ApplicationNOTE

Spectroelectrochemistry – Part 2: Experiments and Data evaluation

Purpose of This Note

This application note is part 2 of a series of notes introducing Gamry's spectroelectrochemistry system.

Part 1 discusses the basics of light spectroscopy and explains important terms and parameters. It describes the setup for spectroelectrochemical experiments and shows Gamry's spectroscopic equipment.

Part 2 discusses the spectroscopic experiments in Gamry's Framework and explains their setup parameters. Data evaluation is shown by using the Echem Analyst. Its new spectroscopy commands are described on the basis of examples.

Introduction

Gamry Instruments offers a new Spectroelectrochemistry software package. It allows the user to perform electrochemical and spectroscopic experiments simultaneously.

The next chapters explain in detail setup parameters and the procedure of all spectroscopic experiments in Gamry's Framework. Afterwards, data evaluation in the Echem Analyst is explained.

Experiments

All spectroelectrochemical experiments are located under "SPECTRO – Spectroelectrochemistry" in Framework's experiment menu, see Figure 1.

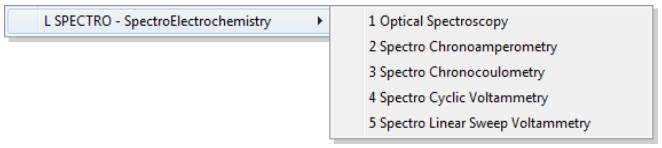

Figure 1 – Gamry's Framework menu showing the new software package "SPECTRO – Spectroelectrochemistry" and its five experiments.

With the exception of *Optical Spectroscopy*, all experiments are combined spectroscopic and electrochemical experiments.

Optical Spectroscopy

As mentioned before, *Optical Spectroscopy* is the only spectroscopic experiment. This experiment records one single spectrum. Its setup is shown in Figure 2.

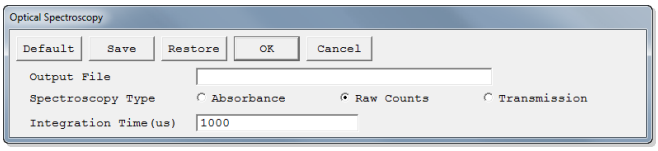

Figure 2 – Setup for the *Optical Spectroscopy* experiment. For details, see text.

The user defines the output file name and the type of data which should be recorded – absorbance, raw counts, or transmission. In addition, the integration time can be set (in microseconds). It defines how long the detector will collect light to obtain a single spectrum.

This experiment is helpful to find the correct integration time or other setup parameters (e.g. analyte concentration or pathlength of the cuvette) for your measurement.

Note: The value for the integration time τ that is set in *Optical Spectroscopy* is used at all spectro-electrochemical experiments which are performed later.

After starting an experiment, the user is asked if a dark spectrum and a blank spectrum should be recorded prior to the actual measurement (see Figure 3). The actual measurement is automatically corrected for both spectra.

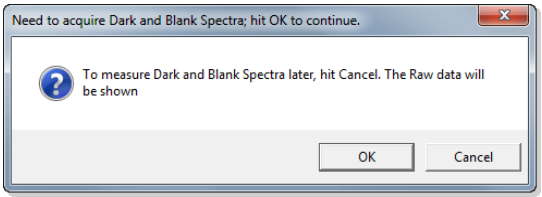

Figure 3 – Dialog box for measuring a dark and blank spectrum prior to the actual measurement.

If Cancel is pressed, the dialog box which is shown in Figure 6 pops up. The actual measurement can be started and a single raw count spectrum is recorded regardless of the type that was chosen in the setup.

If OK is pressed, the box shown in Figure 4 pops up, indicating that a dark spectrum is going to be measured.

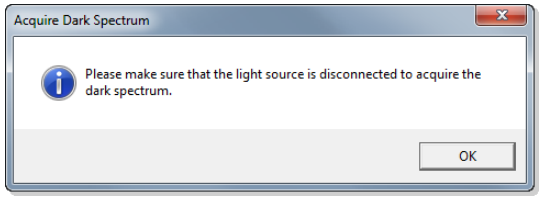

Figure 4 – Dialog box for acquiring a dark spectrum.

Please make sure to darken your cell and close the shutter (S) by turning off the switch on the back side of your light source.

After measuring the dark spectrum, a next dialog box asks you to record a blank spectrum (see Figure 5).

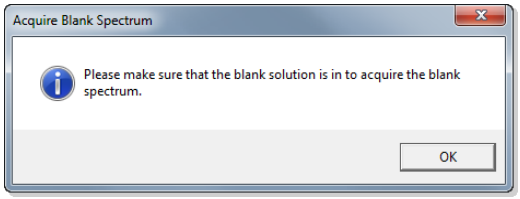

Figure 5 – Dialog box for acquiring a blank spectrum.

Put a cuvette containing a blank solution (commonly the solvent of your analyte) in the cuvette holder and darken it with the cap. Open the shutter and turn on the deuterium (D2) and/or the tungsten (W) lamps to measure a blank spectrum.

> **Note:** Please make sure that both lamps are warmed up for about 8 to 10 minutes before executing an experiment.

After this, a last dialog box pops up (see Figure 6) indicating that the actual measurement can be started.

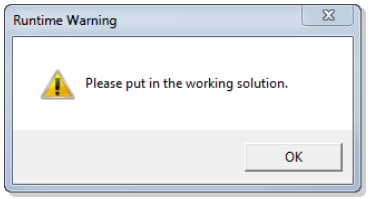

Figure 6 – Dialog box for acquiring an actual spectrum.

Put in the cuvette with your analyte. The light sources are turned on while the shutter is open. The actual measurement is performed by pressing OK.

A single spectrum is recorded. The type is defined prior in the setup – absorbance, raw counts, or transmission.

Figure 7 shows a screenshot of an absorbance spectrum displayed in Gamry's Framework during an *Optical Spectroscopy* experiment. The spectrum is from Methylene Blue in a solution of potassium nitrate (KNO_3). The integration time was set to 0.1 s.

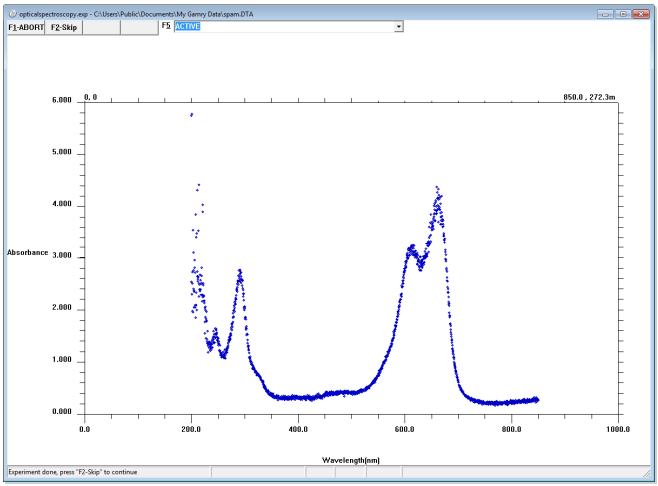

Figure 7 – Absorbance spectrum of 0.1 mM Methylene Blue in 1 mM KNO_3.

The spectrum shows typical absorbance peaks at about 245 nm, 291 nm, 610 nm, and 660 nm. Hence the violet, yellow, and red portion of the electromagnetic spectrum's visible part is mostly absorbed resulting in the intense blue color of Methylene Blue.

Sweep and Chrono techniques

The SPECTRO software package allows the user to perform electrochemical and spectroscopic experiments simultaneously. These measurements include:

- Spectro Chronoamperometry
- Spectro Chronocoulometry
- Spectro Cyclic Voltammetry
- Spectro Linear Sweep Voltammetry

All four experiments are similar to the non-spectroscopic experiments of the PHE200 software package. However, the setup includes one extra line (see Figure 8) to select the spectroscopy type for an experiment.

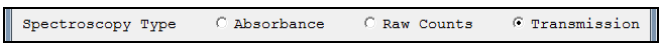

Figure 8 – Section of the setup of spectroelectrochemical experiments from the SPECTRO software package.

Similar to *Optical Spectroscopy*, the user is asked if a dark and blank spectrum should be recorded before the electrochemical experiment starts (see Figure 3 to Figure 6 and the description).

Finally, when both measurements are running, two separate windows are open in the Framework. One

shows all typical graphs which belong to the executed electrochemical experiment. The other window shows the spectrum which is updated each time a whole spectrum is recorded. The duration depends on the integration time which is set in the *Optical Spectroscopy* experiment.

After an electrochemical experiment is finished, a last spectrum is recorded and the spectroscopy measurement stops, too.

Data evaluation

Both spectroscopic and electrochemical data can be evaluated in the Echem Analyst. The next sections discuss the format of the output files and data evaluation in the Echem Analyst with its new spectroscopy commands.

Output files

When performing spectroelectrochemical experiments, two separate *.DTA output files are generated. The first file contains all data for the electrochemical experiment while the second one includes data for all spectra.

The electrochemical output file uses the name that was chosen in the experimental setup. The format is similar to non-spectroscopic experiments in the PHE200 software package. However, it shows some differences.

The tag, specific for an experiment, is varying for spectroelectrochemical experiments. It determines the menus in the Echem Analyst which contain commands and tools for data evaluation. Table 1 shows all experiment-specific tags.

Experiment	Tag
Spectro Chronoamperometry	SPECTROCHRONOA
Spectro Chronocoulometry	SPECTROCHRONOC
Spectro Cyclic Voltammetry	SPECTROCV
Spectro Linear Sweep Voltammetry	SPECTROLSV

Table 1 – Experiment-specific tags for spectroelectrochemical experiments.

In addition, the output file includes one extra line:

```
SPECTRONAME<tab>LABEL<tab>SpectraFor_OutputFile Name.DTA<tab>File Name for Spectra
```

This line links both electrochemical and spectroscopic files by including the file name of the spectroscopic file. The spectroscopic file name consists of the prefix "SpectraFor_" followed by the file name of the electrochemical experiment.

Hence when opening an electrochemical file in the Echem Analyst, corresponding spectroscopic data are automatically added within a new tab.

Note: When changing the file name of a spectroscopy file, ensure to change this name also in the electrochemical data file at the extra line shown before. This can be done by opening the file in a simple text editor. Otherwise, the Echem Analyst will not add spectroscopic data.

When opening a single spectroscopy file, only spectroscopic data are shown in the Echem Analyst.

Spectroscopy commands

When opening a spectroelectrochemical data file in the Echem Analyst, special commands are enabled for spectroscopic data. Figure 9 shows the spectroscopy menu in the Echem Analyst.

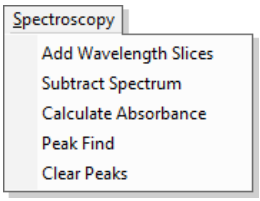

Figure 9 – Echem Analyst's spectroscopy menu including its commands. For details, see text.

The next section will explain each command and its functioning with examples.

Add Wavelength Slices

The command *Add Wavelength Slices* enables the user to select specific wavelengths and display the temporal progress of spectroscopic data (absorbance, raw counts, or transmission) in a new graph.

An application example for this command is shown in Figure 10. It shows five absorbance spectra at different times (1 min, 20 min, 40 min, and 60 min – from darker to brighter) recorded during a spectro chronoamperometric experiment.

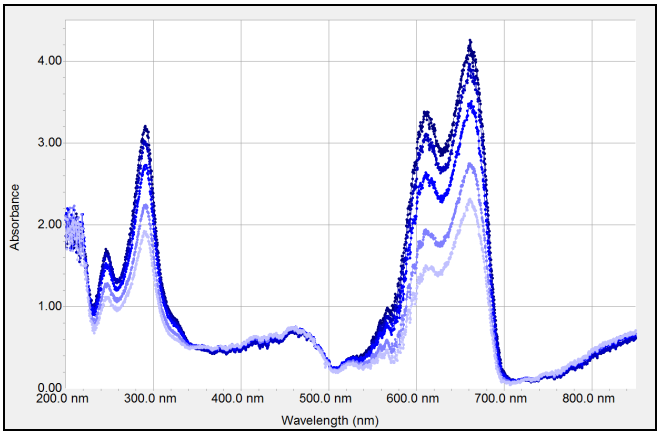

Figure 10 – Absorbance spectra of 0.1 mM Methylene Blue in 1 mM KNO_3 at different times during a spectro chronoamperometric experiment. For details, see text.

The electrolyte is 0.1 mM Methylene Blue in 1 mM potassium nitrate. Methylene Blue (blue) is potentiostatically reduced to Leucomethylene Blue (colorless) on a platinum mesh electrode at -0.35 V vs. Ag/AgCl.

The analyte loses more and more of its blue color as time goes by. Hence absorbance peaks at about 245 nm, 290 nm, 610 nm, and 660 nm are decreasing.

The temporal progress of absorbance during this experiment can be visualized by using the command *Add Wavelength Slices*. When selecting the command, a separate window opens where the user can define up to four wavelengths at a time (see Figure 11).

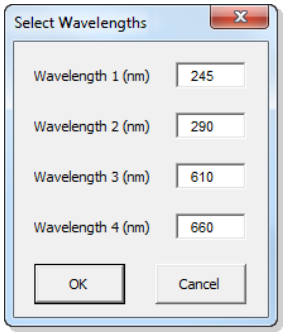

Figure 11 – Setup window for the spectroscopy command *Add Wavelength Slices*. For details, see text.

After pressing OK, a new tab opens in the Echem Analyst showing a new graph with plots for each wavelength (see Figure 12).

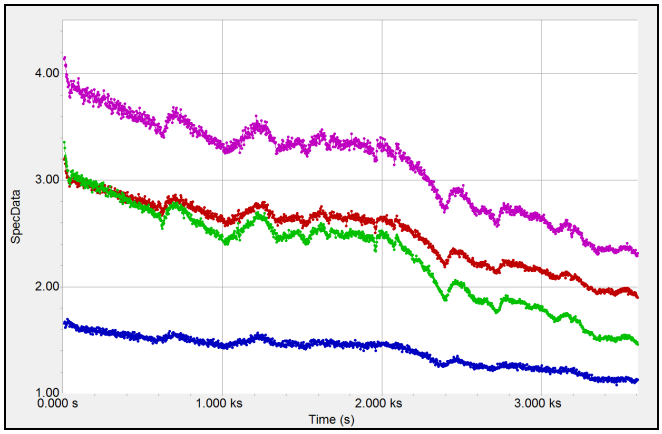

Figure 12 – Temporal progress of absorbance at four different wavelengths during reduction of Methylene Blue. (●) 245 nm, (●) 290 nm, (●) 610 nm, (●) 660 nm. For details, see text.

Repeating the command *Add Wavelength Slices* will add further plots to existing ones. Less than four wavelengths can be plotted by setting a wavelength to zero.

Subtract Spectrum

The command *Subtract Spectrum* allows the user to subtract a spectrum from a current one. Requirement is that spectroscopic data of both spectra (absorbance, raw counts, or transmission) are the same.

The user is asked to select a spectroscopy file that will be subtracted when executing the command. Subtraction is performed on all spectra of the original file. New curves which are called "Subtracted" will be added to the curve selector. Repeating the command will add further plots to the curve selector.

Figure 13 shows a CV and absorbance spectra at different potentials (from darker to brighter) starting from the oxidation peak.

Figure 14 shows relative changes of absorbance at the same potentials compared to the initial cycle by using the command *Subtract Spectrum*.

The electrolyte is 5 mM potassium ferricyanide ($K_3[Fe(CN)_6]$) in 10 mM potassium chloride (KCl). The spectro cyclic voltammetry experiment was performed on a platinum mesh electrode versus a Ag/AgCl reference electrode.

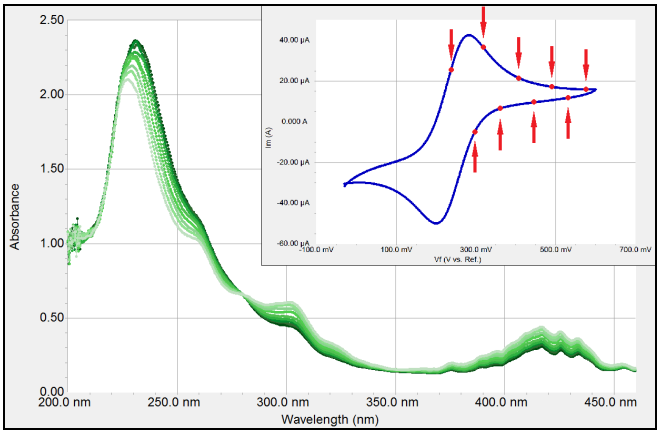

Figure 13 – Absorbance spectra of 5 mM $K_3[Fe(CN)_6]$ in 10 mM KCl at different potentials during a spectro cyclic voltammetry experiment. Picture on top right shows the CV. For details, see text.

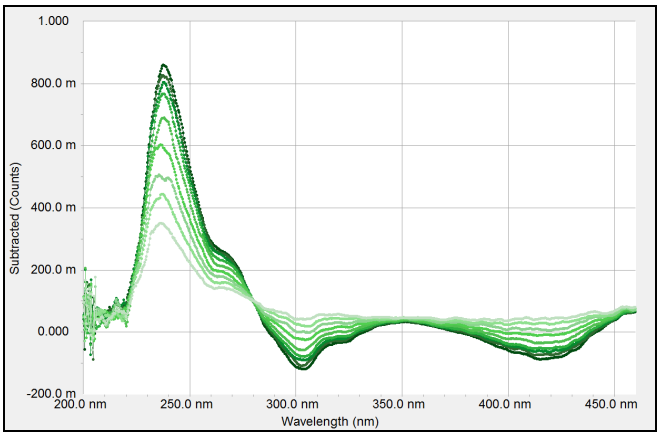

Figure 14 – Relative changes of absorbance by using command *Subtract Spectrum*. For details, see text.

During the measurement Fe(II) is oxidized to Fe(III). Absorbance is decreasing at about 230 nm and 260 nm while it is increasing at 300 nm and around 420 nm.

The whole process is reversible. However, the reduction step is not shown to ensure a better overview at both graphs. All spectra are slightly smoothed using the tool *Smooth Data* due to noise during the measurement.

Calculate Absorbance

Calculate Absorbance is a simple command to convert raw count spectra into absorbance spectra.

The user is asked to open a spectroscopy file with raw count data which is then automatically converted into an absorbance spectrum in the Echem Analyst.

Peak Find

The *Peak Find* command enables the user to find all peaks in the selected portion of a spectrum.

First, the user has to mark a region of the spectrum by using the tool *Select Portion*. By using the command *Peak Find*, all peaks (maxima for absorbance and raw count spectra and minima for transmission spectra) are highlighted and numbered. A detailed table is generated in a new tab which sums up all relevant peak data.

Figure 15 shows an absorbance spectrum of Methylene Blue in KNO_3 with all highlighted peaks. Figure 16 shows the according table.

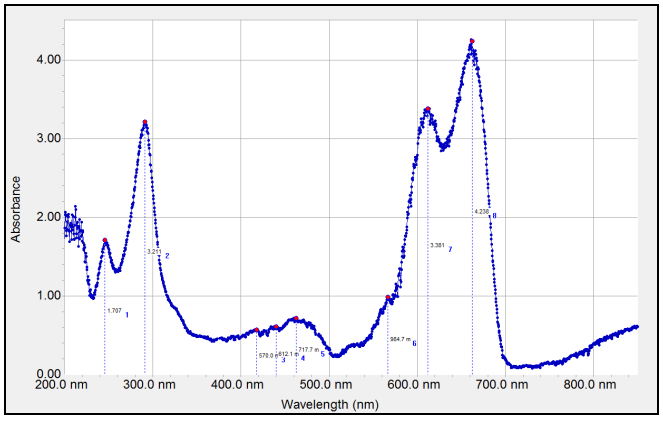

Figure 15 – Absorbance spectra of 0.1 mM Methylene Blue in 1 mM KNO_3 including all peaks. For details, see text.

Spectroscopy_Absorbance | Spectro Peak Locations

Section (Pt# 104 to Pt#726)	Absorbance	@ WaveLength (nm)	Trace	Index	Height ()
Peak 1:	1.707	245.7 nm	1	117	1.707
Peak 2:	3.211	290.9 nm	1	231	3.211
Peak 3:	570.0 m	417.8 nm	1	543	570.0 m
Peak 4:	612.1 m	439.7 nm	1	600	612.1 m
Peak 5:	717.7 m	462.7 nm	1	660	717.7 m
Peak 6:	984.7 m	566.5 nm	1	922	984.7 m
Peak 7:	3.381	612.3 nm	1	1043	3.381
Peak 8:	4.238	662.2 nm	1	1174	4.238

Figure 16 – Table of peak locations for the spectrum shown in Figure 15 generated by command *Peak Find*.

The *Peak Find* command uses an algorithm which is searching for changes in the slope. It makes a linear fit for a pre-defined range and compares signs of slopes. Pseudo-peaks due to noisy measurements are filtered out by the algorithm as far as possible.

Advice: Use command *Peak Find* repeatedly for smaller wavelength portions if too many peaks are found by due to noisy spectra. Additional peaks will be added to the list.

If a spectrum is too noisy, use the tool *Smooth Data*. However, be careful with smoothing as peaks and shoulders could be wiped out.

Clear Peaks

The *Clear Peaks* command clears all peak information generated by the *Peak Find* command. The list containing all peak data is deleted.

Summary

This note is part 2 of a two-part application note series. It explains execution and data evaluation of spectroelectrochemical experiments.

Framework's experimental setup for spectroscopic and spectroelectrochemical measurements is shown and important parameters are discussed. The measurement procedure and the output file format are explained.

Finally, data evaluation in the Echem Analyst including a detailed description of each spectroscopy command is shown by means of examples.

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