User Manual
WheeStat Pico 2.1

Smoky Mountain Scientific: SMS is a 501(c)(3) charitable organization with the mission of developing and building open-source, low cost scientific instruments for science education. Our web site is at SmokyMtSci.com.

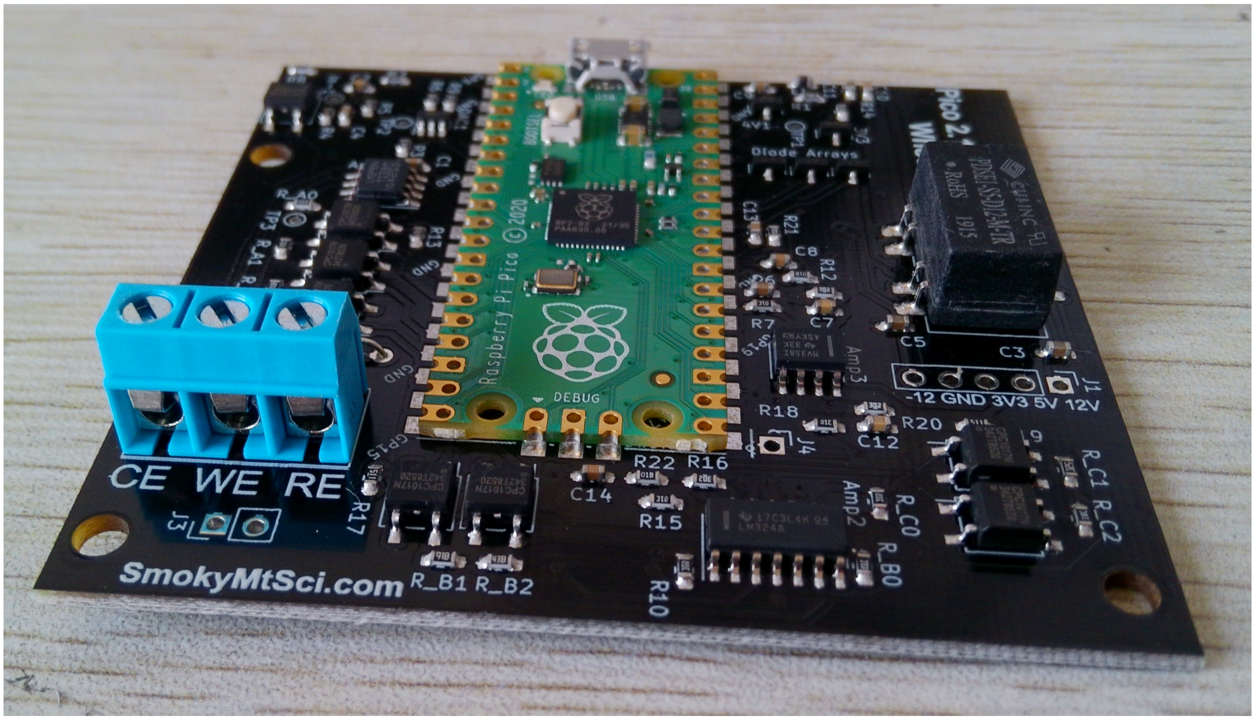
Contents:

See outline to the left.

1. Introduction:

WheeStats are a series of computer controlled, three-electrode potentiostats designed and produced by Smoky Mountain Scientific (SMS). As of 2024, SMS has offered three major versions of the WheeStat, models 5, 7 and the Pico 2.1. The Pico instruments are the most recent. We are currently working to develop a version of the Pico 2.1 with extended current sourcing capacity. All the WheeStat models come with firmware installed and a graphic user interface on a provided USB flash drive. The user interface is compatible with modern versions of Windows operating system.

Legal Disclaimer: While the hardware and software is provided with no guarantee, it is complete and functional to the best of our knowledge at the time of manufacture. If you encounter problems with the instrument or software, contact us and we will try our best to fix the problem. Any updates to the software or this user’s manual will be available through our website, SmokyMtSci.com. While back- compatibility of more modern user interfaces with older hardware is not guaranteed, we will try to address any difficulty of this type that you encounter.



2. Setup:

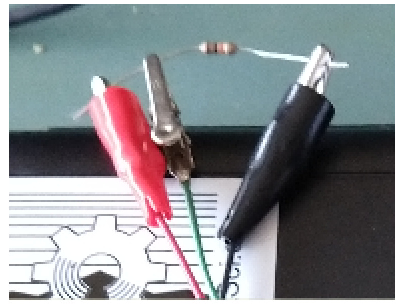
Your instrument should come with a micro-USB cable, a test resistor and a USB memory stick. A three conductor cable with alligator clips extends from one end of the instrument, and the socket for the USB connector is on the other end. Two of the alligator clips have insulating hoods, the third is bare. The clip with the black hood is for the working electrode. The clip with the red hood is for the counter electrode (also called the auxiliary electrode). The bare clip is for the reference electrode. We envision circumstances where it will be desirable to ship instruments with the three conductor cable removed. In this case, it will be necessary to open the instrument case by removing the four screws at the bottom and installing the cable. The three conductors connect to a blue terminal block (on the lower left side of the photo above).. Connectors for the Counter, Working, and Reference electrode leads are labeled CE, WE, and RE, respectively.

Note that micro-USB connections are not reversible. The flat, wide side of the plug must face the top of the instrument (the side with the sticker on it). Forcing the plug in upside down will damage the instrument.

2A. Setting up the User Interface:

The WheeStat user interface is provided as an application on the USB memory stick that came with the instrument. You can find it in a folder named “WheeStat”. While you can run the user

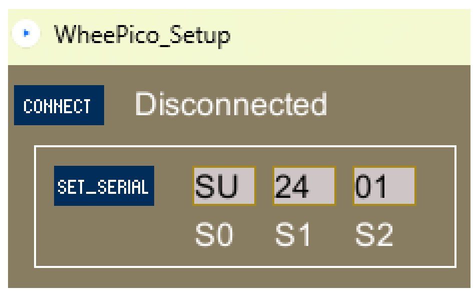
interface from the flash drive, it is better practice to copy the folder to your host computer and run it from there. To run the user interface, open the folder and click on the .exe file.
Testing:
Some functions of the instrument can be tested using a setup where the three electrode leads are connected to a test resistor. Your instrument should have shipped with one terminal of the test resistor connected to the working electrode lead (black hood) and the other terminal connected to the counter and reference electrode leads (red hood and bare clip). This setup is shown in the Figure to the right.



2B. Calibration:

Your instrument was calibrated by SMS prior to shipment and should not require further calibration. If you believe that it requires re-calibration, follow the instructions in the Supplemental section (S1B) in this manual.

2C. Changing the Serial Number of an instrument:



Each instrument can be assigned a unique, six character serial number using the WheePico_Setup program. Open the WheePico_Setup program and connect to your instrument. Only one program can be attached to your instrument at a time, so you need to disconnect from any serial device, including the standard user interface. Then click on the “Connect” button. If it connects, you will see text next to the button that indicates the serial number of the instrument. Change the characters in the S0, S1 and S2 text boxes and click on the Set_Serial button. The characters in the text boxes will be transmitted to your instrument as the new serial number and saved into non-volatile memory.

3. Collecting, Saving and Analyzing Data using the User Interface:

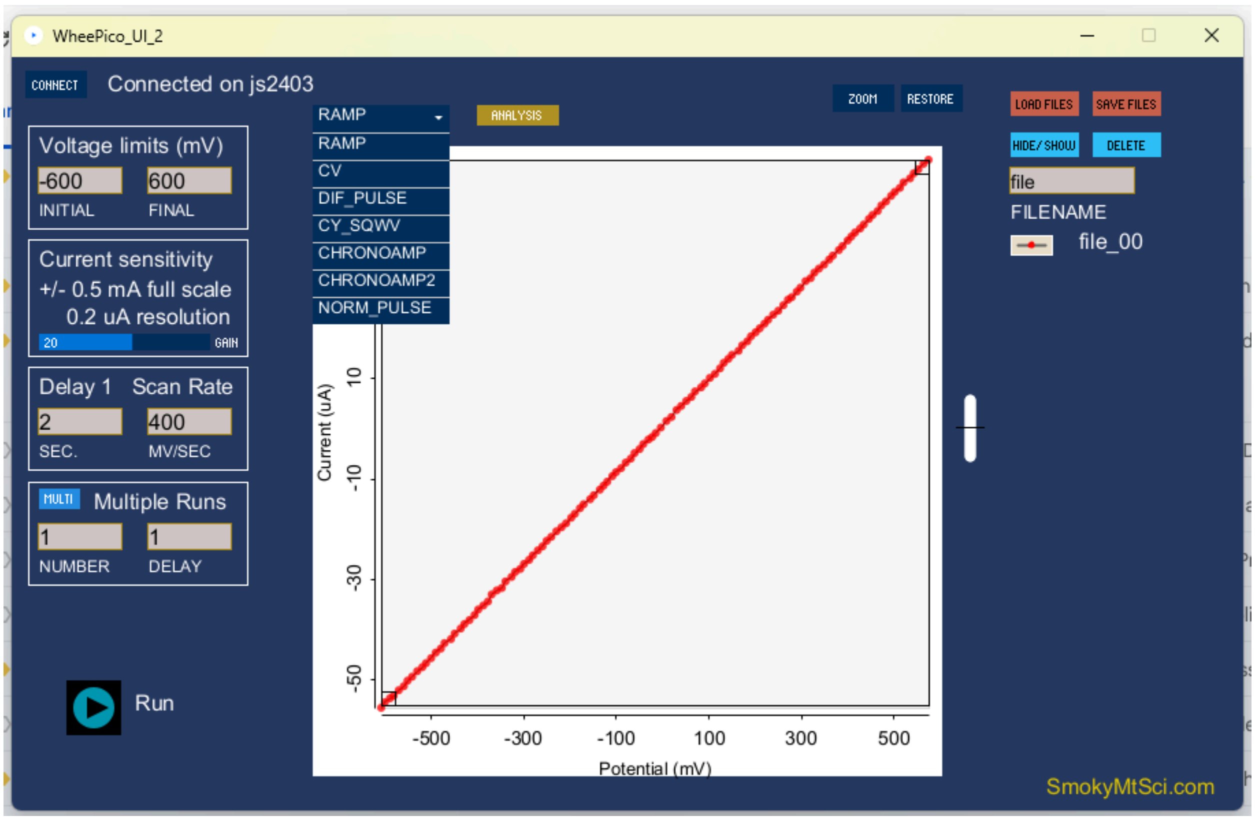
WheePico_UI_2 user interface is used for collecting, displaying, storing and analyzing data.

3A. Video Introduction:

In addition to this text, the interface is described in [this video](#). The video shows the setup of the GUI and some of its functionality. During the video, we show acquiring data when a voltage is applied across a 10 K Ohm resistor, connected as shown in the figure in Section 2A of this manual (above). As expected, Ohm's Law can be used to predict the current / voltage behavior of the voltage ramp experiment.

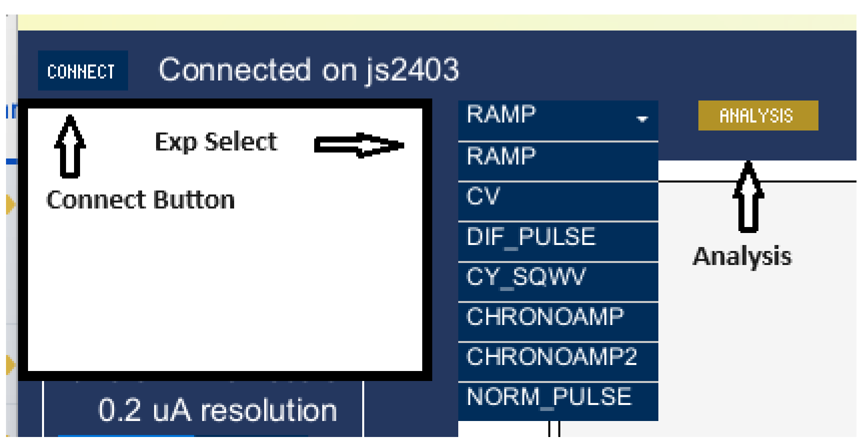
3B. Introduction to the Graphic User Interface:

The graphic user interface allows the user significant control over experiments and allows the user to see the results in real time. A screenshot of the GUI displaying data from a performance test is below.



3B1. Connecting the user interface to the instrument:

When the User Interface is opened it will automatically search for an instrument. If the instrument is plugged into the host computer the interface will connect to it and display the Serial Number of the connected instrument. On the top left of the interface is a button that allows the user to connect to the instrument. If the instrument



is connected to the host computer after the interface is opened, clicking the button will connect the instrument to the interface. If the instrument is connected, clicking the connect button will disconnect the instrument.

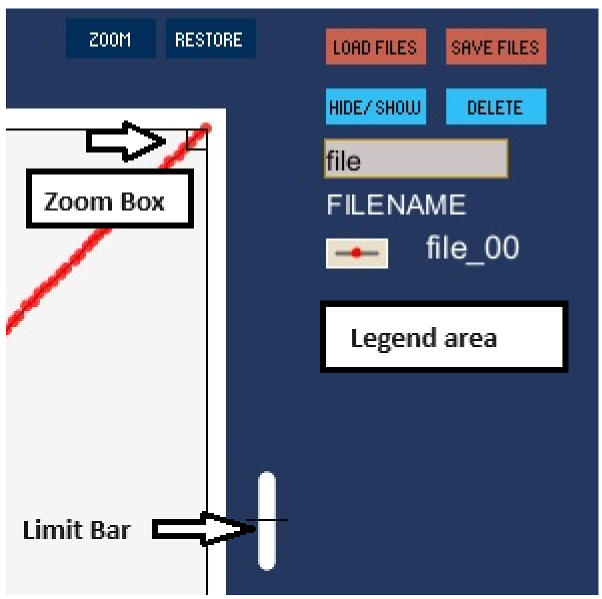
3B2. Experiment Selection:

To the right of the connect button is a dropdown that allows the user to select from a choice of experiments. In this case, the "RAMP" experiment was chosen. Other options include cyclic voltammetry, normal pulse voltammetry, differential pulse voltammetry, and one- and two-pulse chronoamperometry.

3B3. Analysis Mode.

To the right of the experiment dropdown is a gold colored button that allows the user to enter a screen where peak currents may be measured. This screen cannot be accessed unless there is at least one data file that can be analyzed. The background color of the user interface is set to gold when working on analysis. It is dark blue in recording data mode. While multiple data sets can be selected while in acquisition mode, only one data set can be selected when in analysis mode. In analysis mode, the user can define a linear background and find peak voltage and peak currents for each voltammogram of interest.

3B4. Zoom and Restore Buttons:



to the right of the Analysis button are buttons labeled “Zoom” and “Restore”. These buttons are used along with zoom boxes in the data display to zoom in on a region of interest in the data. Zoom boxes are small squares that are originally in the top right and bottom left of the data display area. Dragging the zoom boxes allows the user to select a portion of the voltammogram that will be displayed when the zoom button is clicked. Clicking the Restore button gets back to the original data.

3B5. Load and Save Files Buttons:

Data acquired using the WheeStat can be saved in comma separated value (CSV) format. CSV files can be opened using any spreadsheet program, such as excel. Once saved, Data files can be opened in the user interface by clicking on the “Load Files” button and navigating to the location where the files were saved.

3B6. Hide/Show and Delete Files Buttons:

These buttons are used along with the legend section to help the user keep track of data files, change the display, and delete files when the data is not needed. Only 20 files can be saved in memory at a time. Deleting files allows collection of new data. To hide, show, or delete a file, the file name must first be selected by clicking on it in the "Legend area".

3B7. Filename Textbox.

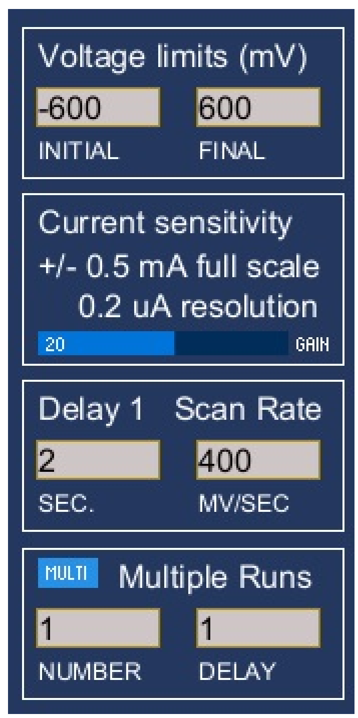
This text box allows the user to assign a name to each file, or to a set of files. This can be helpful in delineating the name of a user, or a page number in a notebook. For example if the users initials are AA and the experiment is described on page 32 of his notebook, then the filename might be assigned as AA32 and individual voltammograms will be named beginning AA32-00. Once a file name is assigned it cannot be changed. The filename will show up in the legend area, followed by a two digit file number. File numbers are assigned by the program sequentially.

3B8. Legend Area:

The legend area allows the user to keep track of the colors of the data points associated with each file.

3B9. Limit bar:

The limit bar is a display feature that allows the user to see what fraction of the instrument A to D converter is used in recording the most recent voltammogram. This allows the user to optimize the instrument gain (current sensitivity) for a given experiment. If the gain is too low, the data can become pixelated. When this happens, the user will notice that the limit bar is short when compared to the size of the graphic display area and there is significant noise compared to the signal. If the gain is too high, the ADC can be saturated, giving flat areas at low and high voltages. In this situation, the limit bar extends to the bottom or top of the display area, or both. The user should adjust the current gain using the Gain slider (figure to the right) so that the limit bar takes up at least half of the size of the data display area.



3B10. Experimental Parameter Input Area.

Below the connect button are a series of controllers that allow the user to input experimental parameters (figure to the right). The top box includes text boxes for voltage limits, in mV. Below that is a box that displays the current sensitivity and resolution. This box also contains a slider that allows the user to change the current gain. The third box has text boxes for the initial delay in seconds, and the scan rate in mV per second. Beneath the text boxes is the Run / Stop button. The majority of the GUI is devoted to a graphic data display that shows the user the experimental data in real time.

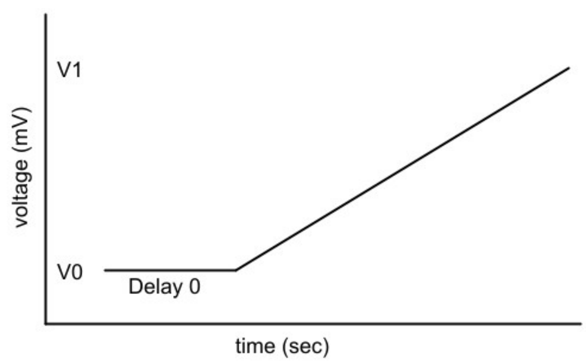
3B11. Saving and Loading Data in CSV files.

Data from our experiments can be saved as comma separated value (CSV) files which can be opened using any spreadsheet program, or can be re-loaded into the user interface at a later date. Any or all of your data files can be saved. To save data, the data file(s) of interest must first be selected. To select a data file, click on the file name in the legend area. Clicking on a selected file will un-select that file. Once you have all the desired files selected, click on the "Save Files" button. This will open a screen that allows you to select a location on your computer to save the files to. Once you save your data, it can be accessed using either a spreadsheet program or the WheeStat user interface. To load the data files, click on the "Load Files" button. This will open a dialog box that prompts you to navigate to the file location and select the file.

4. Experiments:

The WheeStat is programmed to run a number of experiments that are useful for a number of tasks. These experiments are accessed by clicking on the "mode" button at the top of the GUI. Below is a quick discussion of what each does and what it is used for. For greater detail, we refer you to other sources. Some of the links are to content by other instrument manufacturers, such as BioAnalytical Systems, Inc (BASi). Information in these links will describe using instruments from these manufacturers which may not relate directly to the instrument you have.

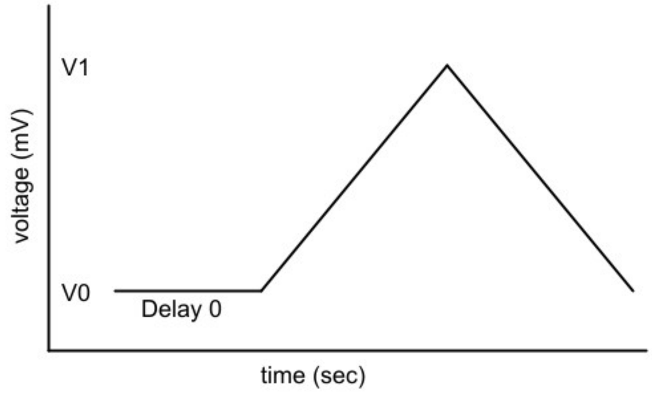
Experiment 1. Voltage Ramp.



The first experiment in the dropdown list is called "ramp". It is a quick experiment that can be used as a test to show that the instrument is functioning properly. The voltage profile is shown in the figure to the right. To run the experiment, the black lead is attached to one side of a test resistor and the other two leads are attached to the other side, as shown in the Figure in Section 2A (above). The voltage / time profile is shown in the Figure below and the experiment is demonstrated in the video demonstrating the GUI, above. The voltammogram shows the current as a function of applied voltage. If the experiment is working correctly, this should be a linear plot extending through the origin (0 current, 0 mV) with a slope equal to 1/R.

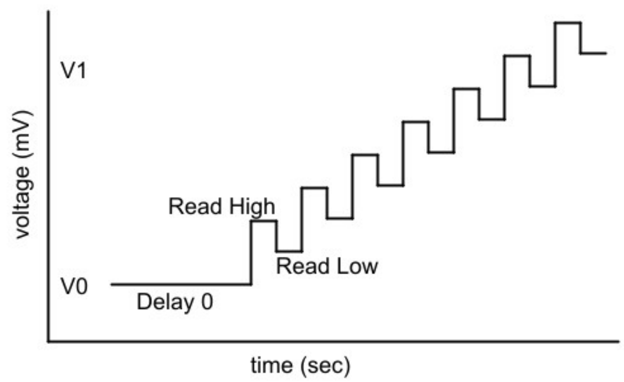
Experiment 2. Cyclic voltammetry (CV):

Cyclic voltammetry is a commonly used method for characterizing redox active materials in solution. In the cyclic voltammetry experiment, the voltage at the working electrode is ramped from an initial value to a final value and then ramped back to the initial voltage. The figure below shows the voltage versus time profile for the CV experiment. A description of cyclic voltammetry can be found in this J. Chem Ed article. A well written teaching lab giving step by step instructions can be found here.

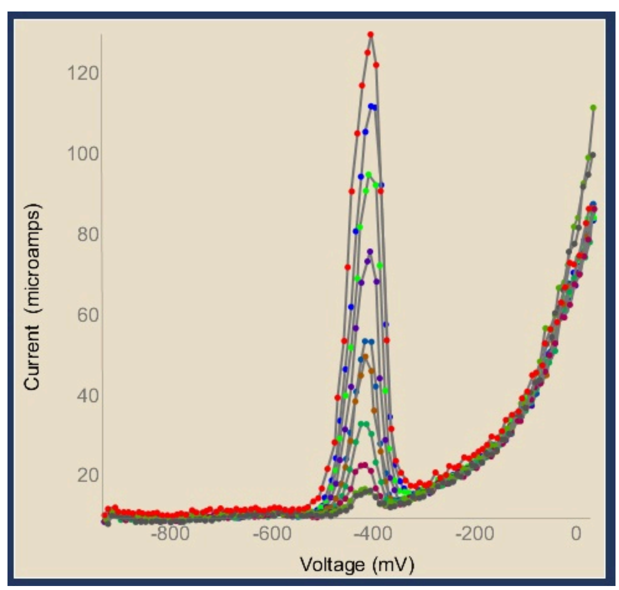


Experiment 3. Differential Pulse Voltammetry (DIF_PULSE):

Differential Pulse Voltammetry is another commonly used method for characterizing redox activity. The technique is one of a set called pulsed voltammetry techniques, some of which are described here by BioAnalytical Systems Inc. The voltage profile for DPV is presented in the figure to the right. In this experiment, voltage is stepped high and the current is measured. Voltage is then stepped low and the current is measured again. The signal in DPV is taken as the difference between the high and low measurements. The benefit of DPV over a ramping technique is that it removes the effects of non-Faradaic processes, such as charging the electrode. The result is that the voltammograms are easier to interpret and explain.



One application of DPV is a technique commonly used for metals analysis called stripping voltammetry. Stripping voltammetry is discussed here. A good laboratory experiment, with step-by-step directions for quantifying lead in water is here. This technique was used to collect the data presented in the figure on the right which was collected using an older model WheeStat. There is a table of elements in this reference that can reportedly be determined by ASV. Unfortunately,

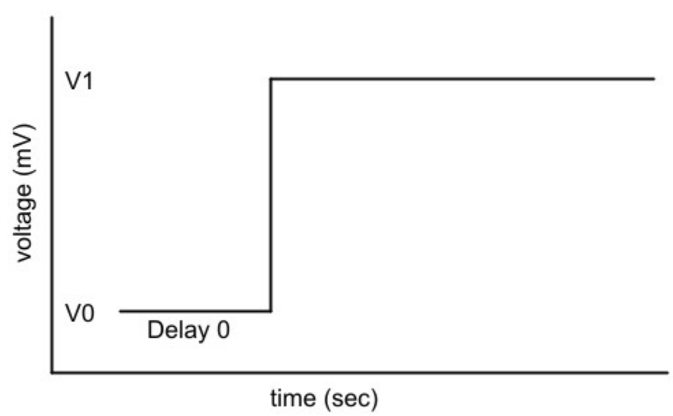


the author does not list his source. Anodic stripping voltammetry (ASV) is a technique that can be used at very low concentrations if the product of reduction is not soluble. For example, if you reduce Cu2+ ions to Cu metal, the metal that is deposited on the electrode stays on the electrode. When this is the case, the analyte can be "pre-concentrated" on the electrode, making it easier to detect during a subsequent analysis step. The WheeStat is set up to do ASV using differential pulse voltammetry during this analysis. The difference between the ASV experiment and the DPV experiment has to do with what goes on before the analysis step. In DPV, you typically hold the voltage at the initial value for a couple of seconds to establish conditions surrounding the electrodes before proceeding. In ASV, you use the pre-analysis time to prepare the electrode and deposit the analyte onto the electrode surface, thereby pre-concentrating it.

Experiment 4. Cyclic Square Wave Voltammetry (CY_SQW):

The voltage profile for Differential Pulse voltammetry is related to that of Cyclic Square Wave Voltammetry. The difference is that in a cyclic square wave experiment, the voltage profile ramps from an initial value to a final value via a series of steps like the differential pulse experiment, and then it ramps back to the original value by another series of steps. By starting and ending at the same voltage, the Cyclic Square Wave experiment is similar to the Cyclic Voltammetry experiment..

Experiment 5. Chronoamperometry (CHRONOAMP):

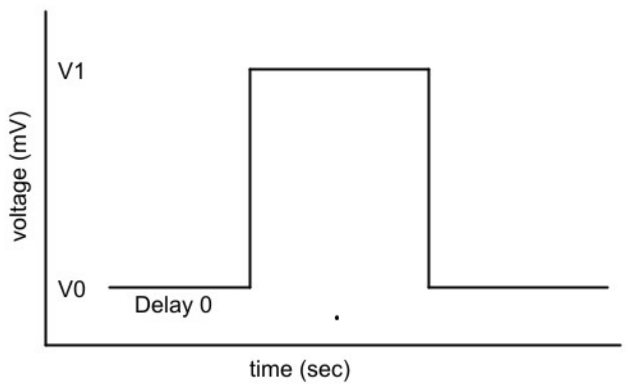


In single step chronoamperometry, the potential of the working electrode is stepped from its initial value to a final value and the current is sampled as a function of time. Description of chronoamperometry by a BASi is here. A nice teaching lab can be found here. Typically, the initial voltage is established where the compound in question is stable and no current passes. The voltage is then stepped to a potential where the compound will either accept or lose an electron to give a second compound. To illustrate, we consider the electrochemical response of the hexacyanoferrate ion ($FeCN_6^{3-}$). In this experiment, the initial voltage was set to +600 mV, where the iron(III) compound is stable. At time = 0, the voltage was stepped to +100 mV. At this voltage, the iron(II) form of the compound is the stable species and the following half reaction occurs at the working electrode:

$FeCN_6^{3-}$ + e- <==> $FeCN_6^{4-}$ (1)

In such an experiment the electrical current passed to the electrode will be a positive value that decays with time. To understand current response using other voltammetric techniques, it is necessary to understand the origin and nature of this decay. Just after the potential step, there is a great excess of the iron(III) compound close to the working electrode, giving rise to a large current. As time evolves, the amount of iron(III) available for reaction diminishes and subsequently, the electrical current decays. The current / time profile in chronoamperometry experiments is governed by the rates at which compounds reach the working electrode. In an unstirred electrolyte solution, the current is determined by the rate at which the compound diffuses. For a planar electrode under these conditions the current is described as a function of time by the Cottrell equation (since I cant figure out how to write equations in this format, click this link).: Note that all the terms in the Cottrell equation are constant with the exception of the current and the time. Thus, the current is expected to be proportional to one divided by the square root of time.

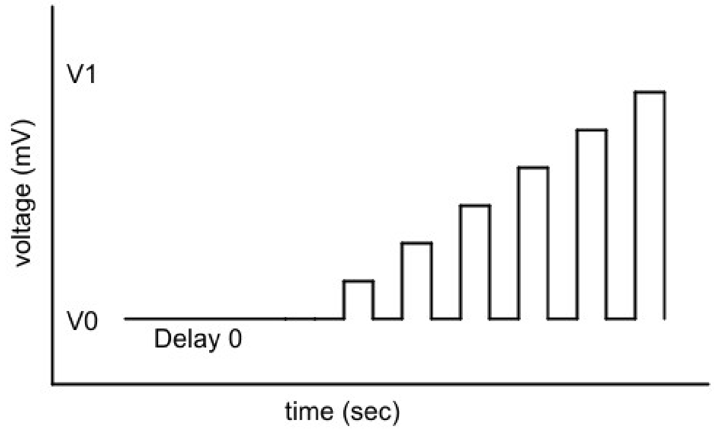
Experiment 6. Double step chronoamperometry (CHRONOAMP2).



The time / voltage profile for a double potential step experiment. In this experiment, the voltage is stepped from the initial voltage to a second voltage and then back to the initial voltage. Current data is collected after each of the two steps. Experiments for Teaching Electrochemistry: 2. Normal pulse voltammetry: . A normal pulse voltammetry experiment consists of a series of voltage pulses with varying heights. It is described here. For our discussion of chronoamperometry, we assumed that the iron(III) form of the compound was the only species stable at the initial voltage and the iron(II) form was the only one stable at the second voltage. At intermediate voltages, however, both oxidation states exist at equilibrium, with their ratio determined by the Nernst equation: $E = E° + RT/nF \ln([Fe3+]/[Fe2+])$ (3) Where E is the applied voltage, E° is the standard reduction potential of the couple, R is the ideal gas constant, T is the absolute temperature, n is the number of moles of electrons transferred and F is the Faraday contant. Thus, Equation 3 tells us that the applied potential (E) and the standard reduction potential (E°) determine the position of the equilibrium mixture of oxidized and reduced species. The relationship that the Nernst equation predicts for a Fe3+ / Fe2+ couple with an Eo of +300 mV is presented in Figure 3 . In this figure, the red line represents the percentage of an Fe2+ ion and the blue line represents the percentage of Fe3+. Notice that at a potential of +150 mV, nearly all the compound exists as the reduced, Fe2+ state, at +300 mV (the Eo for the couple) the mixture contains 50% of each, and at +450 mV, nearly all is in the oxidized, Fe3+ state.

Experiment 7. Normal Pulse:

The Normal Pulse experiment involves a series of voltage steps as shown in the figure to the right. The current and voltage are sampled at the height of each step and returned to the initial voltage between each step. The purpose of stepping back to the initial voltage is to re-establish the initial conditions of the experiment. The normal pulse experiment illustrates how the chosen step potential affects the current profile. Thus, by sampling over a range of voltages where both oxidized and reduced species are present, we can demonstrate that the Nerst equation governs the shape of the voltammogram. The down side of the Normal Pulse experiment is that long periods are required to re-establish the initial experimental conditions, making the experiment long in duration.



Supplemental Section

S1. Hardware:

S1.A Models. There are a few models of the WheeStat Pico 2.1 available. There is a model code stored in non-volatile memory. This code can be read by using a Serial emulator program such as PuTTy or the one that comes built into programs like the Arduino IDE. Connect to the instrument at a baud rate of 115200 and send it the 'R' character. The instrument will respond with a line of text that includes the model code in binary format. As of March 2024, there were five models produced. The different features of the models are presented in the table below. For example, Model 5 will respond to the Serial input of "R" with an output including "model: 101". According to the table, this model will be built on the 2.1d board and have a DAC address of 96 and will not include the high current module. Only two of this model were manufactured. The standard model, without the high current module should source 40 mA power over +/- 4.1 volts.

Model

Note that the DAC address is defined by the DAC model number, which changed during manufacturing. This was a result of our original choice being unavailable at the time. The DAC address that the instrument responds to will not change.

Model code	board	DAC address	High I	Number Mfd

0	2.1e	100	-	81
1	2.1d	100	-	0
4	2.1e	96	-	9
5	2.1d	96	-	2
8	2.1e	100	+	10
9	2.1d	100	+	0
12	2.1e	96	+	0
13	2.1d	96	+	1

The model code cannot be changed through a user interface. The model number can be changed using a serial port emulator at baud 115200 by transmitting the ‘m’ character followed by the character for the model number. For example, changing the model number to indicate an extended current 2.1e with a DAC address of 100, the user sends the text “m8” to the instrument. On receiving this instruction, the instrument will store the value 8 in address 6 of its flash memory. On startup, the instrument will retrieve this value and set parameters accordingly. Additional work is expected to show that the addition of the high current module and a higher current amplifier, will allow the instrument to source greater current output (250 mA). Wire pads to allow easy incorporation of this possible modification added to the 2.1e schematic. Work on high current model put on hold while working on software.

S1.B. Calibrating the DAC zero value:

Instrument design requires the digital value input to the DAC be adjusted to give zero voltage across the Reference and Working electrodes. The approximate value should be half the DAC range. There is an offset that is adjusted in the firmware. The offset needs to be loaded into non-volatile memory. This memory value is read during startup.

The DAC can be calibrated using the WheePico_Setup program. To calibrate, connect leads from RE and CE to one end of 10 K resistor and the WE lead to other end as shown in Figure 1 (In the ”Setup” section of this manual). Connect a volt meter set to mV DC across the test resistor. Open the WheePico_Setup interface and adjust the z offset in the textbox and click the CAL_DAC button. Repeat this process with new values until the multi-meter reads zero volts (or as close as you can get).

S1.C. Reference voltage offset:

The reference voltage is an offset that is required required since the ADC is only capable of measuring exclusively positive voltages. Since the measurement of both current and voltage relies on the reference voltage, both are affected by uncertainty in the reference.

In model 2.1e, this is addressed by measuring the amplified pwm based voltage offset on ADC channel A2. Our early experiments with this model shows it to be an effective method.

For model 2.1d, experiments showed that uncertainty in the reference voltage offset was a serious issue. We found that it could be corrected in software by adding an offset to the outputs. Doing the correction has been automated but you will need to connect a resistor to the electrodes, like was done in the “calibrate DAC zero value” procedure (above). Connect to the instrument using a serial port emulator at 115200 baud and give it the ‘c’ character. When the instrument receives this, it will set the voltage to zero, measure the voltage using the internal ADC and subtract that value from all subsequent measurements. The correction will be saved in non-volatile memory and will be retrieved any time the instrument is powered up.

S.1D. Addressing ADC measurement accuracy: In the 2.1d and previous models, Analog to Digital Converter measurements (ADC) were referenced to the 3.3 volt system voltage. To improve the accuracy, The ADC in the Model 2.1e compares voltages to the output of a precision 3.3 V voltage reference.

S1.E. High Current Models:

Both the 2.1d and 2.1e models can be modified to have high current capacities. Changing the hardware to accommodate higher currents requires using a different amplifier and incorporating a higher current power supply and DC/DC converter.

S1.D1. High Current Hardware:

High current prototype based on model 2.1d2 with high current subassembly. Subassembly fabricated on perf-board: DCWN06A-12 supply, 1A 12V AC/DC converter. High current sense resistor (10 ohm) circuit using existing kill switch circuit board with SSR at 400 mA capacity, substitute Amp1 with higher current AD8397ARZ dual amp, 310 mA per channel. Testing with the modified model 2.1d2 showed that the new DC/DC converter suffered from high levels of noise on the output channels, which will need to be addressed in future versions of the high current module..

S1.D2. Changing the model number to identify high current models.

To avoid problems with users modifying the software without modifying the hardware, we have not incorporated the changing thing into any interface. Instead, changing the model number requires the user to send text to the instrument over a serial port emulator program. Sending the characters “m8” will change the model number to high current version of model 2.1e. Sending “m0” will change back to the standard, lower current version.

S2. Firmware:

Firmware WheePico_2.1 written in Arduino for the Raspberry Pi Pico microcontroller. If you want to change the instrument firmware, make sure that Arduino IDE has board set to wired version of Pico (not the wireless version, PicoW). Setting to Pico W causes big problems with

Serial communications. If you wish to modify the firmware, please contact me. I will provide the source code and advice.
The firmware and user interface will work for the models 2.1d and 2.1e, but requires that the correct model number be in the non-volatile memory of the microcontroller.

S2.A, Non-volatile Memory:

Important parameters are saved in flash memory on the instrument. Model number and serial number are retrieved from flash memory and are transmitted to the user interface at connection.

Table S2.A, Flash memory addresses

Parameter	Address	Range
DAC Offset	8, 9	+/- 2047
Reference Voltage Offset	10, 11	+/- 2047
Model Code	6	0 - 255

S3. User Interface:

S3.A. Standardizing communication between hardware and user interfaces: User interface transmits ‘*’ character, firmware responds with “&aaaaaa,b”. Where aaaaaa represents the six character serial number and b is the model number. If((b & 8) != 0), then the instrument is high current and we need to modify the gain slider and display the model on the interface.
S3.B. Communication with setup interface and hardware. The setup user interface needs to know the DAC offset in addition to the serial number and model. It is not clear whether the 2.1e model will require a reference voltage offset, so we will not be able to finalize code until after the model is received.. In response to ‘R’ character, the instrument sends values of DAC offset and reference offset. Neither of these are needed in the collection or analysis of data. Note: model number can only be changed using serial com port emulator. This is done by sending “mc” command where c is the model number: 0 is standard, 1 is model 2.1d, 8 is standard with high current, 9 2.1d with high current.

S3.C. Changes to user interface for high current model: set up minimum gain values: Gain value of -5 gives range to +/- 325 mA, gain of 2 gives +/- 54 mA.