Construction and Testing of LabVIEW Software to Interface with a Princeton Applied Research Model 273 Potentiostat and an HP Model 8452A Photospectrometer

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With LabVIEW, it was possible to create a program that could operate a Princeton Applied Research Model 273 potentiostat, an HP Model 8452A photospectrometer, and a YSI Model 5000 Dissolved Oxygen Meter from a single interface. Such a program would solve the problems that diverted so much effort away from further experiments and toward watching a potentiostat change potential over the course of several hours (in some cases up to twelve hours). Unfortunately, the dissolve oxygen detection was omitted due to the limits of the instrumentation. However, testing the program's viability with several samples whose redox potentials were given, a program was constructed that could indeed consolidate the functions of a potentiostat and a spectrometer.

INTRODUCTION

In natural and in synthetic oxygen binders– compounds that carry oxygen through the bloodstreams of organisms– the binder itself contains a metal center to which oxygen can attach. These oxygen binders are essential to biological life forms, including humans, and more efficient and convenient binders are a large topic in chemical industry (Fischer-Fodor *et al.,* 2011).One method of changing the transition state of various metals in order to determine the most efficient state for binding oxygen is a process of electrochemistry that involves applying voltages to samples using a potentiostat. A Princeton potentiostat is an instrument that generates and measures voltage across a given sample. The reference electrode used with the potentiostat cell was a silver chloride electrode. Then, an HP Model 8452A spectrometer, emitting both UV and visible light, actuates a shutter and allow the light to pass through a sample and into a diode array. The spectrum is displayed on the PC monitor, and oxygen readings for the sample are taken from a connected YSI 5000 oxygen meter. Utilizing these three instruments, the metals' transition states are altered. Observable oxygen binding can be measured with the data. This process is known as spectroelectrochemistry because of the use of both a potentiostat and a spectrometer.

LabVIEW is a graphical programming environment that uses "virtual instruments" (VIs) in place of traditional written code to compile working instrument software.9 Instrument manufacturers as well as independent individuals make available sets of basic VIs that can be customized and connected as a framework for a more elaborate instrument interface. With the LabVIEW software, a virtual instrument could be compiled that could operate a potentiostat in conjunction with an HP diode array spectrometer and a YSI oxygen meter. The combined advantages from applying LabVIEW to the coordinated operation of the potentiostat, diode array spectrometer, and oxygen meter equal an intuitive process for analyzing oxygen binding samples that reduces experiment time and possible errors in data.
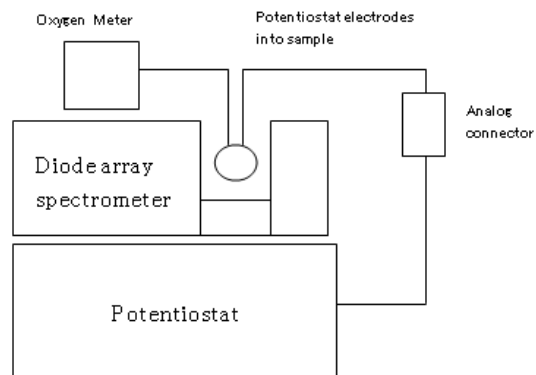

Fig1. Layout of the three instruments involved in oxygen carrier redox analysis.

METHODS

The first focus of this project was to persuade the Princeton potentiostat to receive and implement orders from a PC. A set of VIs written expressly for the PAR Model 273 was downloaded and saved to the PC hard drive (Jamal *et al.*, 1991). While these VIs were written to perform cyclic voltammetry experiments – a different electrochemical process than the one set as the goal of this project – they contained components that had the potential to be useful for spectroelectrochemical trials. An electrometer containing a 10 Ohm dummy cell was connected to the potentiostat and the main VI, "Cyclic Voltammetry", was initialized.

Unfortunately, as it was written the VI would not interact correctly with the potentiostat. The most probable cause of these errors was explicitly mentioned in the text written within the VI. The relative age of the instrument supposedly made it susceptible to errors if a modern PC attempted to

send too many commands in a short period of time. To remedy this, short pauses of 100 milliseconds were placed between each VI. This solution corrected some of the errors, but still allowed others to occur. Using LabVIEW's Highlight Execution function, the VI was slowed so that step of the program was visible, errors included. Many errors were occurring inside of subVIs, so those subVIs were opened and modified to pause at key points to allow the potentiostat more time to process its commands. This produced an operational VI as well as the groundwork for the next potentiostat VI.
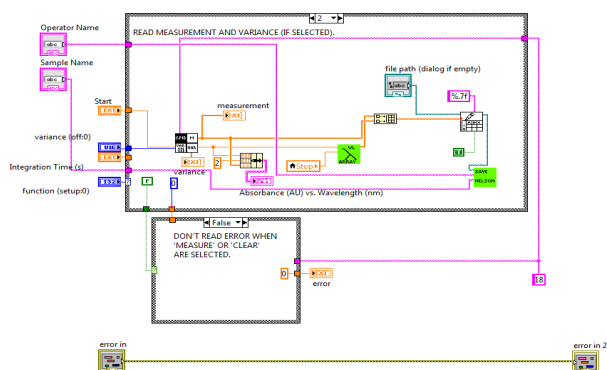

Fig 2. HP 8452A NELSON v2: This version saves a text version of the spectrum.

Once the Cyclic Voltammetry VI was deemed usable, the prefabricated VIs provided by the manufacturer of the spectrometer were opened. The main VI, which allowed the user to take a single spectrum across a range of wavelengths, was complete and required no modifications. A second version of the HP 8752A VI was created that performed the same function, but a series of functions were added that allowed the VI to save the spectrum as a text file complete with a footer containing the date and time the spectrum was taken as well as the operator's name and the name of the sample

With the completion of both the potentiostat's VIs and the spectrometer VIs, a blank VI named "Experimental Potentio-Spec" was created. Several iterations of this VI were completed, but the final version ultimately contained five major frames that performed different functions given proper direction from the operator. The first frame setup the spectrometer. The second frame tells the spectrometer to take a reference spectrum. The third

frame was compiled from a series of the modified VIs used during the cyclic voltammetry experiments The progression of this frame is as follows (with pauses omitted): the potentiostat is set to the default state, the current range is set, the potentiostat's status is determined, the initial potential for a cell is set and held for the number of seconds specified, the potential is stepped and the spectrometer takes ten spectra on the last tenth of the equilibration time, the resulting spreadsheet (the absorbance values are averaged from the ten spectra) is saved with the potential attached to the end of the filename, and the potentiostat acts as it was directed to do on completion. Note that the functions that attach the footers to the ends of the spectra files have been separated from the spectrometer VI and placed into a standalone VI to avoid VI malfunctions. The fourth frame of the "Potentio-Spec" VI is nearly identical to the third frame. The only discrepancy is in the manner by which the VI steps the potential. Whereas the third frame steps the potential in equal steps specified by the operator, the fourth frame calculated each step individually by way of a modified Nernst equation and steps the potential accordingly. This method of stepping the potential is more useful because it can calculate much smaller steps near the zero potential of a sample. Relatively large steps, such as those taken by the third frame of the "Potentio-Spec" VI, can miss the zero potential completely and thereby ruin a time-consuming experiment. The fifth frame of the VI resets any error codes generated by the spectrometer.

Unfortunately, the YSI dissolved oxygen meter supplied was unable to correctly process commands received from the PC and was therefore removed from service for the purposes of these experiments. It has been noted that the purpose of compiling virtual instruments that operate the potentiostat and the spectrometer was to perform redox reactions. To this end, several solutions of ferrocenecarboxylic acid were produced. According to Hillier, et al. the theoretical redox potential for the oxidation of ferrocenecarboxylic acid is 0.4 V, or 400 mV(Hillier *et al.*, 2004). That fact made ferrocenecarboxylic acid an excellent candidate for testing the "Potentio-Spec" VI. However, only solutions whose solvents – in these cases, deionized water – contained a measure of sodium bicarbonate were usable. Those solutions of 0.1125 M ferrocenecarboxylic acid in approximately $4 \cdot 10^{-5}$ M sodium bicarbonate were clear with a distinct orange color. The other "solutions" were actually suspensions of ferrocenecarboxylic acid.

Prior to the completion of the "Potentio-Spec" VI, ferrocenecarboxylic acid samples were used to test the progress of the program. Using the Nernst equation and several spectra taken during those tests, an experimental redox potential for ferrocenecarboxylic acid was calculated. The calculated potential, 417 mV was inserted into the VI and the fourth frame was used to complete a series of potential steps on the sample. The resulting spectra showed that the calculated potential was extremely close to the actual redox potential, and additionally showed that the VI and its components operated in a manner conducive to the successful reduction and oxidation of samples used in electrochemistry and spectroelectrochemistry.
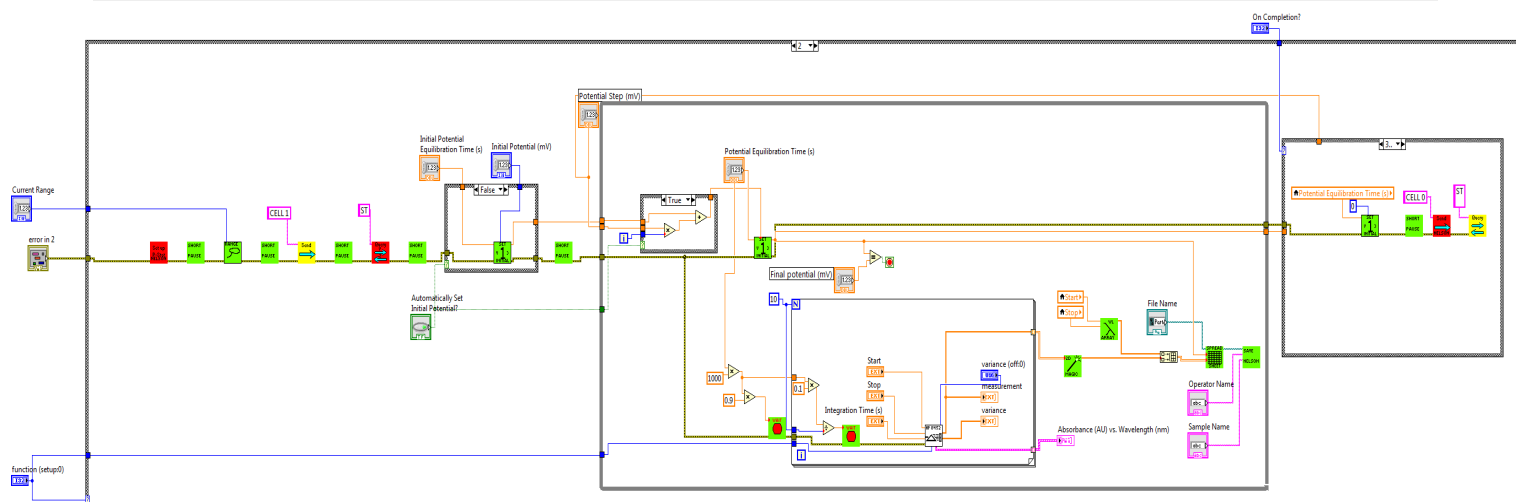

Figure 3. Frame three of the "Potentio-Spec" VI. This frame conducts an equal-step run.

RESULTS AND DISCUSSION

The "Cyclic Voltammetry" VI, though not itself a goal of this project, is important enough to bear discussing. It began as a program developed by a third party who had occasion to work with the Princeton Applied Research Model 273 potentiostat (National Instruments Developer Community). Because of the age of the potentiostat, it was previously meant to be controlled by way of its physical keys or, alternatively, by sending commands through a PC via terminal emulator. Though its digital functions are primitive compared to more modern instruments, it is till controllable through the LabVIEW programming environment. After downloading the cyclic voltammetry package from the party who developed it, it was discovered that the VI generated errors that made impossible the running of a cyclic voltammetry experiment. The subsequently modified VIs, fixed to cope with the hardware setup, were arranged in such a way that the eighth version (the latest version to date) of the "Cyclic Voltammetry" VI would take multiple scans of the same sample and save each one to the same text file. By no means is this latest version perfect – it still generates random errors on occasion – but it functions well enough to use as a standalone program. If the source of the random errors could be identified and corrected, the "Cyclic Voltammetry" VI could potentially be a very useful program.

The program also contributed to the "Experimental Potentio-Spec" VI by donating its subVIs to the production. Once the experimental VI was put together, it could run a full basic stepping routine with either equal potential steps or steps determined by a modified Nernst equation. Early versions of this program could only perform equal stepping runs and were somewhat difficult to test. Several different solutions were used to test the functionality of the "Potentio-Spec" VI: Bindschedler's green dye, rose bengal sodium salt, dichlorophenolindophenol, and ferrocenecarboxylic acid. The external cell used to perform stepping experiments was one of Dr. William Anderson's invention. It was a solvent-resistant shell with hole drilled to allow for the passage of a liquid sample. A thin, transparent layer of gold was sandwiched between Plexiglas plates and acted as the working electrode for the cell.

The Bindschedler's green samples seemed to give only a small peak of less than 0.5 AU near 750 nm on its spectrum. Additionally, runs that stepped the potential from negative potentials or zero to high potentials in excess of 1.2 V failed to reduce or oxidize the samples; the redox potential of the green dye is theoretically 224 mV (Lewis *et al.*, 1948). This could be due to impurities in the lot of Bindschedler's green used; it was also possible that the failure to affect the sample was due to technical issues with the potentiostat's electrometer or with the potentiostat itself. However, when a sample of Rose Bengal sodium salt was used to test the "Potentio-Spec" VI, the redox potential was between 1.7 V and 1.8 V. These readings coincided with the experimental redox potential of rose bengal according to Islam and Ito (Islam *et al.*,1999). The data seemed to discount the theory that an issue was occurring within the electrometer. Unfortunately, the samples of DCPIP (dichlorophenolindophenol) tested also exhibited massive and erratic redox potentials. According to Whitaker et al. the redox potential of DCPIP should be about 217 mV (Whitaker *et al.*, 2012).To make certain that the electrometer and potentiostat were in working order, a voltmeter was applied to the electrodes on a cell with a DCPIP solution inside and the voltmeter returned the same values that the potentiostat displayed on its digital front panel. Based on these observations, there is a strong probability that the Bindschedler's green and DCPIP may be contaminated.

The ferrocenecarboxylic acid solution was used last because of its properties. It could be easily oxidized and reduced and would give clear indicators of the status of its oxidation state such as the color of the solution. Since the overall goal of this project was to create a program that could all but automate the analysis of synthetic oxygen binders, ferrocenecarboxylic acid appeared to be ideal for these sorts of experiments. The redox potential of the ferrocenecarboxylic acid coincided with research conducted at 0.417 V (Hillier *et al.*, 2004). Repeated tests gave consistent results and confirmed that the program as indeed functioning as it should.

With the completion of this program, any who wish to apply it to spectroelectrochemistry have the opportunity to have an automated system in place of a tedious repetition of key pressing. Ideally, the error and tedium of human action has been removed from the process of spectroelectrochemistry (at least in the areas to which the techniques discussed herein can be applied). If an oxygen meter could be incorporated into the process, then operators would be able to measure the oxygen content of a sample as well as its redox potential and analyze how well that sample binds oxygen.
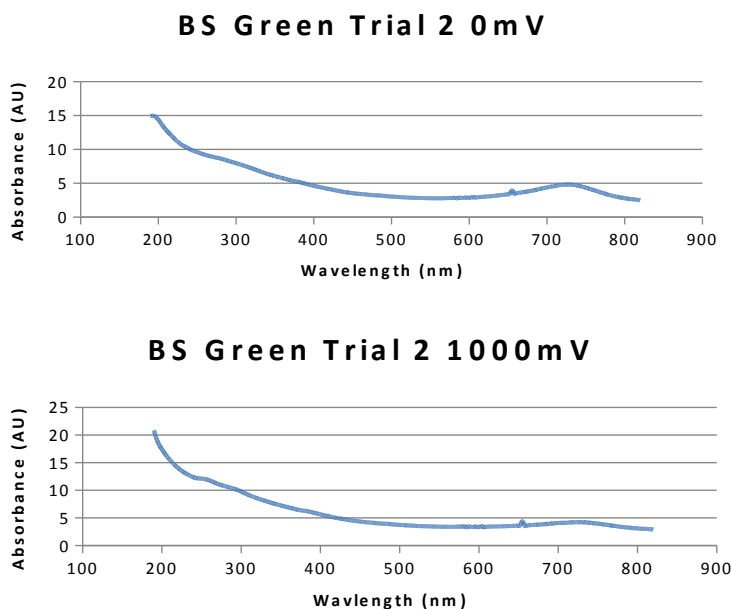

Fig 4. Top: spectrum of Bindschedler's green at 0 mV. Bottom: spectrum of Bindschedler's green at 1000 mV. Both spectra were taken using the equal step method. The absorbance units have been multiplied by ten due to an error in the LabVIEW program. Note the miniscule peak at ~720 nm.

This is especially useful when synthetic binders that utilize metal centers, such as hemoglobin (Berg *et al.*, 2012). It has been noted that the original intent of this project was to create a completely automatic system that combined the processes of potentiometry, UV-vis spectrometry, and dissolved oxygen detection. It has also been noted that the oxygen detector was rendered inoperable by its inability to correctly decode the commands sent to it from a PC interface. However, the main result of the project, the "Experimental Potentio-Spec" VI did successfully combine potentiometry and spectrometry to form a program suitable for performing spectroelectrochemistry. Even though the VI cannot analyze the oxygen content of a sample, it can manipulate the potential applied to a sample and it can take spectra of a sample in order to determine redox characteristics of that sample. Again, if a dissolved oxygen meter could be incorporated into the program, a fantastic VI would come to be.

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