

Integrating CVs: How and Why

Introduction

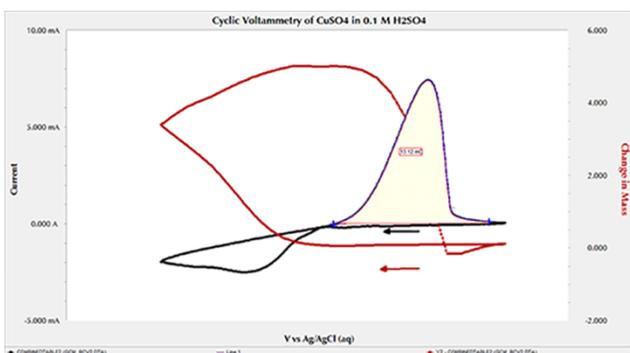
Cyclic voltammetry (CV) is a useful technique for extracting qualitative kinetic data from an electrochemical reaction. Various peaks appear in a CV dataset: each peak corresponds to a particular electrochemical process, and the height of the peak is related to the concentration of the analyte.

Gamry Instruments' software integrates a CV scan via a trapezoidal numerical method, and always integrates current with respect to time. This means that when a CV is displayed as voltage versus current, "behind the scenes" the software still pulls current and time columns from the data file. Hence the units that are generated from integration are always coulombs, regardless of the units shown on the plot on your screen.

Why integrate?

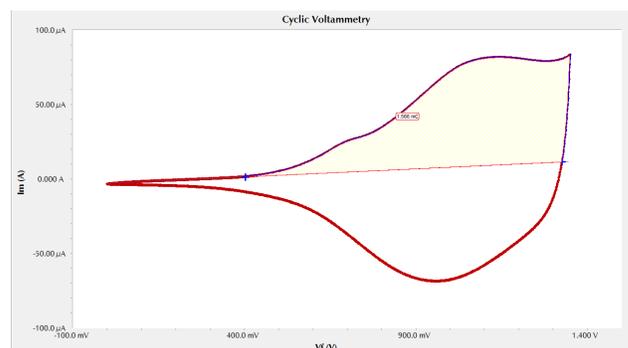
Integration of the CV curve can provide direct information on the amount of charge transferred during the electrochemical reaction. But beyond that, integration can provide "added value" to experiments. Let's look at some examples.

Copper sulfate solution



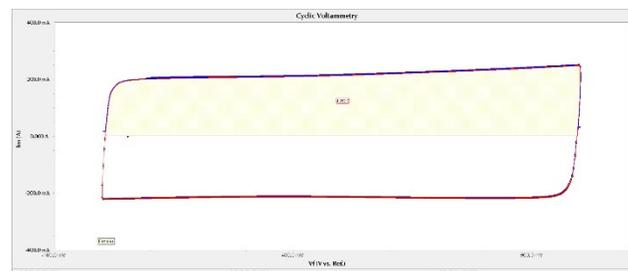
Here is an acidic solution of CuSO_4 run in a CV experiment (black) combined with a set of simultaneous quartz-crystal microbalance (QCM) measurements (red). We can compare the mass of copper removed or added to the charge transferred in each direction of the CV cycle.

Polymer



This CV scan shows a polymer with various electroactive sites. With an accompanying QCM, you can determine an amount of polymer deposited on the electrode. A comparison of the forward and reverse reactions will give insights into the mechanism of reaction.

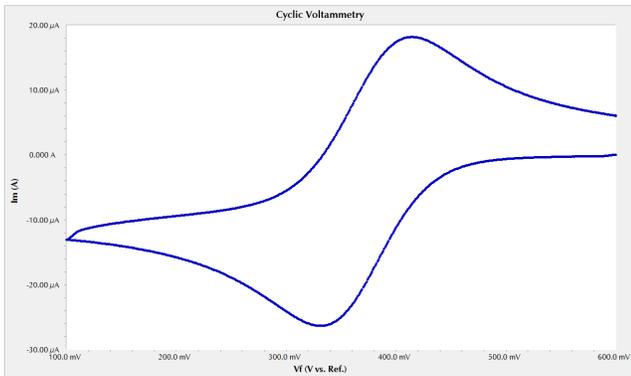
Supercapacitor



Here an integration leads to capacitance, and there is no "reaction" to speak of. To run CV experiments properly with supercapacitors, the potentiostat must be set to **Surface Mode**—and not all manufacturers can do this. (Gamry Instruments' potentiostats can.) **Surface Mode** allows you to measure $1/t$ decay from adsorbed species, unlike the slower $1/t^2$ decay that results from faradaic currents and electrochemical reactions. See our Application Note "[Measuring Surface Related Currents using Digital Staircase Voltammetry](#)" for more details.

How to integrate

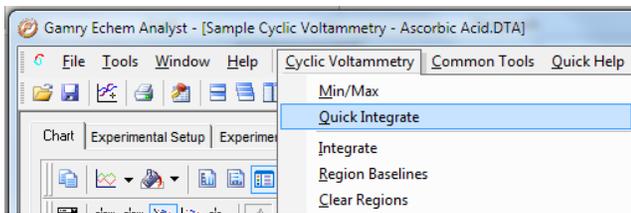
Let's examine an example. Here we use a CV scan of iron ferricyanide in acidic solution:



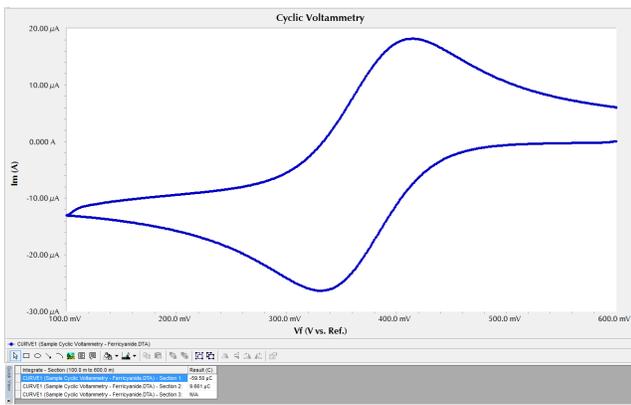
With Gamry Instruments' Echem Analyst™ software, you can integrate under the CV curve with two different ways.

1. Quick Integrate Tool

Under the **Cyclic Voltammetry** menu, the **Quick Integrate** tool splits the dataset into "curves." **Quick Integrate** integrates the entire area under each curve to a zero current. You can, however, specify a particular area to integrate using the **Select X Region** tool .



Below is the result of using **Quick Integrate** on these data:



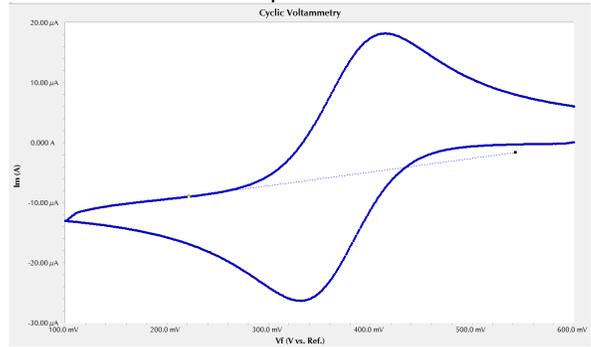
This method is perhaps better for analyzing multi-cycle CV experiments.

2. Integrate Tool

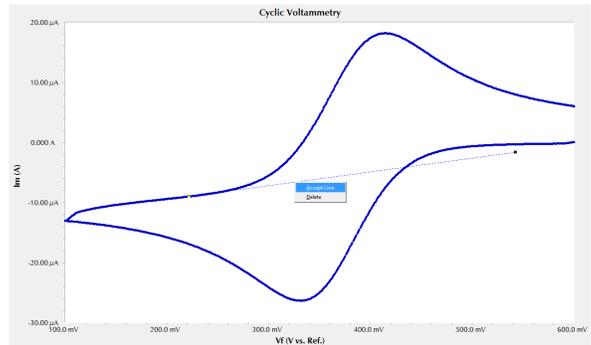
This method lets you choose a bit more carefully precisely which parts of the curve to integrate and how, and what baseline to use.

- Open the data file.
- Activate the **Draw a Freehand Line** button .

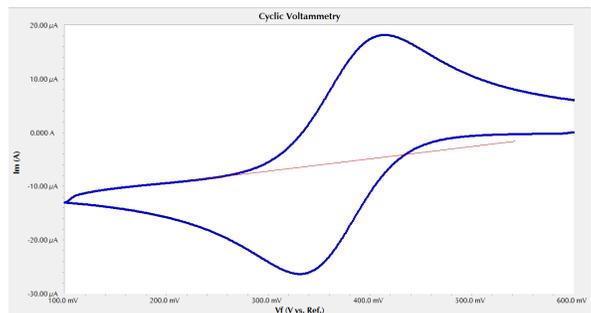
- Left-click and hold on the desired starting point on the graph to place an anchor point. The line is an extrapolation of the background charging current before the peak. We do not want to over- or underestimate the faradaic processes occurring.
- Hold down the mouse button, and extend the dashed line to the final point with the mouse.



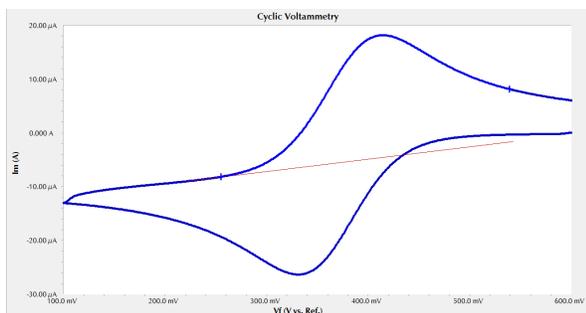
- Right-click directly on the line and **Accept Line** or **Delete** the line:



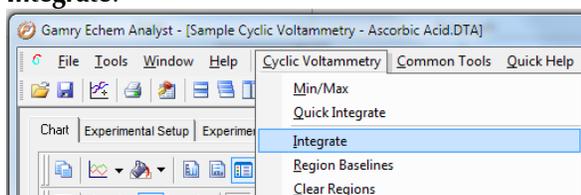
The line turns from dashed to solid if you accept the line, and the slope and intercept are displayed at the bottom:



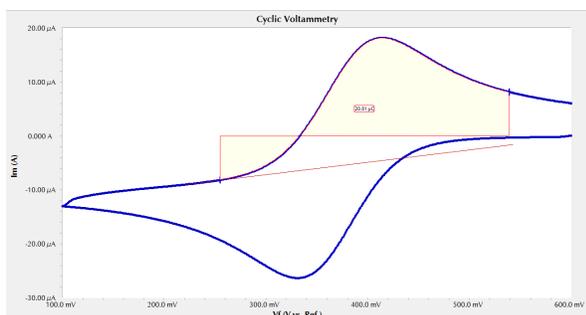
- With the **Select Portion of the Curve using the Mouse** button , select the portion of the curve you wish to integrate:



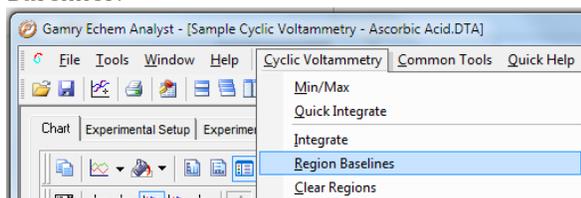
- g. In the **Cyclic Voltammetry** drop-down menu, select **Integrate**:



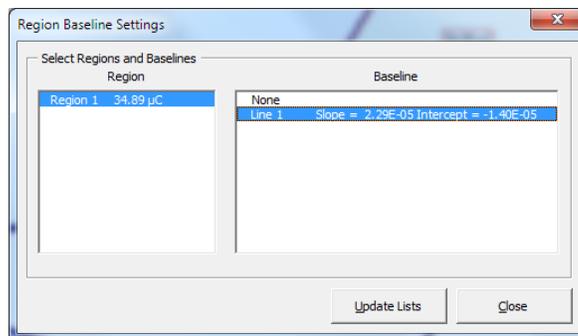
This tool integrates the section between the curve and the zero-ampere line:



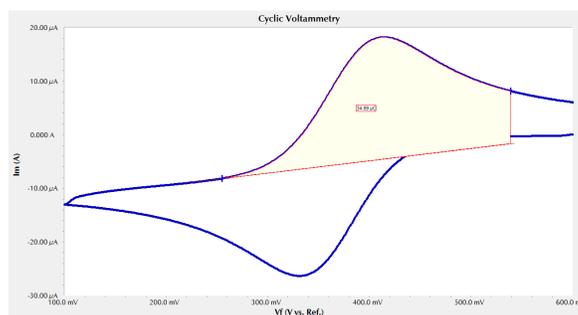
- h. If you wish to change the baseline to the extrapolated line you drew, in the **Cyclic Voltammetry** drop-down menu, choose **Region Baselines**:



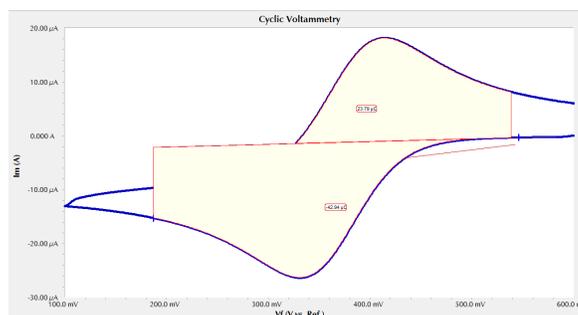
The **Region Baseline Settings** window appears:



- i. In the **Baseline** column, choose the desired baseline, and click the **Close** button. The integrated region shifts from the default zero-ampere baseline to your line.



- j. This CV scan also has a reverse peak, so we can follow the same procedure to integrate the reverse reaction, i.e., draw a line, choose the part of the curve for integration, integrate, and finally shift to the drawn line and re-integrate:



Conclusion

This Application Note shows you how you can use Gamry Instruments' Echem Analyst™ to integrate your cyclic voltammetry data, and provides several ways that CV can assist your research.

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