Application Note S-7

Princeton Applied Research

Subject: Square Wave Voltammetry

INTRODUCTION

The primary advantage of the pulse voltammetric techniques, such as normal pulse or differential pulse voltammetry, is their ability to discriminate against charging (capacitance) current. As a result, the pulse techniques are more sensitive to oxidation or reduction currents (faradaic currents) than conventional dc voltammetry. Differential pulse voltammetry yields peaks for faradaic currents rather than the sigmoidal waveform obtained with dc or normal pulse techniques. This results in improved resolution for multiple analyte systems and more convenient quantitation.

Square wave voltammetry has received growing attention as a voltammetric technique for routine quantitative analyses. Although square wave voltammetry was reported as long ago as 1957 by Barker[1], the utility of the technique was limited by electronic technology. Recent advances in both analog and digital electronics have made it feasible to incorporate square wave voltammetry into the PAR Model 394 Polarographic Analyzer.

Square wave voltammetry can be used to perform an experiment much faster than normal and differential pulse techniques, which typically run at scan rates of 1 to 10 mV/sec. Square wave voltammetry employs scan rates up to 1 V/sec or faster, allowing much faster determinations. A typical experiment requiring three minutes by normal or differential pulse techniques can be performed in a matter of seconds by square wave voltammetry.

THEORY

The waveform used for square wave voltammetry is shown in Figure 1. A symmetrical square wave is superimposed on a staircase waveform where the forward pulse of the square wave (pulse direction same as the scan direction) is coincident with the staircase step. The reverse pulse of the square wave occurs half way through the staircase step.
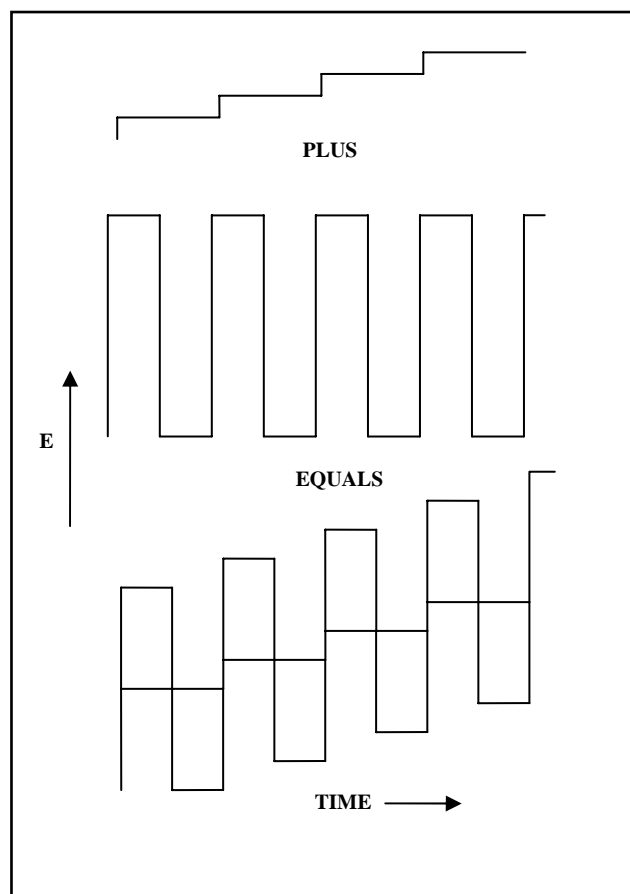

FIGURE 1: Applied excitation in square wave voltammetry.

The timing and applied potential parameters for square wave voltammetry are depicted in Figure 2. τ is the time for one square wave cycle or one staircase step in seconds. The square wave frequency in Hz is $1/\tau$. E_{sw} is the height of the square wave pulse in mV, where $2 E_{sw}$ is equal to the peak-to-peak amplitude. E_{step} is the staircase

step size in mV. The scan rate for a square wave voltammetry experiment can be calculated from the equation:

$$\text{Scan Rate (mV/sec)} = \frac{E_{step} \text{ (mV)}}{\tau \text{ (sec)}}$$

For example, if E_{step} is 2 mV and τ is 0.01 sec (corresponding to a frequency of 100 Hz), the scan rate would be 200 mV/sec.
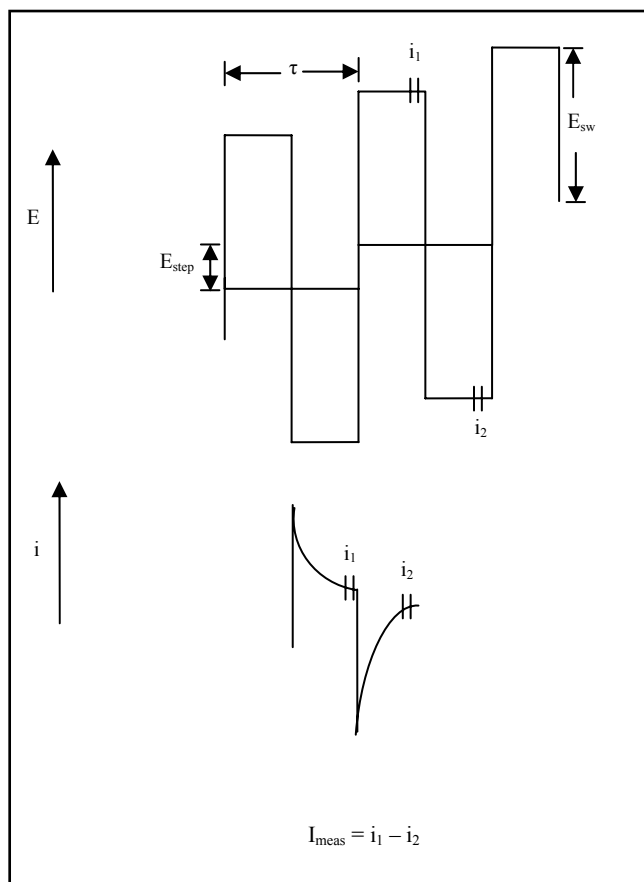

FIGURE 2: SWV timing relationships.

This scan rate is considerably faster than the 1 to 10 mV/sec rate of other pulse techniques.

The current is sampled twice during each square wave cycle, one at the end of the forward pulse, and again at the end of the reverse pulse. The technique discriminates against charging current by delaying the current measurement to the end of the pulse. The difference current between the two measurements is plotted vs. the potential staircase. Square wave voltammetry yields peaks for faradaic processes, where the peak height is directly proportional to the concentration of the species in solution.

Due to the rapid scan rates possible with square wave voltammetry, the entire voltammogram is recorded on a single mercury drop. Early square wave experiments were limited by the Dropping Mercury Electrode (DME). With a DME, the mercury flows constantly during the experiment, resulting in an electrode of constantly changing surface area. The changing surface area causes slope in the baseline and adds complexity to the experiment theory. The PAR Model 303A Static Mercury Drop Electrode (SMDE) eliminates this problem, providing a drop of constant area throughout the experiment.

Frequencies used for square wave voltammetry typically range from approximately 1 Hz to 120 Hz. This frequency range allows square wave experiments to be up to 100 times faster than other pulse techniques. The speed of the technique can result in increased sample throughput over previous voltammetric techniques.

Even greater sensitivity can be attained by doing Stripping Square Wave Voltammetry, in which the species of interest is concentrated into the working electrode by electrochemical means before doing the analysis. With a sufficiently long concentration step (deposition), the concentration of the substance will be much higher in the electrode than in the sample solution. If the electrode potential is then scanned, the substance will be stripped form the electrode, causing an increase in cell current as this process occurs. In Anodic Stripping Voltammetry, the concentration is done at a negative potential and the subsequent scan is in the positive direction. During the concentration process, individual metallic species are reduced and deposited into the mercury drop. The subsequent scan direction is positive, causing the individual species to be oxidized back into the solution.

Cathodic stripping is the "mirror image" of anodic stripping analysis. Generally, an insoluble salt of the analyte is concentrated onto the electrode by oxidation. A cathodic (negative going) scan is then applied in which the salt is reduced. Cathodic stripping analysis is best suited to the analysis of those materials that will oxidize into a mercury electrode. Specific examples include selenium, tellurium and the halogens (iodides, bromides, chlorides). For more details see PAR Application Note S-6, "Fundamentals of Stripping Voltammetry".

EXPERIMENTS

The speed of square wave voltammetry is illustrated by the following example. Consider a sample containing cadmium and lead, which both must be determined. To do this, a suitably prepared sample is placed in a polarographic cell and scanned from -0.2 to -0.8 V vs. Ag/AgCl reference electrode. If differential pulse polarography and square wave voltammetry were both run on the sample, the following experiment conditions would be typical:

PARAMETER	TECHNIQUE		
	DPP		SWV
Drop Time	0.5 s		N/A
Scan Increment	2 mV		2 mV
Pulse Height	40 mV		20 mV
Initial E	-0.2 V		-0.2V
Final E	-0.8 V		-0.8 V
Frequency	N/A		100 Hz
Equilibration Time	N/A		3 s
Effective Scan Rate	4 mV/s		200 mV/sec

The differential pulse experiment will require 150 seconds for the potential scan, while the square wave experiment will only require 6 seconds (a 3 sec equilibration plus a 3 sec scan). The equilibration step is used in square wave voltammetry to allow the solution to become quiescent after extruding the new drop and applying the initial potential. It's obvious from this example that square wave voltammetry can greatly enhance sample throughput.

Since the electronic circuitry required for square wave voltammetry must have short response times, the standard practice of integrating a long time per sample to reduce noise in the measured current signal cannot be used. The Model 394 Polarographic Analyzer can perform multiple scans on a sample, averaging the data to reduce the noise component. If the above experiment required such averaging, five scans could be performed by the instrument in only 30 seconds, which is still five times

faster than the differential pulse experiment. The signal-to-noise ratio increases as the square root of the number of scans averaged.

Figure 3 depicts the experiment results. Cadmium and lead yielded current peaks. Note that the peak heights obtained during the square wave experiment are larger than those of the differential pulse experiment. This enhanced peak height is a function of the time between pulse application and the current measurement. This timing is fixed for the differential pulse technique. The timing for a square wave experiment is frequency dependent and is equal to $\tau/2$. As frequency increases, τ decreases (remember τ has units of seconds) and the measured faradaic current will increase. For a given sample, a low frequency square wave voltammetry experiment will not yield significantly larger peak currents compared to differential pulse polarography.
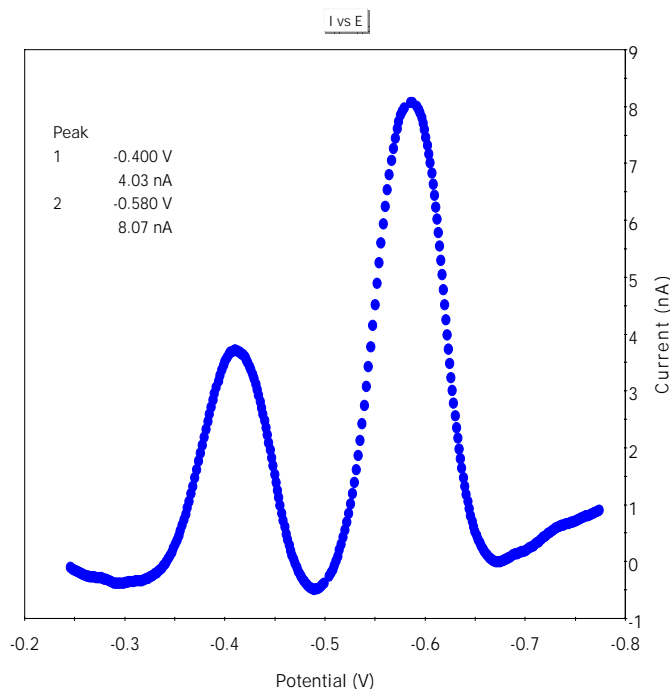

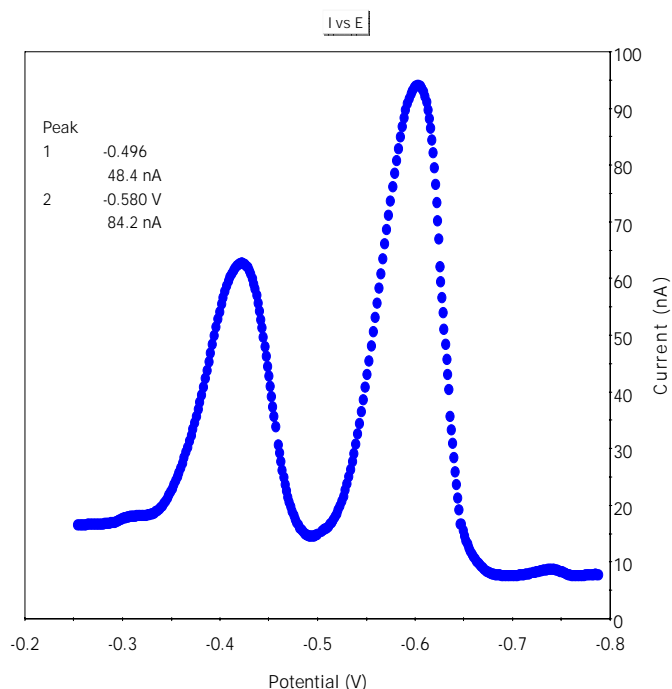**FIGURE 3A: Differential pulse polarogram of lead and cadmium.**

I vs E

Peak
1   -0.496
      48.4 nA
2   -0.580 V
      84.2 nA

Current (nA)

Potential (V)

FIGURE 3B: Square wave voltammogram of lead and cadmium.

I vs E

Peak
1   -0.366 V
      3.34 nA
2   -0.548 V
      5.99 nA

Current (nA)

Potential (V)

FIGURE 4: SWV analysis of 10 ppb cadmium and lead.

If square wave theory stopped at this point, it might appear that an infinite frequency would result in infinite peak heights. Unfortunately, this is not the case. It is possible to scan at a rate faster than the kinetics of the faradaic process will allow, resulting in a kinetically controlled current instead of the diffusion controlled current used in voltammetry theory. Peak height may not be directly proportional to concentration. If the scan rate is significantly faster than the kinetics of the system, no peak would be observed at all. If $\tau/2$ becomes very small, i.e., less than a millisecond or so, the capacitance current caused by the pulse application would not decay completely, resulting in noise and high background currents. A more rigorous treatment of square wave voltammetry theory is presented in References 1 through 5.

Figure 4 is a square wave voltammogram of a solution containing 10 ppb cadmium and lead. Differential pulse polarography cannot easily detect these concentration levels. The sensitivity is the result of a rapid scan rate and averaging multiple cycles (five in this case) to improve the signal-to-noise ratio. Figure 5 is a calibration plot for cadmium at 10, 20 and 30 ppb concentration, demonstrating that instrument response is linear for cadmium at very low levels.
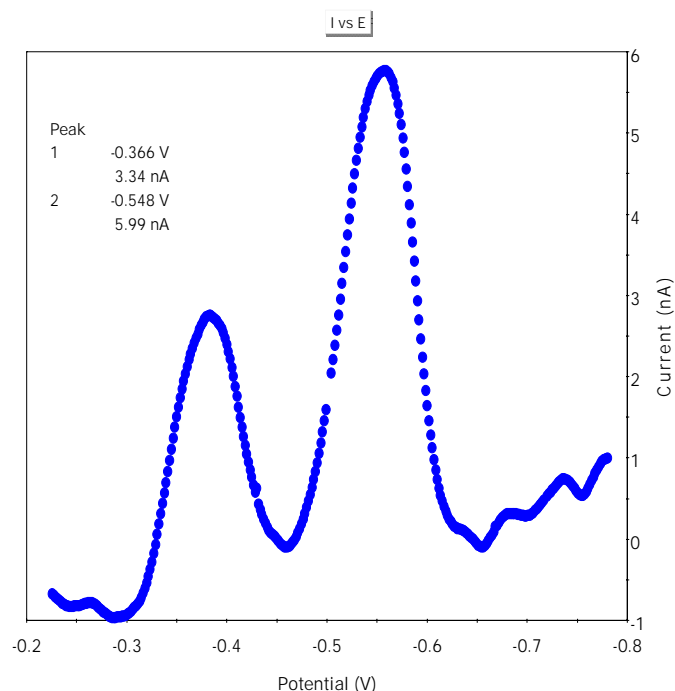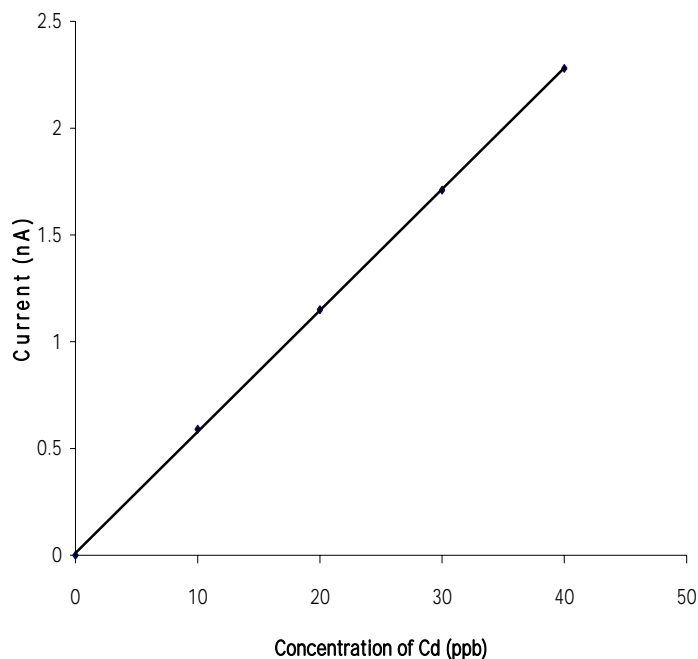

Current (nA)

Concentration of Cd (ppb)

FIGURE 5: Calibration curve for cadmium by SWV.

The ability of square wave voltammetry to rapidly scan wide range to rapidly scan a wide potential range has been used to advantage by researchers. Electrode kinetics and formation constants of complexes have been studied by square wave voltammetry.[5-8] Square wave voltammetry has also been used as a rapid scanning detector for HPLC[9,10], which can be used to generate information on species of different potentials that elute from the column simultaneously.

REFERENCES

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