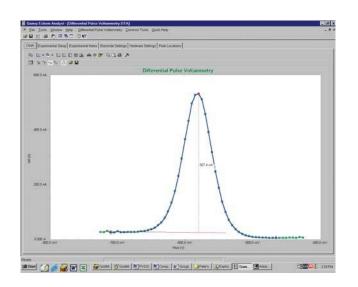
Data Analysis

The analysis of the software data is performed in the Echem

Analyst. Specific analysis routines have been created to handle this software data files. The general features of the Echem Analyst are described in a separate brochure entitled "Overview of Gamry Software."

These specific routines include: **Peak Find:** Use the Region Selector button to select a

portion of the curve that includes the region where the peak is located. Click on the Peak Find button to find the peak position and the peak height. A perpendicular line is drawn on the chart from the peak to the baseline.



Peak Find measures both the potential and the current of the peak. Note the tab labeled "Peak Location". The peak can be measured above zero current or above a baseline drawn with the Freehand Line.

Normalize by Area: Data taken on electrodes of different area can be Normalized. This is done by overlaying the files and choosing the Normalize by Area option from the Pulse Voltammetry menu to automatically calculate the current

density. This feature is particularly useful for comparing data from electrodes of different areas.

Baseline Add: Baselines can be added to the data graph by either drawing a Freehand Line or by extrapolating a part of the baseline with the Linear Fit feature.

Integrate: Integration of the current in Differential Pulse Voltammetry and Square Wave Voltammetry is possible by defining a baseline and then selecting the portion of the curve you want to integrate. Then select Integrate from the drop-down menu and the result is reported on the curve and also on a new tab.

Background Subtract: A background file can be subtracted from the current active data file by selecting Subtract from the menu and choosing the file. This feature is particularly useful when interfering peaks are present in the background solution.

Applications Assistance

If you're using Pulse Voltammetry for the first time, Gamry has the experts to help you. If you have questions, contact your friendly technical advisor at our home office or your local Gamry sales office.

System Information

The Pulse Voltammetry Software requires a Gamry PCI4TM or PC4TM Potentiostat and a computer with Microsoft Windows[®] 98, 2000, or XP. Gamry recommends a computer with at least a 450 MHz processor and 128 MB of RAM.

Gamry Instruments can supply complete systems including the above items and system software installed in a desktop or portable configuration. Custom computer configurations, software, training, and installation are available by special order. Contact the factory or your local Gamry Distributor for further details on these systems.

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Redefining Electrochemical Measurement

The Pulse Voltammetry Software adds Differential Pulse Voltammetry, Square Wave Voltammetry, and other recognized pulse voltammetry techniques to the Gamry software product family. For qualitative and mechanistic studies of low concentrations of electrochemical species, the Pulse Voltammetry Software is ideal.

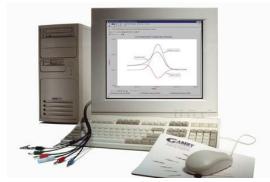
In conjunction with a Gamry potentiostat and its low current measuring capabilities, this software lowers the concentration limits of measurement. The sensitivity of the pulse techniques, achieved by exploiting the difference in the decay rates between the charging and faradaic currents, allows detection of low concentrations of electroactive

species. The Pulse Voltammetry Software is also capable of stripping analysis to further enhance the detection limit.

This software is an excellent companion to Gamry's Physical Electrochemistry Software for cyclic voltammetry, chronoamperometry, chronopotentiometry, and controlled potential coulometry. Physical electrochemists and electroanalytical chemists will find the Pulse Voltammetry and the Physical Electrochemistry Software will meet most of their electrochemical measurement requirements.

Of course, if you need additional electrochemical techniques, Gamry can provide standard software for DC Corrosion Techniques, Electrochemical Impedance, and Electrochemical

Noise. For high sample throughput, the MultEchemTM Electrochemistry System contains eight Potentiostats in one computer for simultaneous measurement of eight cells. For custom experiments, our Open Source Scripting allows unique experiments to be easily accomplished.



The Pulse Voltammetry System plus the PHE200 Physical *Electrochemistry Software is an ideal system for the electroanalytical chemist.*



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This software incorporates the following pulse techniques:

- Square Wave
- Square Wave Stripping
- Differential Pulse
- Differential Pulse Stripping
- Normal Pulse
- Normal Pulse Stripping
- Reverse Normal Pulse
- Reverse Normal Pulse Stripping
- Sampled D.C.
- Sampled D.C. Stripping
- Generic Pulse (User Defined)

In common with most Gamry Software, the Pulse Voltammetry Software and a Gamry Potentiostat use the

 $\label{eq:Framework} \ensuremath{^{TM}}\xspace$ for data analysis.

The common look-and-feel of Gamry software allows you to move easily from one technique to another. Request the brochure "Overview of Gamry Software" for a general description of the Framework and the Echem Analyst.

Square Wave Voltammetry	
Default Save Re	store OK Cancel
Pstat	• My PCI4
Test Identifier	Square Wave Voltammetry
Notes	Tank 23A, 30 minutes after replenishment.
Output File	Electroless Cu.DTA
Initial E (V)	0.1
Final E (V)	-1.1
Step Size (mV)	2
Frequency (Hz)	25
Pulse Size E (mV)	25
Noise Rejection	☑ On
I/E Range Mode	Auto C Fixed
Electrode Area (cm²)	0.15
Max Current (mA)	0.001
Equil. Time (s)	15
IRComp	None O PF
PF Corr. (ohm)	50
Advanced Pstat Setup	🗹 On
Electrode Setup	☑ On

Setup Window for Square Wave Voltammetry makes experiment definition quick and easy.

Square Wave Voltammetry

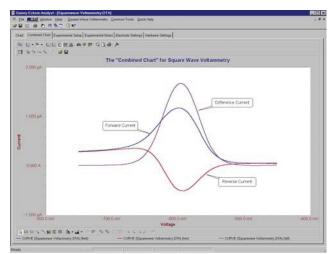
Pulse techniques are favored by electroanalytical chemists to measure low concentrations of electrochemically active compounds. In recent years, Square Wave Voltammetry has become very popular because the timescale is much faster than other pulse techniques. The scan rate in Square Wave may be as high as 50 V/sec with little or no sacrifice in sensitivity compared to Differential Pulse! The pulse profile is superimposed on a voltage staircase and the current is sampled at the end of each half-pulse. The resulting graph is the difference between the forward and reverse currents.

The experiment proceeds from the starting potential specified in Initial E to the finishing potential specified in Final E. The Step Size and the frequency determine the scan rate with the pulse always having a 50% duty cycle. The Pulse Size determines the sensitivity and resolution.

Current measurement can be made in fixed or auto- ranging mode. For faster experiments, fixed mode is recommended, whereas auto-ranging mode allows the potentiostat to pick the best current range for optimum sensitivity.

At very low concentrations, noise may be a concern. All the pulse techniques allow you to perform noise rejection. When Noise Rejection is used, the signal is averaged over one AC line cycle (16.66 ms for 60 Hz or 20 ms for 50 Hz) to acquire the current.

In the software, the forward currents, the reverse currents, and the difference currents can be plotted on the same graph. This is useful in determining the reversibility of your redox system. Large forward currents with no corresponding reverse currents indicate a non-reversible or quasi-reversible system. Results of a square wave voltammetry experiment are shown below with the forward, reverse and difference currents traces.



Square Wave Voltammetry displayed in the Echem Analyst shows the difference current as well as the forward and reverse currents.

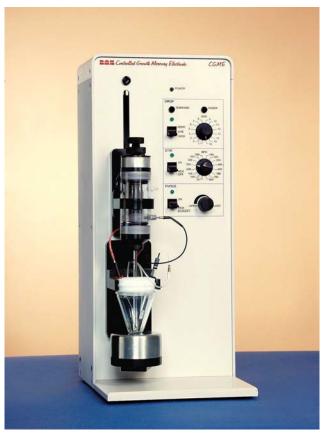
A variety of different electrode configurations can be used with this software. These include solid electrodes, mercury electrodes, and rotating disk electrodes.

Selection is made at the beginning of the experiment with the Electrode Setup panel. If you're using a mercury electrode, you have a choice of configurations: dropping, hanging, or static mercury drop. If you are using a rotating disk electrode, you have full control of the rotation rate from the Pulse Voltammetry Software.

When you check the Rotating Electrode radio button, a new dialog box appears enabling you to select the rotation rate.

Electrode Setu	p					
Default	<u>S</u> ave	Restore	<u>0</u> K	<u>C</u> ancel		
Electrode Ty	pe	O Non	e O Sc	lid O	DME	C SMDE
		• HME	DE C Ro	otating		
Purge/Stir C	ell	🗹 On	Time (s)	60	Quiet (s)	10

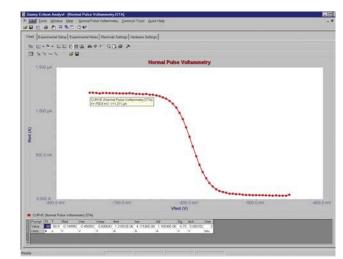
Electrode Setup: Choose your electrode and the PV220 does all the work. The software is compatible with rotating electrodes, solid electrodes, and mercury electrodes.



Controlled Growth Mercury Electrode is just one of the supported electrode types in the software. Operation of the CGME is completely automated. It's a great electrode for high-sensitivity voltammetry.

As with the Physical Electrochemistry Software, the Pulse Voltammetry allows the user to alter the potentiostat settings through the Advanced Pstat Setup dialog box. By tweaking the settings of the potentiostat electronics, an optimum balance can be achieved between noise and sensitivity.

Normal Pulse, Reverse Normal Pulse, and Differential Pulse Voltammetry.



A Normal Pulse Voltammogram of 10μ M cadmium at a hanging mercury drop electrode. Measurement details of any data point can be easily displayed on the monitor.

During Normal Pulse Voltammetry, pulses of increasing amplitude are applied from the Initial Potential. The current response is measured at the end of the pulse and then plotted against potential. Measurement of the current at the end of the pulse allows for differentiation between the charging current and the faradaic current of interest.

At the start of the experiment, the potential specified in Initial E is applied. This potential is then incremented by the value of the Step Size until the potential specified in Final E is reached. The sample period and pulse time define the duration of each pulse cycle. The pulse time is the length of time that the pulse is applied at the end of the cycle. The effective scan rate is (step size)/ (sample period).

Differential Pulse Stripping Voltammetry				
Default Save [Restore QK Cancel			
<u>P</u> stat	Gamry			
Test Identifier	Diff Pulse Stripping			
Notes				
Output <u>F</u> ile	Nockamixon_M237.DTA			
Initial <u>E</u> (V)	-1.2			
Final <u>E</u> (V)	0.1			
Step Size (mV)	4			
Pulse Size <u>E</u> (mV)	25			
Sample Period (s)	0.5			
Pulse <u>⊺</u> ime (s)	0.1			
Noise Rejection	⊡ On			
I/E Range Mode	Auto Fixed			
Electrode <u>A</u> rea (cm²)	0.03			
Max Current (mA)	0.3			
Conditioning	□ Off Time (s) 15 E (V) 0			
Accum. Time (s)	90			
Equil. <u>T</u> ime (s)	10			
IRComp	© None © PF			
PF Corr. (ohm)	50			
Advanced Pstat Setup	₽ On			
Electrode Setup	₽ On			

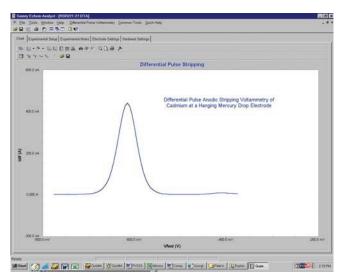
Experiment Setup Dialog Box for Differential Pulse Stripping Voltammetry.

During Reverse Normal Pulse Voltammetry, the voltage profile is inverted compared to Normal Pulse. The first part of the pulse cycle has the voltage stepped and then the voltage is returned to the Initial Voltage and the current is measured. This profile enhances the response of reaction products whereas Normal Pulse favors the reactants.

In Differential Pulse Voltammetry, the pulse waveform is superimposed on a voltage ramp. The current is sampled immediately prior to the application of the pulse and at the end of the pulse and the difference is recorded. This gives rise to a differential current response. This technique is used when very low quantities of compound are present.

Sampled D.C. Voltammetry

Sample DC Voltammetry involves sweeping the voltage with a staircase waveform and sampling the current immediately prior to each voltage step. The measured voltammogram exhibits a much smoother response than traditional DC polarography, increasing the detection limit.



Differential Pulse Stripping of a solution containing Cadmium at a Hanging Mercury Drop Electrode. Stirring can be automatically controlled during accumulation to enhance sensitivity, then disabled during the voltammetric scan.

Generic Pulse

The software also incorporates a user-defined pulse technique, which allows you to apply a repeating pulse waveform of any size and duration. Generic Pulse functions in both potentiostatic and galvanostatic modes. The potentiostatic mode has applications in chromatographic detection and also electrode conditioning. The galvanostatic mode is particularly useful for applications such as pulse plating.