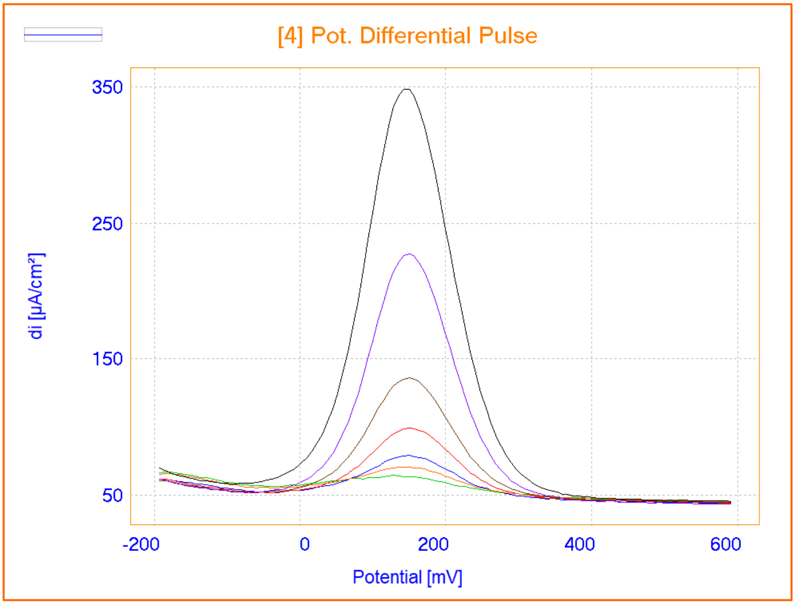
Application Note

General Electrochemistry
AP-GE10

Differential Pulse Method



In this Application Note differential pulse voltammetry method was used for quantitative analysis. Different concentration of Ferri Cyanide solutions were used for this reason.

Origalys

Introduction

Pot. Differential Pulse is a voltammetric method used to perform quantitative electrochemical measurements. The potentiostatic differential pulse generates pulse superimposed to a potential ramp between two applied potential set points.
The direct and differential currents are recorded as a function of the potential applied. Raw data (potential, current, time) and differential data (potential, current, time) can be saved in two individual curves. You can set the potential set points versus the OCP, the reference electrode or the last imposed potential. Auto ranging or manual ranging for current measurement is also available.

Figure 1 shows the scheme of imposing potential pulse on linear sweep ramping of potential.

Most important parameters:

1: Step of potential (mV)
2: Pulse time (msec)
3: Pulse value (mV)
4: Current ranges

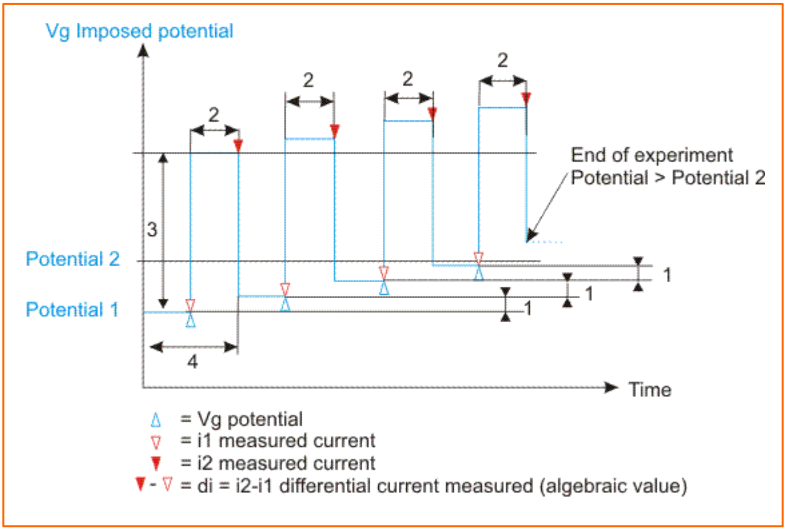
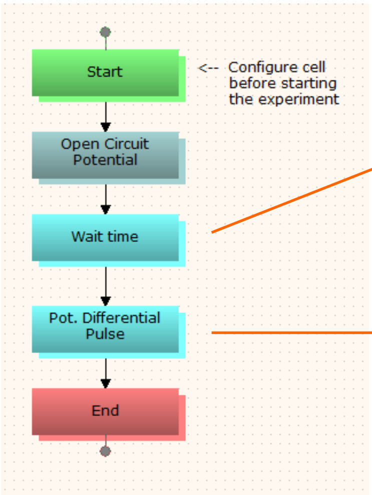


Figure 1: Scheme of imposing pulse of potential

Parameters

This experiment was performed by OrigaMaster software. The parameters of the method are shown in figure 2.



Single Chrono Amperometry	
Potential (mV)	-200
Duration	10, sec.
Open circuit at end	Yes
Save points	Yes
Auxiliary input	No

Pot. Differential pulse	
Potential 1 (mV)	-200, REF
Potential 2 (mV)	600, REF
Scan rate (mV/sec.)	10
Step (mV)	7
Pulse (mV)	90
Pulse time (msec)	20
Minimum range	100 nA
Maximum range	1 mA
Digital Filter	0
Open circuit at end	Yes
Save raw data	Yes

Figure 2: The parameters of the Pot. Differential Pulse

With the above default settings, the start potential is defined as -200 mV versus REF. The potential step is 7 mV. Differential measurements are obtained by difference of currents measured at the end of each pulse. The experiment is completed when the applied potential reaches 600 mV versus the REF.

TIPS: Before perfoming the Pot. Differential Pulse, we advise you to perform two methods, in order to get a more stable working electrode:

- OCP for 1 minute
- Chrono Amperometry for 10 seconds. The goal here is to impose the same starting potential as the Pot. Differential Pulse, called Potential 1. That's why, in this case, we imposed – 200 mV for 10 seconds.

It results that the beginning of the Pot. Differential Pulse will be much more stable.

HOW TO SET THE PARAMETERS

To get good results, some parameters need to be chosen with care. Indeed, if the parameters are not optimized, the curve could be too noisy and so useless for publications and post-treatment.

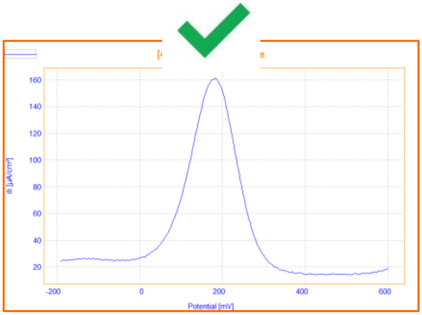


Figure 3: Good curve

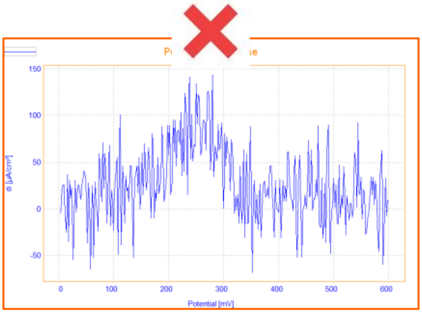


Figure 4: Bad curve, too noisy

	Pot. Differential pulse	
	Potential 1 (mV)	-200, REF
	Potential 2 (mV)	600, REF
	Scan rate (mV/sec.)	10
	Step (mV)	7
1	Pulse (mV)	90
4	Pulse time (msec)	20
2	Minimum range	100 nA
3	Maximum range	1 mA
5	Digital Filter	0
	Open circuit at end	Yes
	Save raw data	Yes

Figure 5: Optimized parameters for OGS100

TIPS: Parameters can be optimized to get a smooth curve. But it does not prevent from also optimizing the electrode connections : shielded cables, Faraday cage, and so on.

Most important parameters:

1: Pulse
This is the height of the pulse (see figure 1 on page 2). Higher it is, less the noise is.

2: Minimum range
More accurate is the current range, better is it for the quality of the signal. Adapt the current range to the flowing current.

3: Maximum range
The Maximum current range could be the highest one or fit the highest level of current, flowing in your cell. You can consult the raw data to determine it.

4: Pulse time
Important too. It has to be optimized. Generally, it's between 20 and 50 msec.

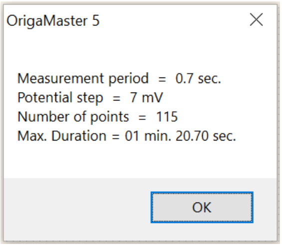
5: Digital filter
If optimizing the first parameters are not enough, you can put a digital filter, from 0 (no filter) to 20 (maximum).

HOW TO CHECK THE SHAPE

During method programming, you can get two kind of information:

- The shape of the imposed signal, by clicking the icon of the Pot. Differential Pulse Properties tool box.
- Some data on the experiment, by clicking twice on the method block.

1 Experiment conditions



These data are deduced from the parameters and give you very important information on how the experiment will be performed.
"Number of points" is an important data, because it gives you the size of the curve. Too many points can engender lagging in the analysis process.

Figure 5: Infomation about DPV experiment

2 Shape of imposed signal

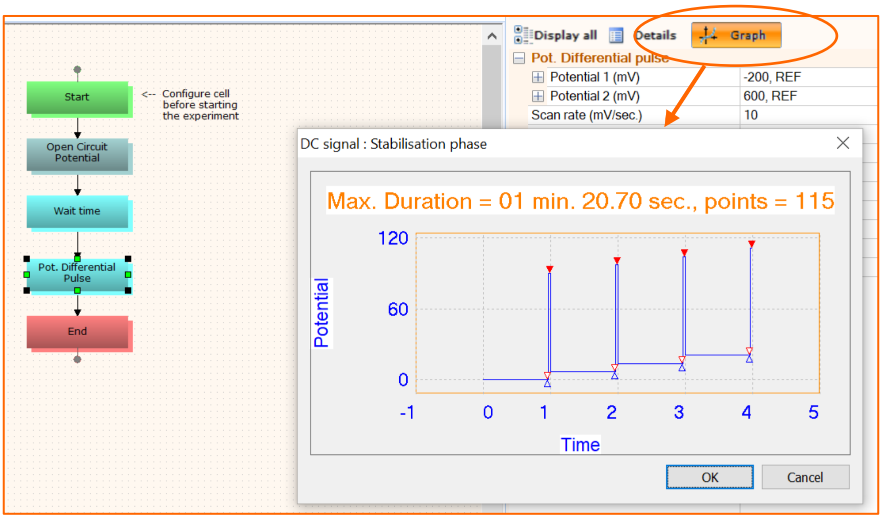


Figure 6: Shape of imposed signal

Results

The pulse method was performed on Ferri Cyanide solution by different concentration from 5 mM to 0.07 mM.

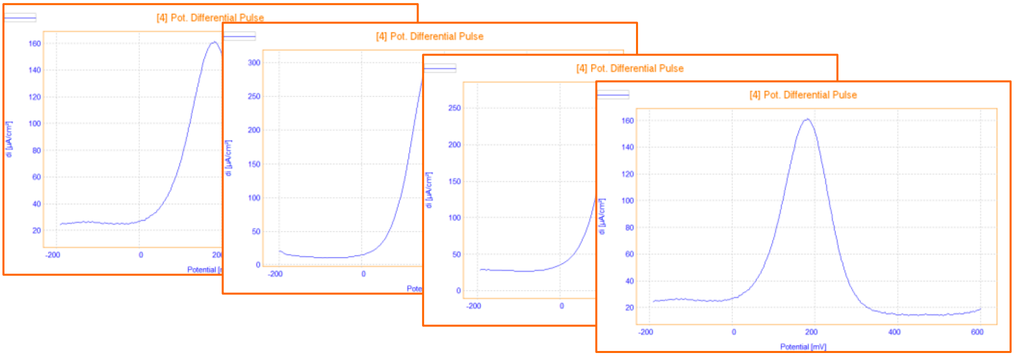


Figure 7: Examples of individual Differential Pulse curves

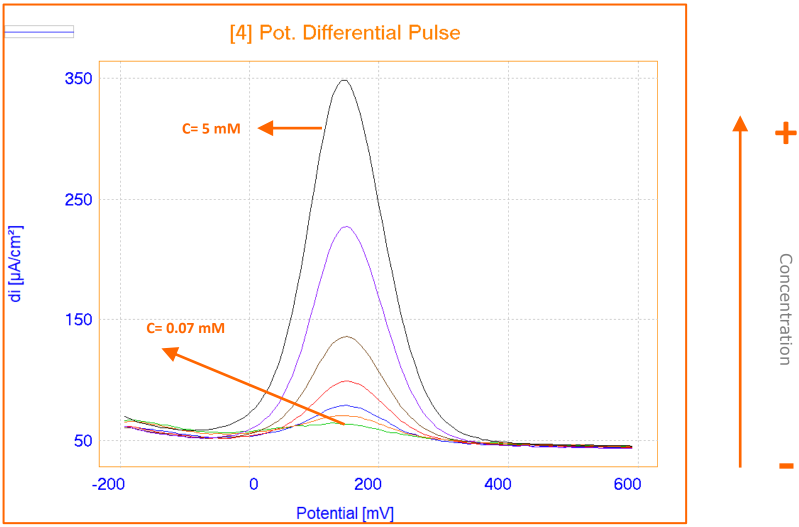


Figure 8: Overlay of 7 Differential Pulse Voltamogramms

CONCLUSION: Most applications of pulse methods are for quantitative approaches in low concentrations. In figure 8, it can be seen by increase in concentration; the current is increased as well.

APPLICATION: Talking about low concentration is talking about probe application. It means determination of a metal or a chemical element in an environment. Examples: heavy metals in mineral water, efficiency of treatment by determining if concentration of a toxic element can still be found, …

Instrument and Electrodes

Figure 9: OrigaStat OGS100

Electrode setup	
Reference Electrode (REF)	Calomel Type: OGR003
Counter Electrode (AUX)	Platinum wire Ø1mm Type: OGV005
Working Electrode (WRK)	Platinum Ø5mm Type: EMEDTPTD5
Sample	Ferri solution 5 x 10^{-3} - 7 x 10^{-5} M in KCl
Instrument	OrigaStat OGS100
Software	OrigaMaster

Figure 10: Electrochemical cell

REF
Calomel

AUX
Platinum wire Ø1 mm

WRK
Platinum Ø5 mm

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