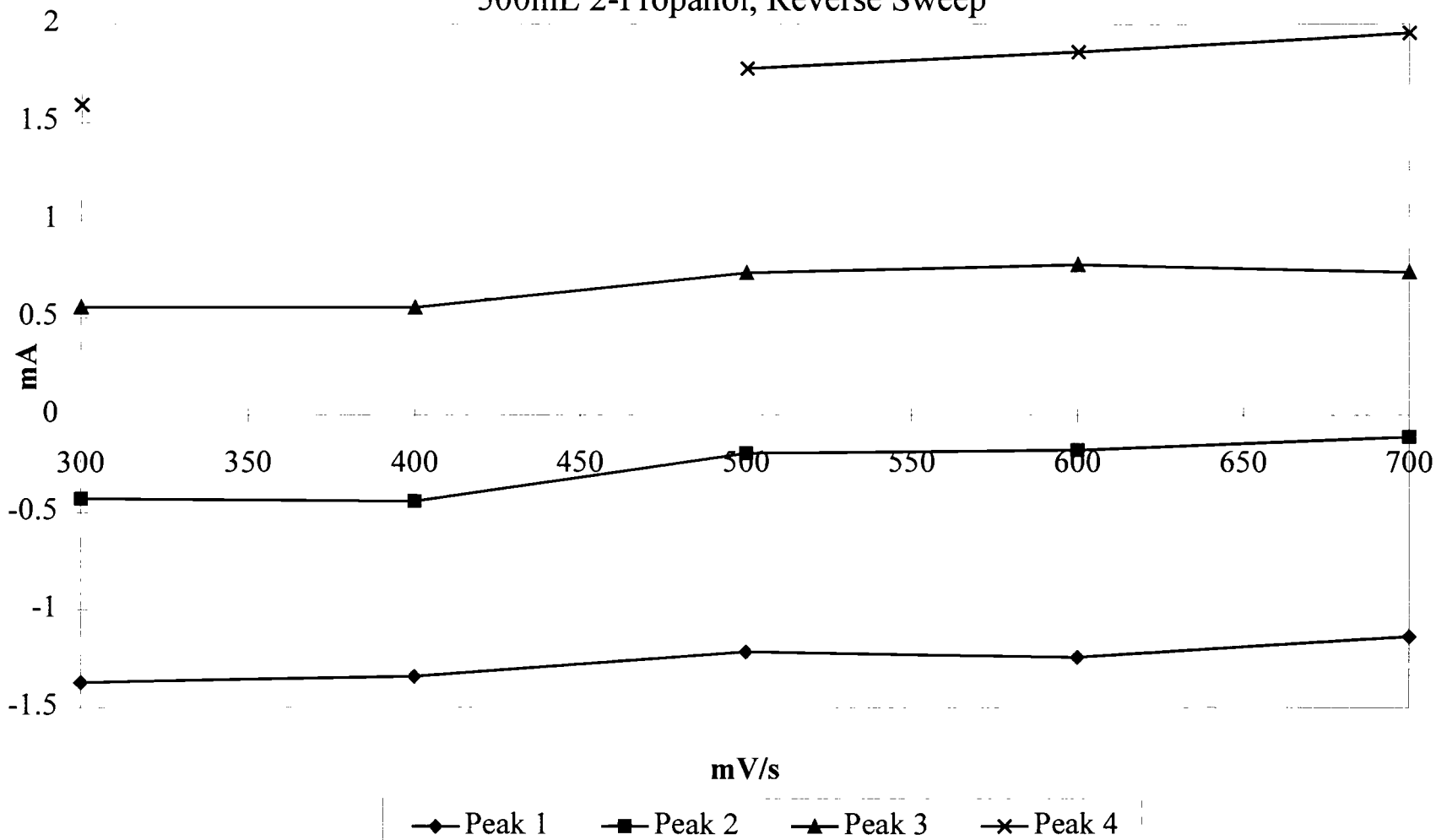


Figure 7: Peak Center vs. Volume of IPA
300mV/s, Forward Sweeps

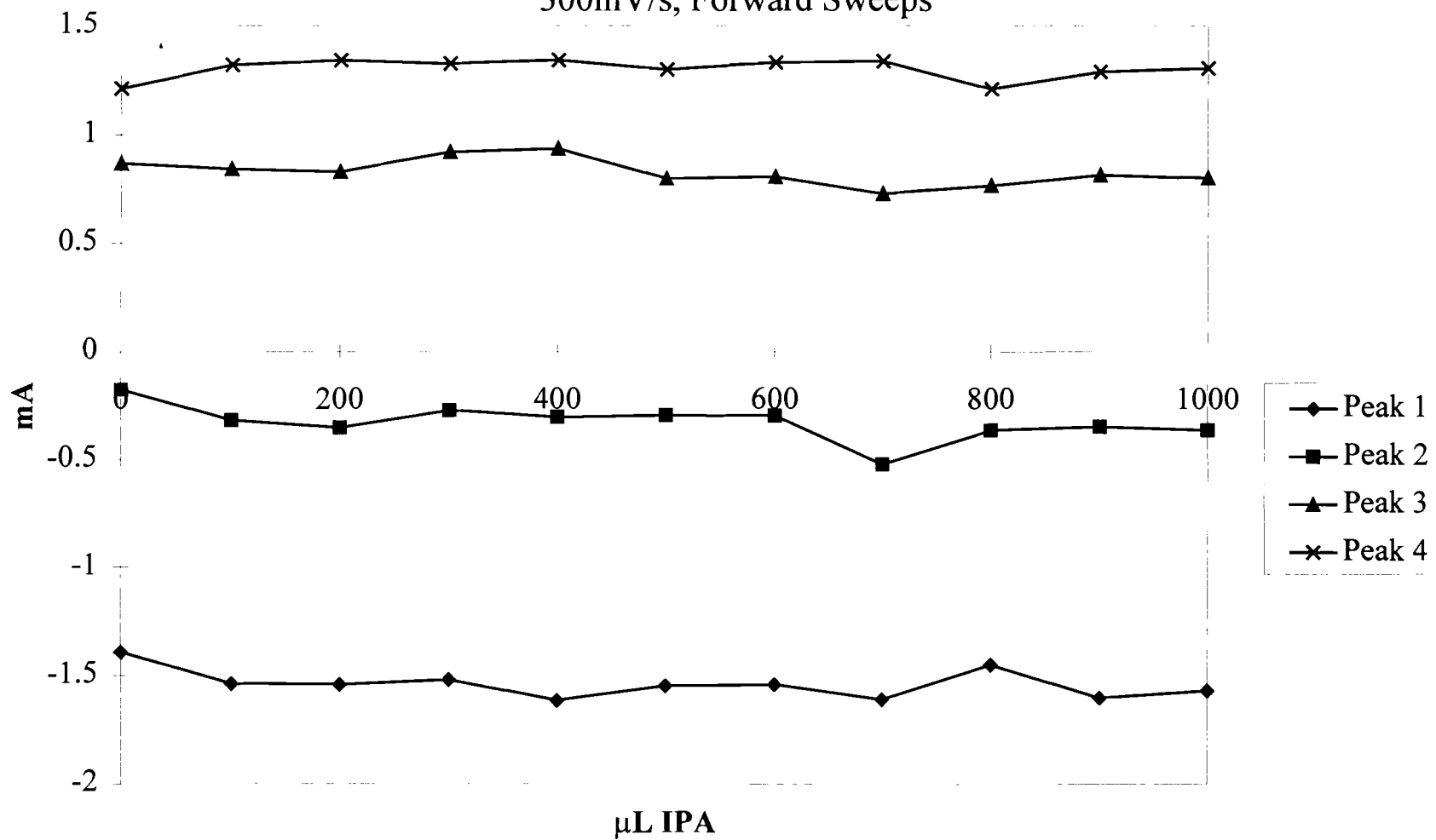


Figure 8: Peak Center vs. Volume of IPA
300mV/s, Reverse Sweeps

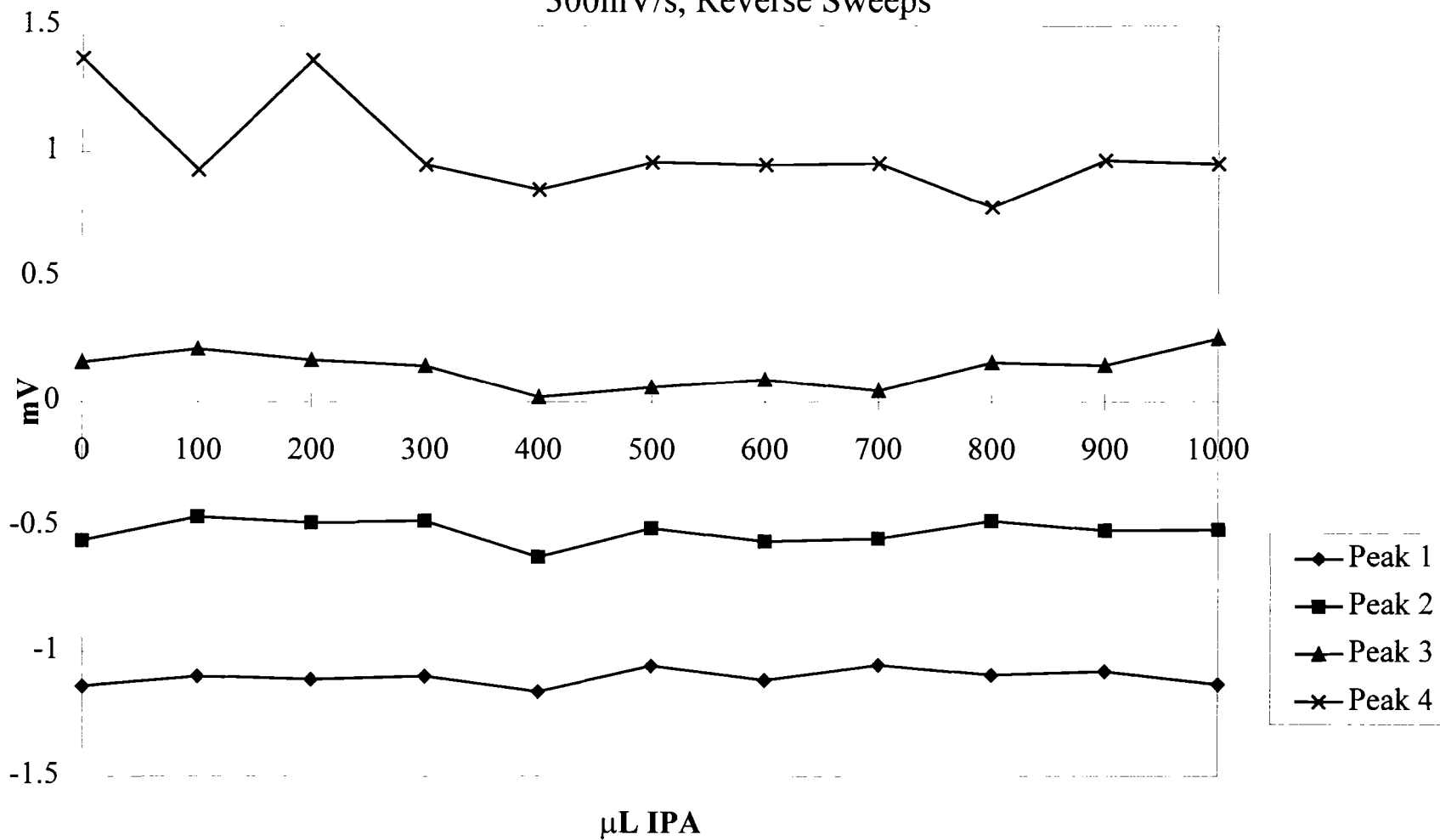


Figure 9: Peak Height vs. Volume of IPA

300mV/s, Forward Sweeps

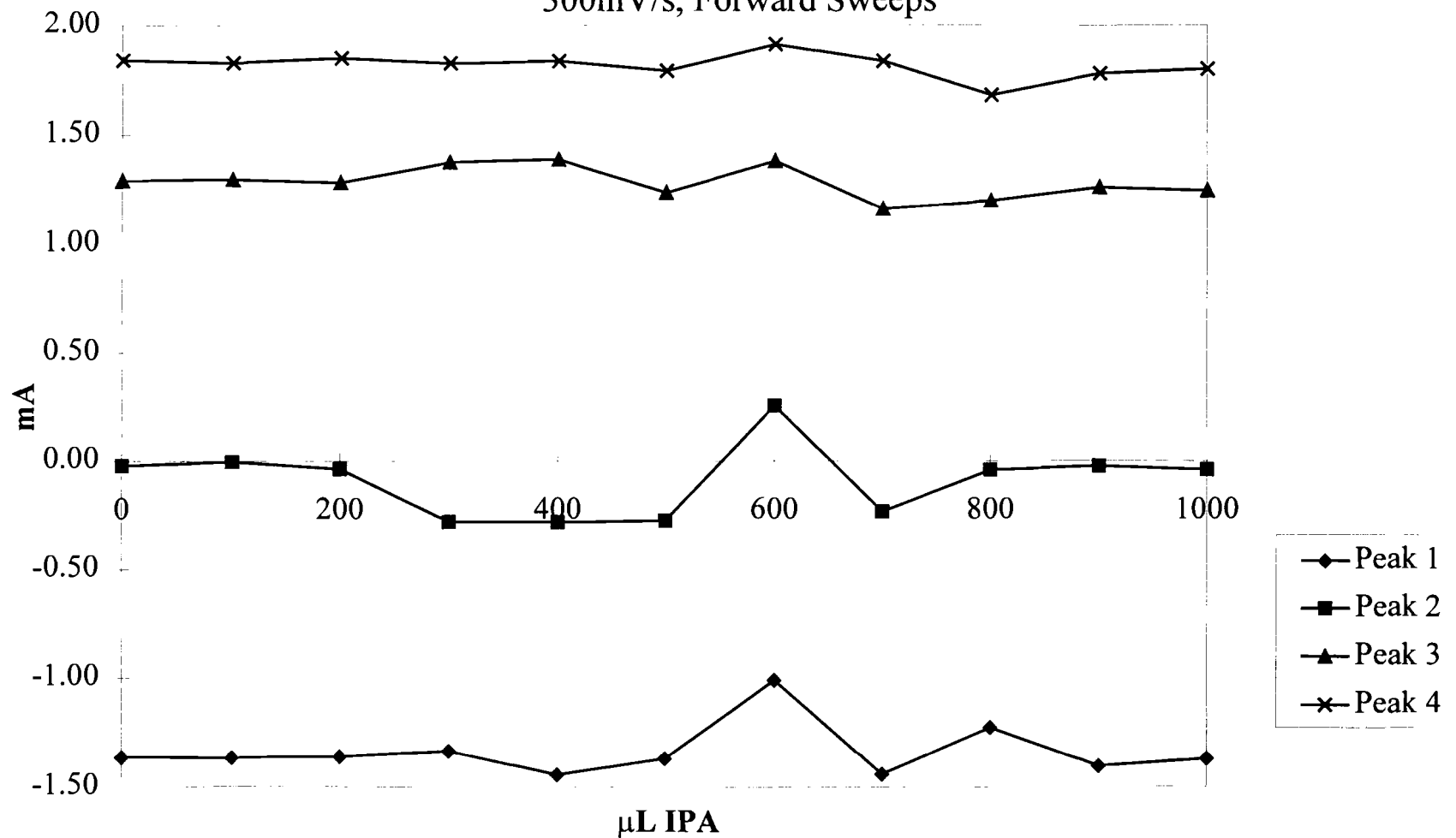


Figure 10: PeakHeight vs. Volume of IPA
300mV/s, Reverse Sweeps

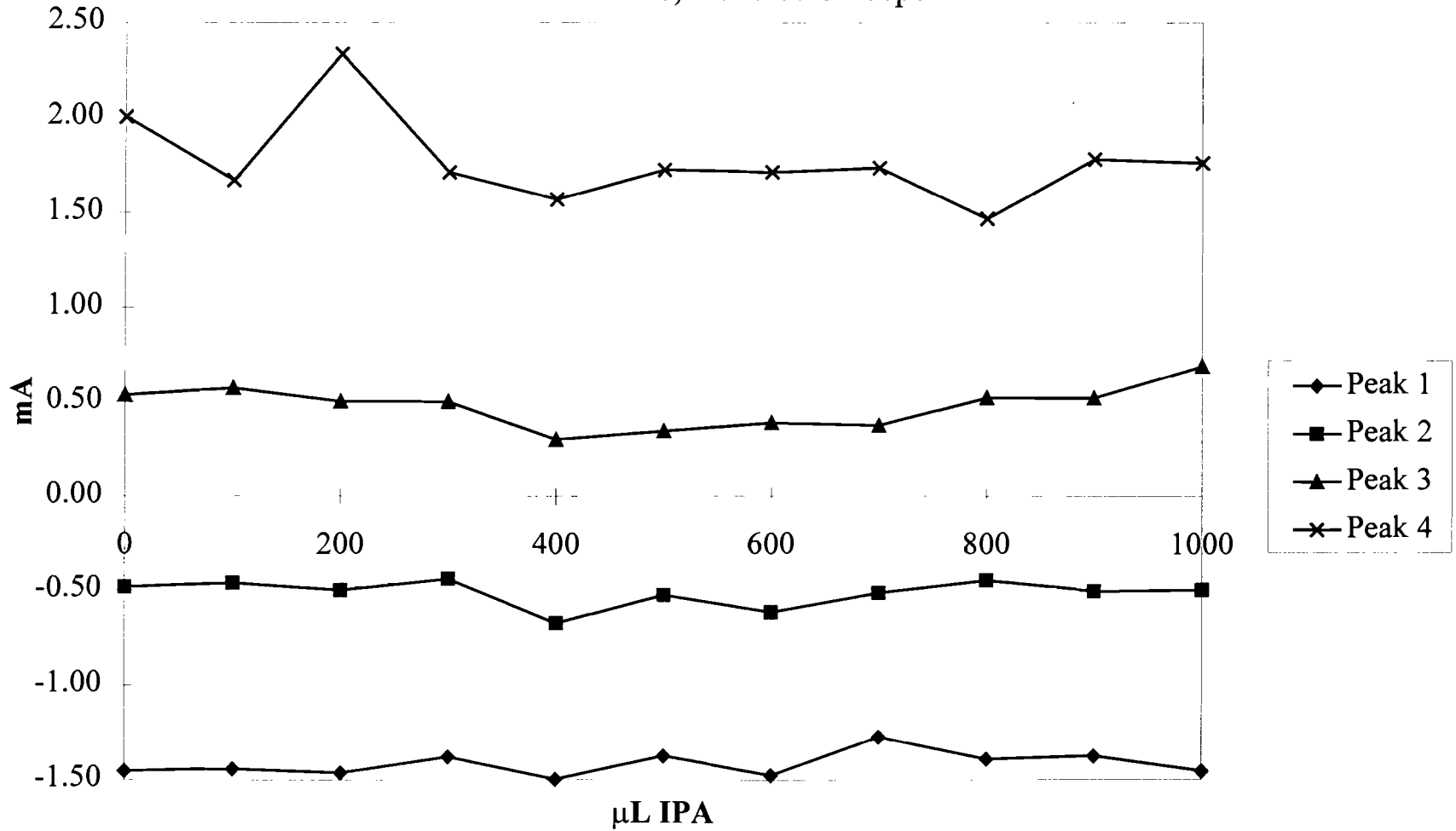


Figure 11: Copper(II) Reference

100 mV/s

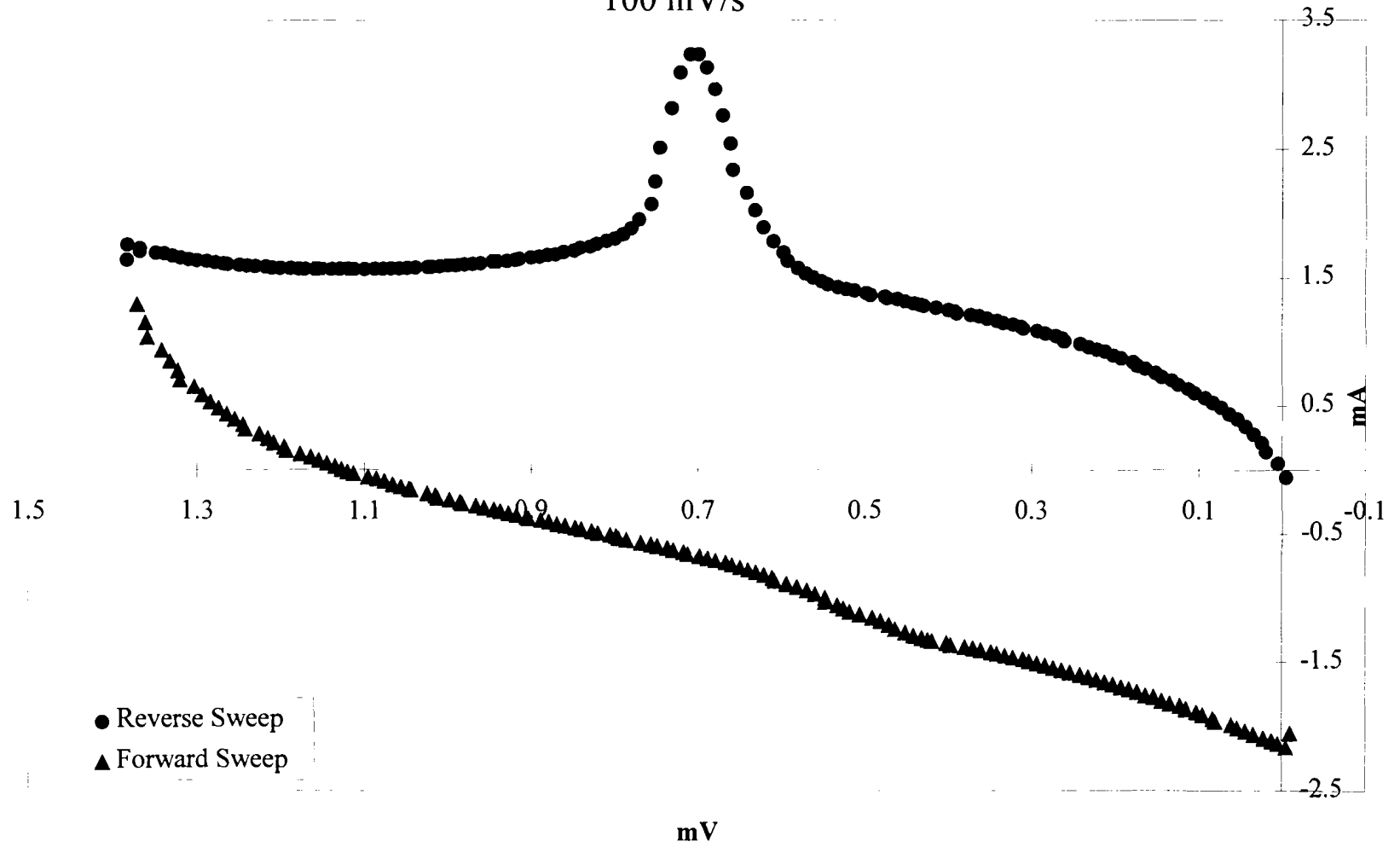


Figure 12: Deconvoluted Sweep
100 μL IPA, 300 mV/s, Reverse Sweep

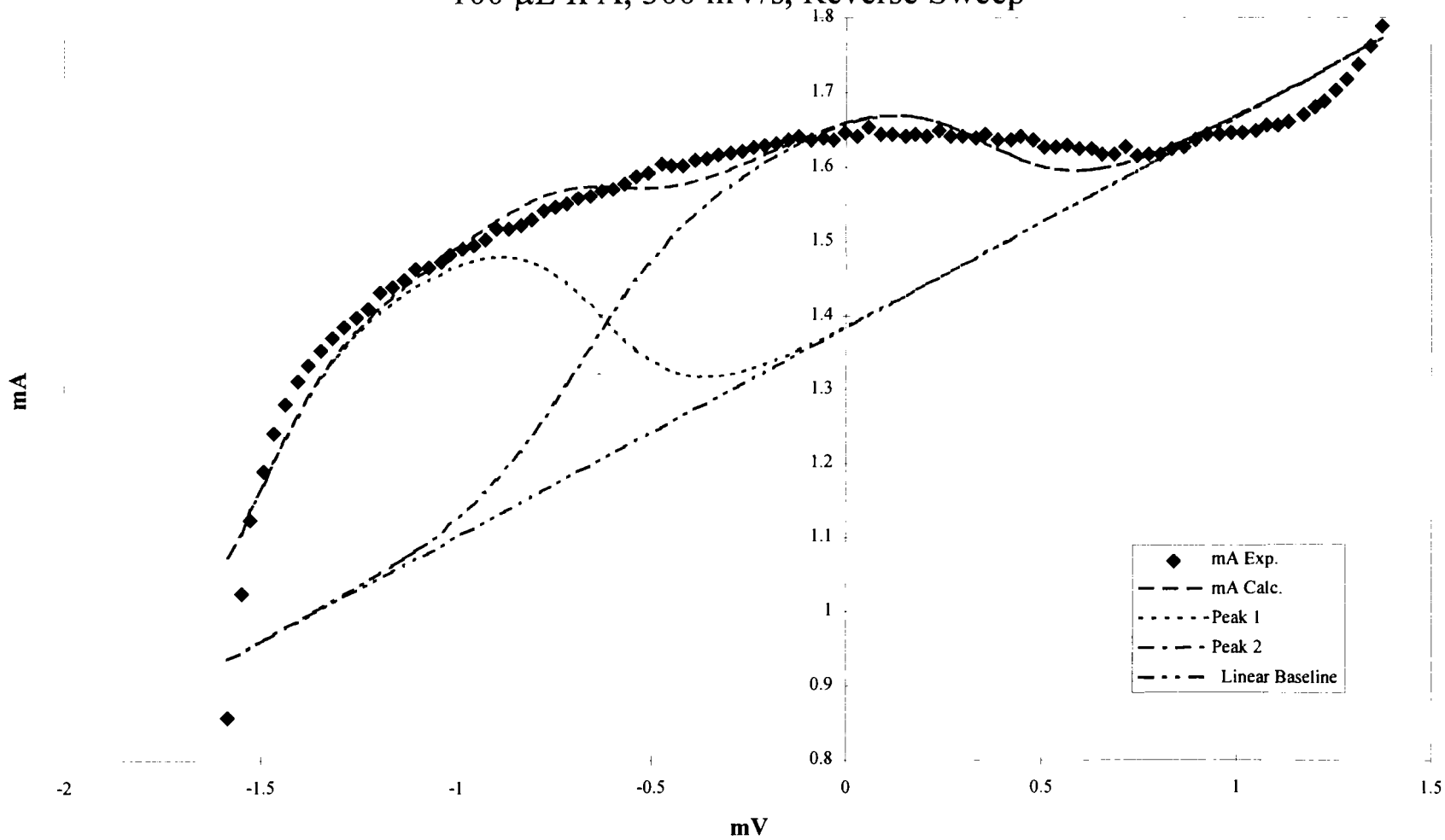


Figure 13: Diagram of Electrical Connections

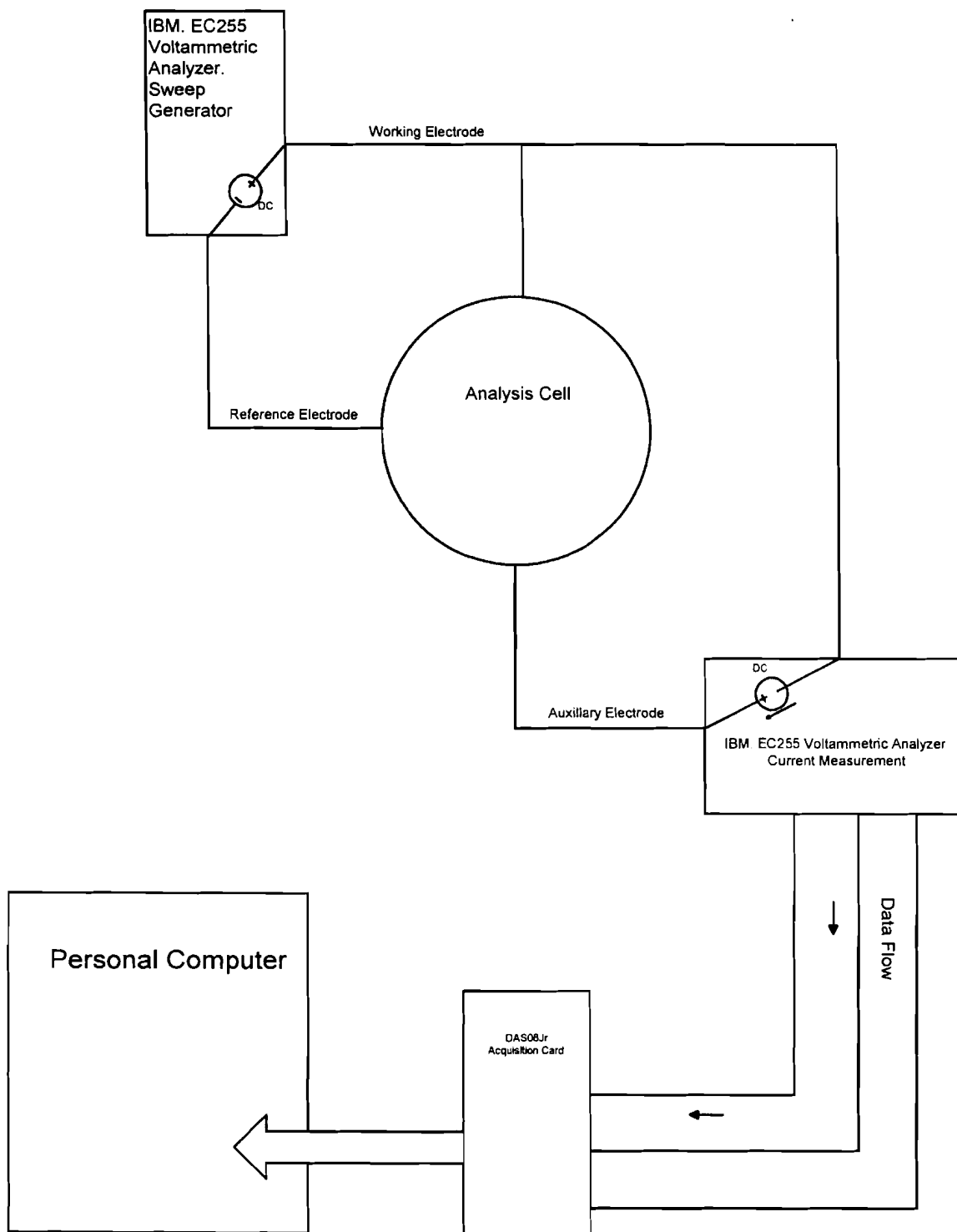
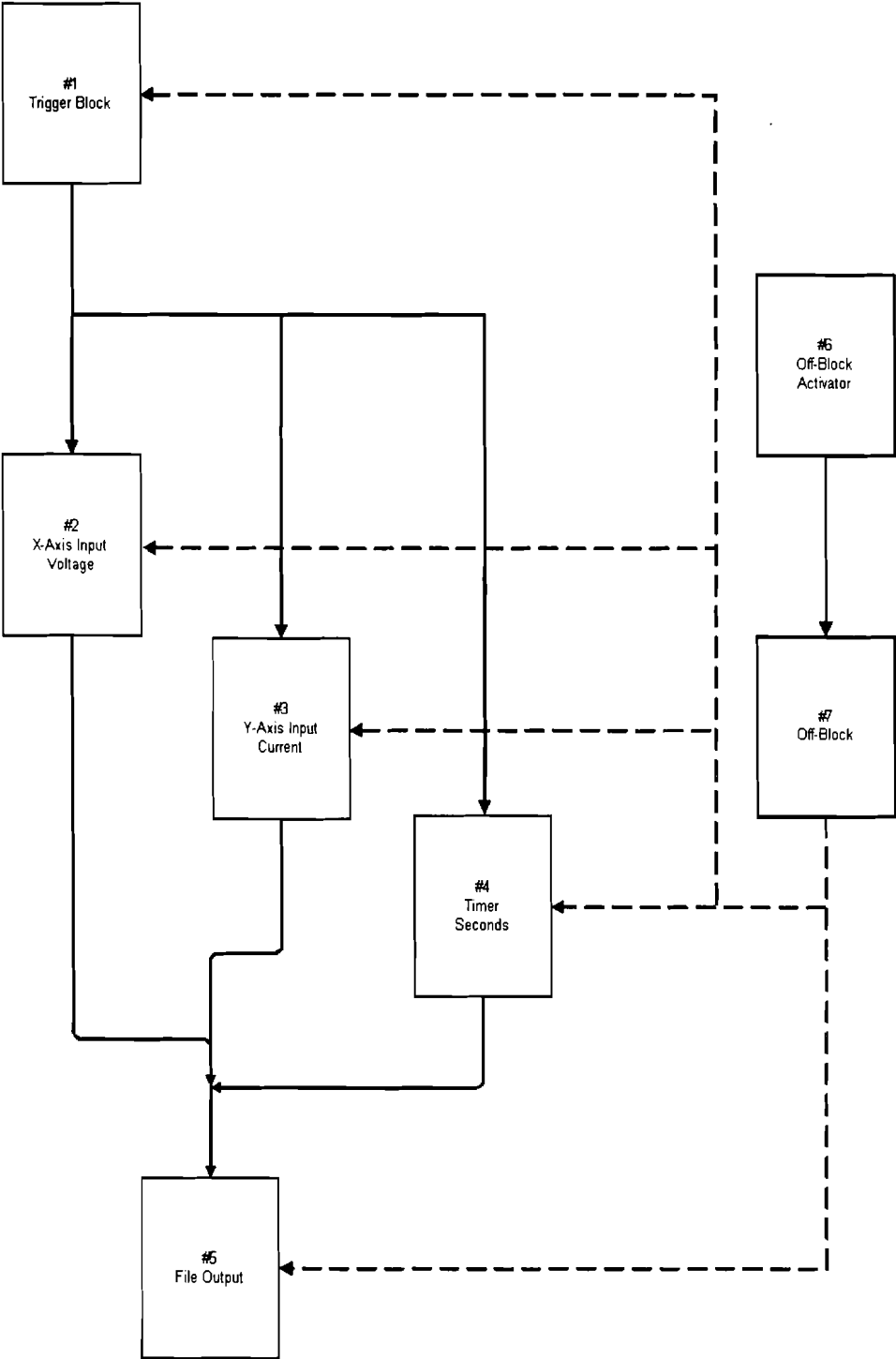


Figure 14: Block Layout and Flow of Data



Legend:

Data Input	←——
Termination Signal	←- - -

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Brian P. Armstrong
Signature of Author

12-19-97
Date

Cyclic Voltammetry of Heteropolytungstate Complexes
with Computer Controlled Data Collection.
Title of Thesis

Cozy Cooper
Signature of Graduate Office Staff Member

December 18, 1997
Date Received