

Echem Analyst[™] Software Operator's Guide



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Introduction to This Guide

Echem Analyst[™] software is Gamry Instruments' dedicated data-analysis program, the companion to Gamry Instruments' data-acquisition program called Framework[™]. Data files generated by experiments in Framework software then can be analyzed in the Echem Analyst. The Echem Analyst is a single program that runs data-analysis for all types of experiments, such as those used in DC Corrosion, EIS, and Physical Electrochemistry.

The Echem Analyst is designed with the specific functions to make data analysis as straightforward as possible. This manual explains the most common analysis routines. The tools discussed here in the examples are common to many data files created by other experiments. This document is a guide, and is not intended to have the same scope as the on-line help or a complete operating manual. In order to create a concise document, we assume you have a working knowledge of Windows[®]-based applications. We ignore details about common functions, such as opening, saving, and closing files, so as not to obscure the goal of this guide.

This textbox indicates a helpful hint to know about Echem Analyst.



Installation

Echem Analyst installs separately from other Gamry software. If Echem Analyst is not installed yet, you can find it on the CD-ROM, or—if you already own one of our potentiostats—on our website at <u>www.gamry.com</u>.

You may install copies of the Echem Analyst on multiple computers. Often users prefer the convenience of performing data-analysis at an office workstation, rather than the laboratory setting.

File Formats

Gamry data files acquired using Framework software have the extension *.DTA. DTA files are ASCII text, and therefore you can open them directly into various programs, such as Excel[®] or Origin[®]. When DTA files are opened in Echem Analyst, then saved, their extension becomes *.GData. Gdata (Gamry Data) files include information on curve-fits and graphing options, thus Gdata files are only viewable in Echem Analyst.



Do not delete your DTA files! They are the raw data and may need to be reloaded for certain analyses, such as area normalization.

To Open a Gamry Data File

There are several different methods to open data files in the Echem Analyst:

- Launch the Echem Analyst icon on your desktop. Then use the File > Open function.
- 4. Use the link on your desktop to open the **My Gamry Data** folder. Double-click on the data file. You may have to instruct your computer to associate the *.DTA extension with the Echem Analyst program.



- 5. There are two quick ways to open a recent Gamry Data File.
 - a. A recently generated file can be opened using the hotlink in the *Analysis* menu in the Gamry Framework. (The last eight generated data files are listed there for quick access.) The Echem Analyst automatically launches and opens your selected data file.
 - b. A recently opened file in the Echem Analyst is shown at the bottom of the **File** menu. This is similar to how other Windows®-based programs display links to *Most Recently Used* documents.

By default, files acquired in the Framework are saved into the **My Gamry Data** folder. A shortcut for **My Gamry Data** installs on the Windows[®] desktop. You can change this default under **Tools** > **Options**, which opens the **Gamry Analysis Framework Options** window. Choose the **General** tab, and change the **Path** for each type of data file as desired.

Don't change the directory for *Analysis Script* Files. These are the VBA programs that do the actual analysis.

≥ Don'T

The data set appears in the main window. The menu items, tabs, and toolbar are adjusted for the particular type of data set you chose. In the example below, a Potentiostatic EIS data set is shown:



Note the tab-based display. The **Experimental Setup** tab displays all the information from the parameters used to run the experiment, such as voltage, time, etc. The **Experimental Notes** tab stores any notes written into the setup screen in Framework. The **Open Circuit Voltage** tab shows the voltage measured during the initial delay of the experiment. The **Hardware Settings** tab records information on the filters, ranges, gains. Additional information on date of last calibration, software version, etc. is also stored here.

Working with Plots in Echem Analyst

Introduction

Echem Analyst boasts a number of graphical tools to help you get the most information out of your data. After you open a data set, these tools appear in the toolbars immediately above the plot:

In the data file, Framework writes a line that indicates the type of experiment used to generate that file. Echem Analyst displays both general and specific menus containing the analysis routines pertinent to your experiment.

Toolbars:

🤌 Gamry Echem Analyst - [Sample Cyclic Voltammetry - Ascorbic Acid.DTA]	
6 Eile Iools Window Help Cyclic Voltammetry Common Tools Quick Help	_ & ×
📔 🛃 🖄 😫 🗮 🖬 👘	
Chart Experimental Setup Experimental Notes Electrode Settings Hardware Settings	
📗 🖻 🗠 🕶 💩 🕶 🖿 📾 🔚 🎟 🔛 🗠 🗇 🎯 🔎 🖄 ≽ ≻	
)) 🗊 🖄 🖄 🏷 🚔 🙀 📝 🛃 💌	
0	- LL-Barrenselers

The main toolbars are:

General	General functions for replotting and printing in various formats
Toolbar	🖻 🗠 🕶 🦄 🕶 🛍 📾 📰 🎟 🜇 🖛 🗇 🎯 🔎 🙆 🔌 🥕
Selection	Tools to select and view data points
Toolbar	🛛 🖬 🔺 🕉 🔚 🦎 📝 🕞 💿

The following charts are references for buttons on the default toolbars. Descriptions of the most commonly used functions are highlighted in blue.

Button	Name	Action
Ð	Copy to clip- board	Copy the selection to the Windows [®] clipboard. Can paste directly in Mi- crosoft programs for reports or presentations.
	Gallery	Choose, via the dropdown menu, from scatter (no line), line, curve, and steps between data points
- 🌭	Color	Choose the color of the selection from the dropdown menu. To change the color menu, use the <i>Palette</i> button on the PaletteBar .
	Vertical Grid	Toggle between showing and hiding vertical grid lines on the plot
	Horizontal Grid	Toggle between showing and hiding horizontal grid lines on the plot
	Legend Bar	Toggle between showing and hiding a legend bar underneath the plot
	Data Viewer	Toggle between showing and hiding numerical data to the left of the plot
	Properties	Open the GamryChart Properties window, so that you can adjust effects, colors, markers, 3-D effects, lines, etc.
64	3D/2D	Toggle between two-dimensional and three-dimensional graphing
4	Rotate	Rotate the three-dimensional graph. Only active if the graph is 3D.
	Z-clustered	Offset two data sets so that they can be distinguished within one plot. Only operates in 3D mode.
<i>,</i>	Zoom	Zoom in on a selected region. Also open a zoom slider at the bottom of the graph for continuous adjustment of zoom.
	Print preview	Open the Page setup window to adjust orientation of plot and printer mar- gins
\$	Print	Print the plot
>	Tools	Open a dropdown menu, for choices of various toolbars and viewers to appear on the screen

General Toolbar Functions

Selection Toolbar Functions

Button	Name	Action
	Show curve selector	Open the Curve Selector area to the right of the plot, so that you can choose which data are used as the x-, y-, or y2-coordinate, and which curve is the active trace.
	Select x region	Select a desired region of the plot across the x-axis. Commonly used to specify a region for Quick-Integrate .
	Select y region	Select a desired region of the plot across the <i>y</i> -axis Commonly used to specify a region for Quick-Integrate .
Ø	Select Portion of Curve using the Mouse	Left-click on the active trace using the mouse to select a section of the curve
	Select Portion of Curve using the Key- board	Open an area to the right of the plot, in which you can choose a segment of the trace numerically. See below for more details.
***	Draw Freehand Line	Draw a line on the plot
	Mark Found Peaks	Place a tag on peaks that the software finds. A portion of the curve must be selected first.
1	Apply Template	Open the Apply User-Defined Chart Template window, and choose a previously created template to apply to the plot
	Save Template	Open the Save User-Defined Chart Template window, and save the template
۲	Show Disabled Points	Show data points not being used in the plot

Changing the Axes on a Plot (the Curve Selector):

To choose a different variable plotted on an axis, use the **Curve Selector** button

as follows:

(The example shown below is a Differential Pulse Voltammetry plot.)

1. With the plot open and displayed on the screen, click the Curve Selector but-



The **Curve Selector** area appears on the right side of the window.

2. Choose which trace is active by clicking the drop-down menu in the **Active Trace** area.

The Active Trace is the data series on which the analysis will be performed. Use this if multiple files or cycles are displayed on the graph.

3. Choose which trace is visible on the plot by activating the checkbox next to the desired trace(s) in the **Visible Traces** area.

Visible Traces also contains any data fits that are performed.

- 4. Choose which variable is plotted on the *x*-axis by highlighting the variable in the **X-Axis** column.
- 5. Choose which variable is plotted on the *y*-axis by highlighting the variable in the **Y-Axis** column.
- 6. Choose which variable is plotted on the second *y*-axis by highlighting the variable in the **Y2-Axis** column.



If there is a data column graphed on the **Y2-Axis**, those data appear in a different color and a different scale.

Selecting Portions of a Curve for Analysis

For certain types of analysis, you must select a region of the curve, for example, within the **Peak Find** function in Cyclic Voltammetry or **Tafel Fit** function in Potentiodynamic. You can select regions by mouse or keyboard.

- 1. Left-click the mouse on the **Mouse** button in the **Selection toolbar**.
- 2. Use the left mouse-button to select each endpoint of the curve. Each endpoint is marked with a blue cross. The selected portion of the curve is shown as a thick blue line. (In the figure below, the color of the data was changed to red for contrast to the selected region).



3. Another click on the **Mouse** button clears the selected region, and readies the graph for a different region to be selected.

Cutting and Pasting Images and Data

Many users want to present, publish, or otherwise share their data and charts from the Echem Analyst.

To create a bitmap image of the graph,

As a Bitmap:

- 1. In the General Toolbar, click the **Copy to Clipboard** button
- 2. In the drop-down menu select As a Bitmap.



3. A bitmap image of the graph enters the clipboard. You can paste this bitmap into a presentation program such as Word[®] or Powerpoint[®].

This is a quick and easy way to import a picture of the graph for a presentation or report.



As Text:

Because Gamry Data Files are ASCII text, they can be opened easily in other graphing programs, such as Excel[®] or Origin[®]. Right-click on the DTA file, select **Open With...**, and select your desired program. These programs, however, do not contain fitting routines specific to the analysis of electrochemical data. This **As Text** feature lets you fit the data in Echem Analyst and then copy and paste the data and fit into another graphing program.

This is a quick and easy way to import both the data and the fit into another graphing program.



If you are using the **As Text** feature, be sure to note the currently graphed parameters. The coordinates of this currently displayed graph are copied and can be pasted to graphing programs.

Plotting Conventions

By right-clicking the mouse on a non-zero value on an axis, you can choose to show that axis in **Log Scale** (logarithmic) or linear scale (when **Log Scale** is inactive), or to reverse the direction of the numbers (when **Reversed** is active).



Or you can use the **Transform Axes** selection (if available) under the **Common Tools** menu.



Getting On-Line Help and Version Number:

In the toolbar, choose **Help**.

a. Click **Gamry Help** to obtain information about various commands and functions within Echem Analyst.

A separate Gamry Echem Analyst Help

 Camry Echem Analyst

 File Tools Window

 Bile Tools Window





On-line help is a great resource for more involved questions. **Help** is divided up according to software package.

b. Click **About the Gamry Echem Analyst** to view the software version number.

While each type of experimental data has its own method and parameters, there are certain commands that are common to many analyses. This section shows you these **Common Tools**.

Accessing Common Tools

1. Open a dataset.

In the toolbar, the function **Common Tools** appears.



3. Select the desired command.

In this example, chronoamperometry's **Common Tools** includes three commands: **Add I Constant**, **Linear Fit**, and **Smooth Data**.



List of Common Tools

Command	Type of experiment	Result
Add E Con- stant	Cyclic Voltammetry, DC Voltammetry, Dif- ferential Pulse Voltammetry, Galvanic Corro- sion, Normal Pulse Voltammetry, Pitting Scan, Polarization Resistance, Potentiody- namic Scan, Square-Wave Voltammetry	Adds a constant po- tential to all voltages in the plot. Used to easily convert be- tween different Ref- erence Electrode's scales.
Add I Con- stant	Chronoamperometry, Chronopotentiometry, Cyclic Voltammetry, Galvanic Corrosion, Pit- ting Scan, Polarization Resistance, Poten- tiodynamic Scan	Adds a constant val- ue to all currents in the plot.
C from CPE, omega(max)	Potentiostatic EIS, AC Voltammetry, Mott- Schottky	Calculates capaci- tance from previ- ously fit CPE values

		and data from the Nyquist plot.
C from CPE, R(parallel)	Potentiostatic EIS, AC Voltammetry, Mott- Schottky	Calculates capaci- tance from previ- ously fit CPE and fit R data.
Linear Fit	Chronoamperometry, Potentiostatic EIS, AC Voltammetry, Chronocoulometry, Chronopo- tentiometry, Cyclic Voltammetry, DC Volt- ammetry, Differential Pulse Voltammetry, EMF Trend, Galvanic Corrosion, Mott- Schottky, Normal Pulse Voltammetry, Polari- zation Resistance, Potentiodynamic Scan, Square-Wave Voltammetry	When a region of the plot is selected, fits the data to y = mx + b.
Post-Run iR Correction	Cyclic Voltammetry, Polarization Resistance, Potentiodynamic Scan	Corrects a previous- ly run scan for volt- age-drop caused by <i>iR</i> .
Smooth Data	Chronoamperometry, Chronopotentiometry, Cyclic Voltammetry, DC Voltammetry, Dif- ferential Pulse Voltammetry, EMF Trend, Galvanic Corrosion, Normal Pulse Voltamme- try, Pitting Scan, Polarization Resistance, Po- tentiodynamic Scan, Square-Wave Voltam- metry	Smooths the data. Useful for locating peaks in regions of high data-density.
Transform Axes	Galvanic Corrosion, Pitting Scan, Polarization Resistance, Potentiodynamic Scan	Changes x- and y- axes from linear to logarithmic, etc.

Experimental Setup

🖉 Gamry Echem Analyst - [Sample Cyclic Voltammetry - Ferricyanide.DTA]						
6 Eile Tools Window Hel	C File Iools Window Help Cyclic Volkammetry Common Tools Quick Help					
📔 🖬 🗠 🖂 🛃						
Chart Experimental Setup E	xperimental Notes Electrode Settings Hardware Settings					
Initial <u>E</u> (V)	0.6 © vs. Eref © vs. Eoc	Scan Limit <u>1</u> (V)	0.1 💿 vs. Eref 🔿 vs. Eoc			
Scan Limit <u>2</u> (V)	0.6 © vs. Egef C vs. Ege	Final <u>E</u> (V)	0.6 © vs. Eref C vs. Ego			
Date	8/31/2004					
Test <u>I</u> dentifier	Cyclic Voltammetry					
Time	11:34:58					
<u>S</u> can Rate (mV/s)	100					
Step Size (mV)	1					
Electrode <u>A</u> rea (cm²)	0.0707					
Equil. <u>T</u> ime (s)	5					
Max Current (mA)	0.04					
Conditioning	☐ <u>0</u> # 15 Time(s) 0 E(V)					
Init. Deļay	□ _0ff 30 Time(s) 0 Stab.(mV/s)					
Cycles (#)	1					
IRComp	None					
Open Circuit (V)	0					

This particular **Experimental Setup** tab is from a Cyclic Voltammetry experiment. This example has many of the same parameters as other experiments. It shows:

Initial E, Scan Limit 1, Scan Limit 2, Final E	The potentials defining the waveform, and whether measured vs. a reference electrode (E_{ref}) or the open circuit potential (E_{oc}).
Test Identifier	Read from the Framework Setup. This field also becomes the default title of the plot.
Time	Time the experiment was started
Scan Rate	How fast (in mV/s) the scan was taken
Step Size	The interval between potentials
Electrode Area	The size of the electrode
Equil. Time	How much time was spent letting the electronics settle before the scan was started
I/E Range Mode	Automatically adjusted or fixed I/E (Current) Range mode.
Max Current	The current value that sets the I/E Range in Fixed Mode and determines the range in which to start in Auto Mode
Conditioning	Whether off or on, for how long, and under what potential. This Potential is vs. Reference.
Init. Delay	Whether off or on. This is when the $E_{\rm oc}$ is measured.
Cycles	Number of how many voltammetry cycles were run
IR Comp	If IR Compensation was used and the mode.
Open Circuit	The value of the open-circuit voltage (Corrosion Potential). It is the value of the last point in the Initial Delay.
Sampling Mode	Data-acquisition mode (for Reference family Potentiostats)

Experimental Notes

Click the **Experimental Notes** tab:

Any notes entered in the Framework software are automatically displayed here. You may enter any additional comments about the experiment in the **Notes...** field.

		e fottammetry - Ferri	cyanide.DTAj
C <u>File T</u> ools <u>W</u> ind	dow <u>H</u> elp <u>Cyclic Volta</u>	ammetry <u>C</u> ommon Tools	Quick Help
🚰 🖬 🗠 🗃	2 = = 11 🤊	@ 12 ⁹	
Chart Experimental S	Setup≻ Experimental Note	Electrode Settings Har	dware Settings
<u>N</u> otes	Pt electrode 1M NaCl 10 n +200 ul 0.1M +200 ul 0.5M	nl FeCN6 [2mM Fe(CN)6] H2SO4 [10 mM H2SO4]	

This is a version of a modern laboratory notebook. Enter as many details about your experiment as you can. Information here can help you avoid having long strings of descriptive file names.

Hardware Settings



This section documents the hardware settings that were used when the experiment was run, e.g., everything from the offsets, filters, and gains to the last time the potentiostat was calibrated.

This information is used primarily by Gamry Instruments' Technical Support staff to help troubleshoot. Gamry Instruments determines default settings based on experience. Advanced users can adjust these settings manually before the experiment is run.

For DC Corrosion experiments, the **Hardware Settings** are set in the experiment code. For Physical Electrochemistry experiments, you have access to these features through the **Advanced Panel**, but we recommend that only advanced users make changes to these settings. Consult **Help** or Gamry Instruments' Technical Support for advice.

Click the Hardware Settings tab:-

1	Chart Experimental Setup Ex	perimental Notes Open Circuit Voltage Herdware Settings		
	Potentiostat	PC14G750-45060	Pstat Model	Series-G 750
	Control Mode	Potentiostat	Current Convention	Anodic
	Control Amp Speed	Medium	I/E Stability	Slow
	I/E AutoRange	√ <u>O</u> n	I/E Range	75 mA
	Ich Auto Range	l▼ <u>O</u> n	Vch Auto Range	<u>₩</u> <u>0</u> n
	Ich Range	3V	Vch Range	30 V
	Ich Filter	5 Hz	Vch Filter	5 Hz
	Ich Offset Enable	<u> </u>	Vch Offset Enable	<u> </u>
	Ich Offset (V)	0	Vch Offset (V)	0
	Positive Feedback IR Comp	<u>п</u> 04	Positive Feedback Resistance	0
	I/E Range Lower Limit	750 nA	Ach Range	3 V
	DC Calibration Date	6/6/2008	AC Calibration Date	6/6/2008
	Framework Version	5.5		

The hardware settings displayed here are:

Potentiostat	Shows the potentiostat's label
Control Modo	How the experiment was controlled
Control Mode	now the experiment was controlled
Control Amp Speed	Shows the speed of the control amplifier
I/E AutoRange	Shows if the I/E autorange function was enabled
Ich AutoRange	Shows if the I _{ch} autorange function was enabled
Ich Range	Shows the I_{ch} range (gain). 3 volts = $\times 1$ Gain.
Ich Filter	Shows the I _{ch} cut-off filter frequency
Ich Offset Enable	Shows if I _{ch} Offset was enabled
Ich Offset	Shows the I _{ch} offset voltage
Positive Feedback IR	Shows if the IR positive feedback was enabled
Comp	
I/E Range Lower Limit	Shows the lowest available I/E Range available to use in this experiment
Ach select	Shows the input connector for A _{ch}
DC Calibration Date	Shows the date of last DC calibration
Framework Version	
Pstat Model	Gives the model number of the potentiostat

Current Convention	Shows which currents are positive
I/E Stability	Shows the I/E stability speed
I/E Range	Shows the I/E (or current) range used
Vch AutoRange	Shows if V _{ch} autoranging is enabled
Vch Range	Shows the maximum value for V _{ch}
Vch Filter	Shows the V _{ch} cut-off filter frequency
Vch Offset Enable	Shows if V _{ch} Offset was enabled
Vch Offset	Shows the I _{ch} offset voltage
Positive Feedback Re-	Shows the positive feedback resistance applied to the system
sistance	
Ach Range	Shows the voltage range of the auxiliary channel
Cable ID	(for Reference family potentiostats only.) Gives the type of cable connected to the system
AC Calibration Date	Shows the date of last AC calibration
Instrument Version	Shows the Firmware Version of a Reference family potentiostat

Detailed explanations of these parameters are beyond the scope of this guide.

Open Circuit Voltage (Corrosion Potential) Data



Because default plotting of graphs is auto-scale, please note the y-axis's scale when the **Open Circuit Voltage** first appears.

Analysis of Cyclic Voltammetry Data

This is a sample cyclic voltammetry file that installs in My Gamry Data when Framework software installs.



Cyclic Voltammetry Special Tools

This menu analyzes the cyclic voltammetry data.

- 1. In the main menu, choose **Cyclic Voltammetry**.
 - A drop-down menu appears.
- 2. Choose the desired tool:



Тоо	Function	Notes
Min/Max	Finds the minimum and maximum currents and	
	voltages within the dataset. Results appear in a win-	
	dow below the plot.	
Quick Integrate	Integrates to find the total charge. Results appear in	For multi-cycle CV
late mete	a window below the plot.	experiments
Integrate	the total charge.	must be selected
Region Baselines	Defines a line as the baseline for a specified region.	Region must be se-
Clear Regions	Clears all baselines from the dataset.	Region must be se-
elear regione		lected
Normalize by Scan	Normalizes the dataset based on the scan rate.	
Rate		
Normalize by Square	Normalizes the dataset based on the square-root of	
Root of the Scan Rate	the scan rate.	
Peak Find	Finds peaks within a specified region of the dataset.	Portion of the curve
		must be selected
Clear Peaks	Clears all peaks found within the dataset.	fied
Automatic Baseline	Finds the baseline automatically.	Peaks must be identi-
		fied
Peak Baselines	Defines a line as a baseline for a specified peak.	Peaks must be identi- fied
Clear Lines	Clears all lines from the dataset.	Lines must be associ-
		ated with graph
Delta Ep	Finds the potential difference between two peaks.	fied
Subtract Background from File	Subtracts a background amount from the dataset.	
Export to DigiElch	Exports the file to a DigiElch ⁻ compatible format.	
Options	Changes units and grids for plotting the data.	

Integrating the Voltammogram

All integration methods integrate current versus time to get the total charge. There are two different ways to integrate under a curve with Echem Analyst.

Quick Integrate

Quick Integrate breaks the data into "curves." Each curve is integrated to a zero current. **Quick Integrate** integrates the entire area of each curve, unless an area is specified using the x-region icon.

Integrate

Integrate requires you first to select a portion of the curve. (See how to select a portion of the curve in the "Starting Echem Analyst" chapter.) After an integration is performed, you can change the baseline from the default 0 A to another line, either a line that you draw, or an **Automatic Baseline**.

- 3. Open the data file.
- 1. Select the **Draw a Freehand Line** button.
- Left-click and hold on the graph to place an anchor point. Holding down the mouse button, extend the line with the mouse. Move or extend the line as you wish.



Directions to accept the line are printed at the bottom of the window.

- Right-click the mouse on the line and either Accept or Delete.
 After you accept the line, it turns from dashed to solid.
- Select the portion of the curve to integrate. This function is described in detail earlier.



5. Select Integrate from the Cyclic Voltammetry menu.

This integrates the section between the curve and the zero A line.

6. To change the baseline to the desired userdrawn line, select Region Baselines from the **Cyclic Voltammetry** menu.



The Region Baseline Settings window appears.

7. Select the desired **Baseline** from the available lines. You may draw multiple lines from which to choose.

The integrated region moves from the default 0 A baseline to the user-drawn line.







Polarization Resistance Special Tools

This menu analyzes the polarization resistance data.

1. In the main menu, choose Polarization Resistance.

II III are main	
A drop-	Gamry Echem Analyst - [Sample Polarization Resistance.DTA]
down	<u>6</u> Eile <u>T</u> ools <u>W</u> indow <u>H</u> elp <u>Polarization Resistance</u> <u>Common Tools</u> <u>Quick Help</u>
menu	😂 🛃 🛃 🚍 🧮 Quick Integrate
appears.	<u>Min/Max</u>
	Chart Experimental Setup Experi Polarization Resistance ge Hardware Settings
2. Choose the	desired tool:
Tool	function
Quick Integrate	ntegrates to find the total charge. Results appear in a window below the plot.
Min/Max	rinds the minimum and maximum currents and voltages within the dataset. Re- sults appear in a window below the plot.

Polarization Re- sistance	Within a selected portion of the curve, finds the polarization resistance.
Options	Changes units and grids for plotting the data.

Finding the Polarization Resistance

Method 1: Manual Entry of the Tafel Constants

- 1. Select the desired portion of the curve. (See section "Selecting Portions of a Curve for Analysis")
- 2. In the main menu, choose Polarization Resistance.



Method 2: Automatic Selection of Voltage Region

Echem Analyst offers another way to select automatically the voltage region over which this analysis is done.

1. In the Polarization Resistance menu, choose Options.



The Polarization Resistance Options window opens.

2. Select the **Automatic** radio button, specify the region around Ecorr to use, and click the **Save as Defaults** button. You are prompted directly for Tafel constants when a polarization resistance file is opened.

This is how Gamry Instruments' RpEc Trend experiments calculate corrosion rate.

Polarization Resistance ()ptions 🔰 🚺
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Use for Open Circuit Data	3
Units for Voltage	Data Grid
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💿 vs. Ere <u>f</u>	
- Upits for Current	Set Region
C Current Density	C Automatic
Current	Ecorr (mV) +/- 5
	Manual
Alternate IV	Save as Defaults
Voltage on <u>Y</u> Axis	
C Voltage on <u>X</u> Axis	ApplyOse

Modeling Potentiodynamic (Tafel) Data

A Tafel experiment is also a very popular electrochemical corrosion technique. The following analysis is performed on the sample Potentiodynamic data file.

Tafel Fit

3. Select the region over which to perform the Tafel fit.

This region must encompass the Ecorr (open-circuit potential).

4. Select Tafel Fit from the Potentiodynamic menu:



1. A **Tafel Fit** window appears where you may input seed values optionally for the fit. The better the information we provide the fitting routine, the more likely it will be able to generate an acceptable fit.

If you have reasonable starting parameters for the fit, input them in the **Seed Values** area, and check the **Use Seed Values** checkbox. If you do not have any confidence at all in your range of parameters, do not check the **Use Seed Values** checkbox.

We recommend using the seed values supplied by the Echem Analyst.



2. Click the **Calculate** button. -

When you click the **Calculate** button, the changes can be subtle. The following events occur:

- The parameters in the **Tafel Fit** window become the fit parameters.
- A fit line is displayed on the graph.

• A new **Tafel** tab is created (to the right of the **Hardware Settings** tab) that holds the information about the fit.

	Gamry Echem Analyst - [Sample Potentiodynamic Dummy Cell).DTA]	L 6 🗙
T-6-1 FM	C Elle Iools Window Help Botentiodynamic Common Tools Quick-Help	- 8 ×
Tarel FIT 🔼		
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-5.28E-05	600 N HA	
Beta A 2.1224		
Beta <u>⊂</u> 2.1115		
Weighting		
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	4000 mV	1.000-004
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E Log I Fit

The **E Log I** fit is a useful fit if you want to fit the data one branch (anodic or cathodic) at a time. This can be important if one branch doesn't show linear behavior, but the other does.

The fit is called **E Log I** because of the semi-logarithmic nature of a Tafel plot. The *x*-axis is the logarithm of current, while the *y*-axis is potential on a linear scale.

Method

5. Select a portion of the curve.

Here you need only the linear section of one of the branches. This selection does not include **Ecorr** [Eoc (open-circuit potential)].

2

- 1. In the **E Log I Fit** window, enter an approximate value for **Ecorr**.
- 2. Click the **Calculate** button. A single branch of the Tafel data is fit. The fit is shown on the graph, and the results of the fit are contained in a new **E Log I** tab.

You can run a Polarization Resistance fit on these Potentiodynamic data, if the axes of current are changed to the linear scale. Generally

	Close	⊆alculate	
in approximate			-
mry Echem Analyst - [Sample Potentiodynamic (Dummy Cell).D	TA]		- 8 🗙
jie Isols Window Belp Botentiodynamic Common Tools Quick Help ▲ [12] (3) [2] [3] [3] [3] [2] [4] [4]			- 8 ×
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10.00 nA 100.0 nA 1.000 µA	10.00 µA Im (A)	100.0 µA 11	An 000

E Log I Fit

-9.28802E-06 Volts

Ecorr

we suggest running a separate experiment on a new sample of the same material because of the more-polarizing, more-destructive nature of the Potentiodynamic experiment. The data-analysis features shown here are common to many of the AC-based techniques. By far the most popular type of AC experiment is Potentiostatic EIS.

Bode and Nyquist Plot View

Click the **Bode** tab or the **Nyquist** tab of the plot you prefer to work with. All fits are displayed on both the Bode and Nyquist plots. Because they are different representations of the same data, the fit results are identical.



EIS Special Tools

EIS data-analysis uses an equivalent-circuit approach. This menu creates and runs fits for EIS data. Commands in this menu allow you to build an equivalent-circuit model in the **Model Editor**, then fit that model to your data. This menu also lets you run advanced procedures, such as **Subtract Impedance**, and run Kramers-Kronig transforms.

6. In the main menu, choose Impedance.

A drop-down menu appears.

7. To create 🖉 Gamry Echem Analyst - [Sample Potentiostatic EIS.DTA] or edit an Impedance Tools Window 6 File Help Common Tools Quick Help equivalent circuit, Model Editor 🚰 🛃 2 choose Fit A Model (Levenberg-Marquardt Method) Model Edi-Bode Nyquist Experimental Setu Fit A Model (Simplex Method) Subtract Impedance... tor. Kramers-Kronig The Impedance <u>⊂</u>lear All Fits - ix iy 🗞 ៉ 🔖 Model Ed-Options itor win-

dow appears. See the next page for how to use it.

- 1. Choose your fitting method.
 - To fit the data using the Levenberg-Marquardt method, choose **Fit A Model** (Levenberg-Marquardt Method).
 - The Select Model File window opens.
 - Choose the appropriate model file, and click the **OK** button.
 - To fit the data using the Simplex method, choose **Fit A Model (Simplex Method)**.
 - Simplex method weighs the user's seed values less. We recommend using the Simplex method.
- 2. To subtract an impedance from the data, choose **Subtract Impedance...**.

The Impedance Subtraction window appears.

Choose:

Element Choose a circuit element from the drop-down menu. Model Browse for a previously defined model.

Spectrum Browse for a data-set.

Click the **Close** button.

3. To use the Kramers-Kronig method, choose Kramers-Kronig.

Kramers-Kronig is a model-independent transform that checks the EIS data for consistency.

The Kramers-Kronig window appears.

- 4. To clear all fits from the plot, choose Clear All Fits.
- 5. To change time or impedance units, choose **Options**. This option let you normalize the data and fits to the normalized area.

The Model Editor

The **Impedance Model Editor** allows you to create an equivalent circuit, via a drag-and-drop method.

> DON'T

ed.

ORGET

are several preloaded models. Often users find it convenient to start with

one of these models and edit it as need-

There



Circuit Elements

Symbol	Element	Comments
	Resistor	Abbreviated as R. $Z = R$
	Capacitor	Abbreviated as C. $Z = -i/\omega C$
-ll-	Inductor	Abbreviated as L. $Z = iL \omega$
-Ø-	Constant Phase Element	Models an inhomogeneous property of the system, or a property with a distribution of values. Often abbreviated as CPE.
	Wire	Connects one element to the next.
-G-	Gerischer ele- ment	Models a reaction in the surrounding solution that happened already; also used for modeling a porous electrode. Often abbreviated as G.
-W-	Infinite War- burg	Models a linear diffusion to an infinite planar electrode. Often abbreviated as W.
-W-H-	Bounded War- burg	Models diffusion within a thin layer of electrolyte, such as electrolyte trapped between a flat electrode and a glass microscope slide. Often abbreviated as T.
- W H	Porous Bound- ed Warburg	Models diffusion through a thin layer of electrolyte, such as electrolyte trapped between an electrode and a permeable membrane covering it. Often abbreviated as O.
Bisquert Open(BTO)	Bisquert Open (BTO)	Transmission line with $Z_B \equiv \infty$ boundary condition. Only pore reactions are considered; base electrode is insulating.
Bisquert Short(BTS)	Bisquert Short (BTS)	Transmission line with $Z_B \equiv 0$ boundary condition. Only pore reactions are considered; electrode is non-insulating.
Unified (UTL)	Unified (UTL)	Transmission line with a variety of free parameters.

Building an Equivalent Circuit

1. Adding an element

a. Click on an element symbol.

- The element appears in the central window.
 - b. Place the mouse cursor over the element. Left-click and drag to move the element to its desired position.
- 2. Connecting elements
 - a. Click on the Wire symbolb. Left-click one end of the wire and drag the
 - end to the element.

The element's border turns green when the wire's end reaches the element.

- 3. Deleting an element
 - a. Right-click on the element.
- The **Delete** command **Delete** appears.
- b. Left-click on the **Delete** command. The element vanishes.

Here is an example of a simple equivalent circuit (a Randles model) constructed in the **Impedance Model Editor**:



4. Relabeling and fixing parameters for an element

This lets you rename the element, and specify a Lower and Upper Limit for its value. Renaming the element helps you distinguish between elements of the

same type during fitting. Giving the program limits on the parameters may help the mathematical algorithm. For example, we know values are generally positive, so a Lower Limit = 0 is reasonable to set.

a. Left-click on the name of the element (here, R1).

The Parameter window appears.

- b. Enter a new Parameter Name.
- c. Enter an **Initial Value**, i.e., the first trial value for fitting.
- d. In the **Lower Limit Test** and **Upper Limit Test** fields, enter lower and upper limits, and check the **Enable** checkbox, as desired.
- e. Click the **OK** button.

The **Parameter** window closes, and the element is set to these parameters.

Parameter		
Parameter Na	ame: Rsolution	
Initial Va	alue: 10000	ohms
<u>L</u> ower Limit T	est	
🔲 Enable	0.00E+00	ohms
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🔲 Enable	0.00E+00	ohms
	<u> </u>	<u>C</u> ancel



Compiling the Equivalent Circuit

When the equivalent circuit is complete, the circuit can be compiled before use to check for connectivity of the wires. Compiling is only used to check connections 號 Impedance Model Edito

- 1. Click the **Test Compile** button ¹ in the toolbar. -The software compiles the equivalent circuit. If there is a problem, such as a missing connection, an error message appears, and a red box outlines the problem element:
- 2. Click the **OK** button to continue.
- 3. Inspect the schematic and make necessary corrections.



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A A A

If the equivalent circuit compiles properly,

the Model Editor window appears:

- 4. Click the **OK** button to continue.
- 5. Save the equivalent circuit with a *.mdl extension by clicking the Save button 🖬 .

Model Editor Model_Test Compile Complete. The model is properly constructed. ÖΚ 號 Impedance Model Edito 1 🔁 🖬 🕸

The File Save As window appears.

The default folder for saving model equivalent circuits is the Models folder.-

6. Name and save the file here, or choose a different folder. The model shown above was saved as trial model.mdl.

> The File Save As window closes.



Fitting the Data to the Equivalent-Circuit Model

 With the data open and plotted, click Impedance, and choose Fit A -Model (Simplex Method).

The **Select Model File** window appears.

2. Choose the desired model.



The default folder for models is the Models folder. This Models folder is in the C:\Documents and Settings\All Users\Application Da-

ta\Gamry Instruments\Echem Analyst\Models by default. As our example, we choose the model trial model.mdl created previously.

- Select Model File **?**× Look in: 🛅 Models 💽 🔶 🖻 🗕 🚽 Size Type Date 🔼 Name 🔺 À 🐹 cpe.mdl 1 KB Gamry Impedance ... 2/9/2 My Recent 🐹 FuelCell.MDL 2/9/2 2 KB Gamry Impedance ... 📆 G.MDL 1 KB Gamry Impedance ... 2/16/: B 谎(L.MDL 1 KB Gamry Impedance ... 2/16/: 職 paint.mdl 1 KB Gamry Impedance ... 2/9/2 Desktop 🐹 PBW.MDL 1 KB Gamry Impedance ... 3/29/: 🐹 Q.MDL 1 KB Gamry Impedance ... 2/16/: ₩R.MDL 1 KB Gamry Impedance ... 2/16/: 🖏 randles.mdl 1 KB Gamry Impedance ... 2/9/2 My Documents 🐹 reap2cpe.mdl 2 KB Gamry Impedance ... 2/9/2 職 rebar.mdl 1 KB Gamry Impedance ... 2/9/2 🐹 Rotated Disk.MDL 1 KB Gamry Impedance ... 2/9/2 trial model.mdl 1 KB Gamry Impedance ... 1/26/: My Computer 📆 W.MDL 1 KB Gamry Impedance ... 2/16/ < > My Network File <u>n</u>ame: trial model.mdl <u>O</u>pen Files of type: Model Files(*.mdl) • Cancel
- 3. Click the **Open** button.

The **Select Model File** window closes, and the **Impedance Fit by the Simplex Method** window appears.

4. Click the AutoFit button, or set parameters.
When setting parameters, choose the Maximum Iterations to loop before stopping the fit. Enter estimates for all the circuit elements in the Model Parameters area. Fix particular elements by ena-

<u>C</u> alculate	Contin	ue	Preview	<u>AutoFit</u>	Close
Fit Parar	neters —				
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FIUUEIF					
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	Rp Ru	Rese 2500 100	ohms	/alues	< Rp < Ru

bling their Lock checkboxes.

In our example, we try 100 Ω for Ru, 2500 Ω for Rp, and 100 nF for Cf and leave all of them free (unlocked).

5. If you don't use the **AutoFit** button, click the **Calculate** button to start the fit. The software attempts to fit the model to the data. When finished, the fitted parameters appear next to each circuit element.

Our model results give



Like other Echem Analyst fits, the fit also appears superimposed upon the data and a new tab is created that contains those results.



If you try another fit using the same model, this fit will be overwritten. If you fit to another model, the fit results of both models will be displayed.



This new tab shows the residual errors and goodness of fit, along with the various plotting tools. Residuals are a point-by-point **Goodness of Fit**, which quantifies how closely the data match the fit. A smaller number indicates a better fit.

The blue data (**Zreal**) correspond to the *y*1-axis (on the left); the green data (**Zim-ag**) correspond to the *y*2-axis (on the right).

Headings in Data-File Columns

DC Data Files

Abbreviation	Meaning
Pt	Point number
Т	Time
Vm, Vf	Measured voltage
lm	Measured current
Vu	Uncompensated voltage
Sig	Signal from the signal generator
Ach	Auxiliary channel
IE Range	I/E (Current Measurement) range on which measurement was made
Over	Any overloads. Numeric record of different overload types
0	No overloads

EIS Data Files

Abbreviation	Meaning
Freq	Frequency
Zreal, Zimag, Zmod, Zphz	Calculated values of impedance
Idc, Vdc	DC component of current and voltage,
Yreal, Yimag	Admittance (calculated from Z)

Current Conventions According to Framework[™] and Echem Analyst

The current convention in the Framework software for all experimental packages is that an anodic/oxidation current is positive.

To change the current convention (whether anodic/oxidation currents or cathodic/reduction currents are positive), in the menu **Tools** > **Options** > **Units** tab, specify the current you want represented as positive. The current convention can be changed by editing the experimental script (contact Gamry Instruments or your Gamry Instruments representative if you need to do this). Regardless of the current convention used in the Framework, it can be changed in the Echem Analyst to the one you desire (see below for exceptions).



To change the current convention in the Echem Analyst, in the menu **Tools** > **Options** > **Units** tab specify the current you want represented as positive.

To change the current convention in other experimental packages (DC Corrosion, EIS, etc.) please contact Gamry Instruments or your Gamry Instruments representative.

To Edit Visual Basic Scripts:

1. In the toolbar, choose **Tools**.. _____ A drop-down menu appears.



> DON'T

Echem Analyst runs on "Open Source" scripts written in VBA. Most customized analysis routines are done by Gamry Instruments in the factory for you, the user, and that makes Echem Analyst extremely flexible. The typical user will never need to edit the scripts for electrochemical analysis.



Simulating an EIS Curve

It is often useful to simulate the response of an equivalent circuit.

- 1. Launch the Echem Analyst.
- Select Tools > Run Named Script. Select EIS Model Simulation Script.Gscript.

This opens a blank chart.



3. Select **EIS Simulation** > **Simulate** (use the Model Editor to build or edit the model).

The EIS Model Simulation window appears.

IS Model Sin	nulation				
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-				10 20 Close	
Stop	300000.0	Hz	1	Simulate	
Model Para	meters		Pa	arameters may be edited i	in\
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	Ru	1.000 ohms			
	Cf 86.6	53e-12 F			

- 4. Select the saved model, and input parameters for the experiment (frequencies and data-point density) and values of all circuit elements.
- 5. Click the Simulate button.-

The simulation appears under new tabs.



This is a simulated Bode plot.



This is a simulated Nyquist plot.

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