Raman Intensity (a.u.)

200

100

Raman Shift (cm⁻¹)

2200
2150
2100
2050

-0.20
+0.20
+0.60

Potential (V)

Tools for monitoring Spectroelectrochemistry experiments in DropView SPELEC

Spectroelectrochemistry is a multirresponse technique which provides valuable information associated with electrochemical and spectroscopic processes. In that way, this Application Note explains the usefulness of two different tools included in DropView SPELEC for relating electrochemical and optical information.

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INTRODUCTION

As was firstly explained by Kuwana in 1964 [1], spectroelectrochemistry is an instrumental technique which offers global information through simultaneous, quick and in-situ measurements related to chemical processes. On one hand, electrochemistry provides information about the electron transfer process that takes place in a chemical reaction produced on the surface of an electrode; while on the other hand, spectroscopy provides molecular, thermodynamic and kinetic information about this reaction. Then, optical and electrochemical information about the same dynamic process are simultaneously obtained. Due to the high versatility of the technique, the field of applications is considerably wide [2-5].

This Application Note explains different tools included in DropView SPELEC software to understand spectroelectrochemistry experiments as well as to relate the spectroscopic and electrochemical information. With this aim, the usefulness of different tools such as "Spectra vs EC" or "Spectra peak height vs EC" will be shown, allowing to obtain the maximum information from a single experiment.

INSTRUMENTATION AND SOFTWARE

Measurements displayed in this Application Note were obtained with SPELEC and SPELEC RAMAN instruments, both controlled with DropView SPELEC. These equipments allow obtaining detailed, clear and concise information about the electrochemical processes that take place on the electrode surface. DropView SPELEC is a dedicated software that provides spectroelectrochemical information and includes tools to perform an adequate treatment and analysis of the obtained data.

RESULTS

Spectroelectrochemistry is very versatile due to the wide variety of spectroscopic and electrochemical techniques available. However, the usual classification is made according to the spectroscopic technique used.

according to the spectroscopic technique used. In this Application Note, one UV-VIS absorption spectroelectrochemistry and Raman spectroelectrochemistry experiments will be analysed using two interesting tools:

• "Spectra vs EC" represents the value of the optical signal at a single wavelength with potential. This representation is relevant and allows the understanding of spectroelectrochemistry experiments. Furthermore, baseline correction can be additionally applied to the spectra. Similarly, "Spectra vs time" tool allows monitoring the spectroscopic signal at a specific wavelength with time.

• "Spectra peak height vs EC" is a tool particularly interesting for Raman measurements because it provides the evolution of Raman intensity at a single Raman Shift with potential. To measure the peak height, a baseline is automatically subtracted in order to obtain only the value that corresponds to the peak. Similarly, "Spectra peak height vs time" tool allows monitoring the Raman signal with time.

"Spectra vs EC"

For a better understanding of the tool, it will be applied on the results obtained in the UV-VIS spectroelectrochemical study of adrenaline. A cyclic voltammetry was performed scanning the potential between +0.20 and +0.80 V at 10 mV/s in 5 mM adrenaline in 0.1 M HCl solution using a screen-printed carbon electrode (DRP-110). Spectra were recorded using 300 ms as integration time.

When a spectroelectrochemical experiment is carried out, two types of signals are recorded, electrochemical (Fig.1a) and spectroscopic (Fig. 1b). Cyclic voltammogram (Fig. 1a) shows two electrochemical peaks, an anodic process at +0.69 V and a cathodic process at +0.17 V, corresponding to the oxidation and reduction of the adrenaline, respectively.

Simultaneously, spectroscopic information is obtained. This information can be represented in different ways, being one of the most useful the representation of absorbance (a.u.) vs wavelength (nm). Several absorption bands associated with the generation of adrenoquinone during the adrenaline oxidation are observed. Fig. 1b shows the most representative band of electrogenerated adrenoquinone located at 385.2 nm. In case of a noisy signal is obtained, electrochemical and/or spectroscopic responses can be smoothed using the different tools included in DropView SPELEC.
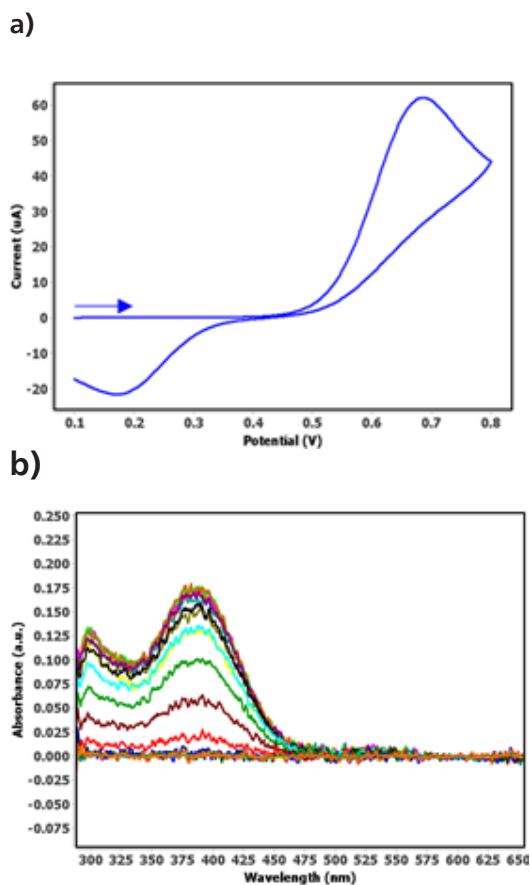
a)

b)

Figure 1. (a) Cyclic voltammogram and (b) UV-VIS spectra recorded in 5 mM adrenaline in 0.1 M HCl scanning the potential from +0.20 to +0.80 V and back to +0.20 V at 10 mV/s scan rate.

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Once the characteristic wavelength of the molecule has been located, "Spectra vs EC" tool is applied for monitoring the evolution of this band with potential. Short integration times, 300 ms in this example, enables the acquisition of huge number of spectra, 466 in adrenaline experiment. In that way, time-resolved or operando spectroelectrochemistry provides information at all times and not only at several potentials.

Short integration times, 300 ms in this example, enables the acquisition of huge number of spectra, 466 in adrenaline experiment. In that way, time-resolved or operando spectroelectrochemistry provides information at all times and not only at several potentials. "Spectra vs EC" tool is selected in two different ways: (1) right click on the recorded experiment in the "Graphic Control Area" (Fig. 2a) or (2) selecting it in the "Experiments" section of the menu bar (Fig. 2b). Then, just introducing the selected wavelength, in this case it is 385.2 nm (Fig. 2c). As can be observed in Fig. 2c, autobaseline correction can be also applied at the same time that evolution of this band is calculated. Finally, smoothing of the signal can be done introducing the parameters of Savitzky-Golay filter (Fig. 2d).

Figure. 2 Steps for using the "Spectra vs EC" tool.

After performing the steps mentioned, representation shown in Fig. 3 is obtained. As can be observed, absorbance at 385.2 nm is represented with potential, being this representation known as voltabsorptiogram.
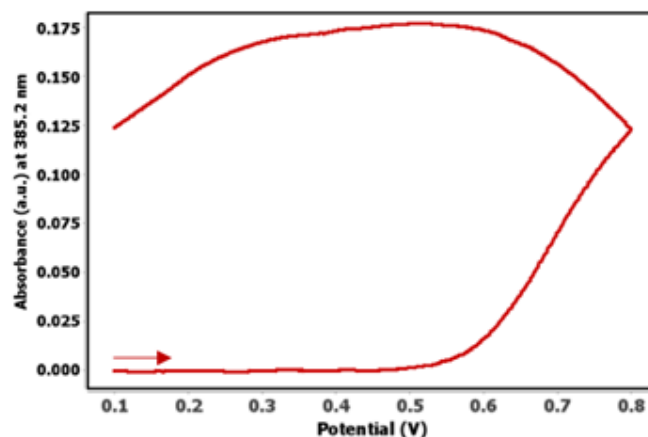

Figure 3. Evolution of absorbance at 385.2 nm with potential.

Figure 3 shows that the absorbance at 385.2 nm is initially 0 a.u. in the range of potentials where adrenaline is not oxidized. It increases during the oxidation scan, from +0.55 V, when the oxidation of adrenaline to adrenoquinone starts. Absorbance continue increasing at more positive potential in the forward scan and also in the backward scan while the oxidation process continues and the maximum value (0.175 a.u.) is reached at +0.50 V. From this potential, absorbance decreases due to the reduction of adrenoquinone takes place. Decrease of absorbance is more pronounced at lower potential than +0.35 V, when the reduction peak is detected in the electrochemical profile.

Several options are available by DropView SPELEC software when the voltabsorptiogram is plotted:

• Film: this tool shows the evolution of absorbance at the specific wavelength with potential as a video. It can be also saved as a video file.

• Information: provides information about the experimental parameters selected for performing the experiment.

• Smooth: as was previously mentioned, this tool is used to smooth the signal using Savitzky-Golay filter. However, if a heavy smoothing is applied it will significantly modify the signal, leading to misinterpretation of the studied process.
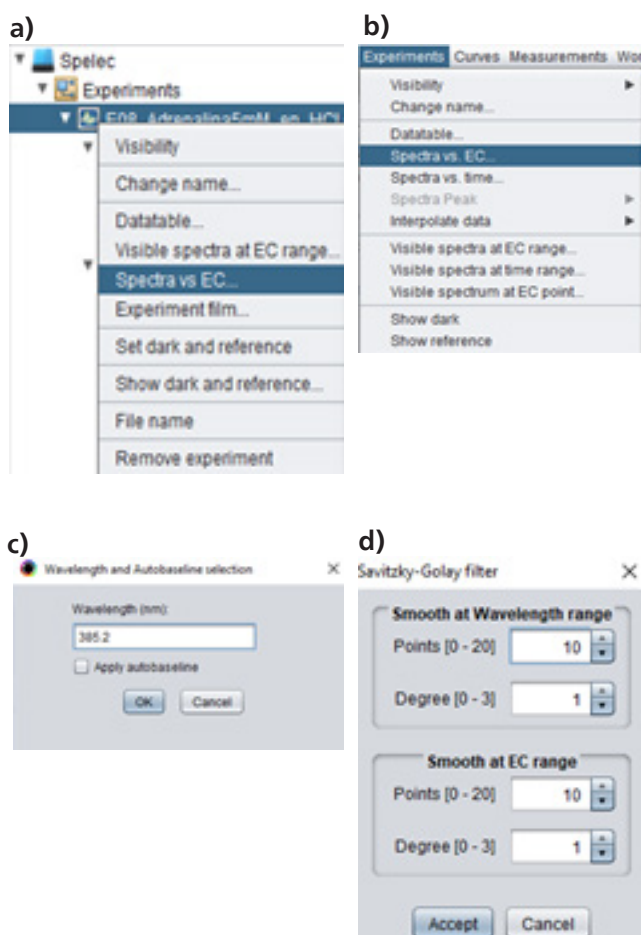
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- Send to ws (workspace): it sends the generated signal to a new window, called workspace, which is very useful for comparison purposes. When this option is selected, a pop up window appears in order to select in which axis (primary or secondary), the signal will be represented (Fig. 4). If any signal is not plotted in the workspace, select the principal axis. If there is another signal in the workspace and the scale is different, selection of the secondary axis is recommended.
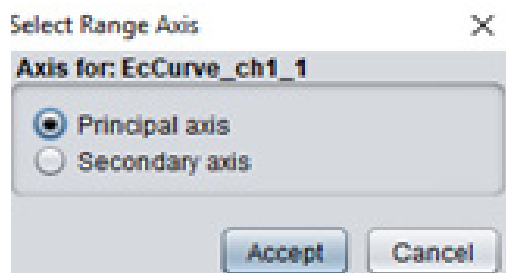

Figure 4. Axis selection of workspace.

- Export curve: it saves the data in .csv format.

- Reset curve: it allows resetting to the initial curve by removing the applied tools.

- Derivative: it calculates and represents the derivative of the absorbance at the selected wavelength with potential as a function of time.

In order to compare electrochemical and spectroscopic responses, EC curve as well as the voltabsorptiogram at 385.2 nm, are sent to the workspace. EC curve is sent to workspace by right clicking on the EC curve in the "Graphics display area" and selecting principal axis to be represented. Voltabsorptiogram at 385.2 nm is plotted following the previous procedure and is sent to the seconday axis of the workspace. Fig. 5. shows the workspace with both signals.

As can be noticed, the x-axis is the same for both signals (potential) while two different y-axis are plotted, principal (on the left) for the electrochemical signal (current) and the secondary (on the right) for the optical information (absorbance). Absorbance at 385.2 nm increases at the same time as the oxidation peak is observed in the forward scan in the voltammogram, while it decreases during the cathodic process, when the cathodic peak emerges in the voltammogram.
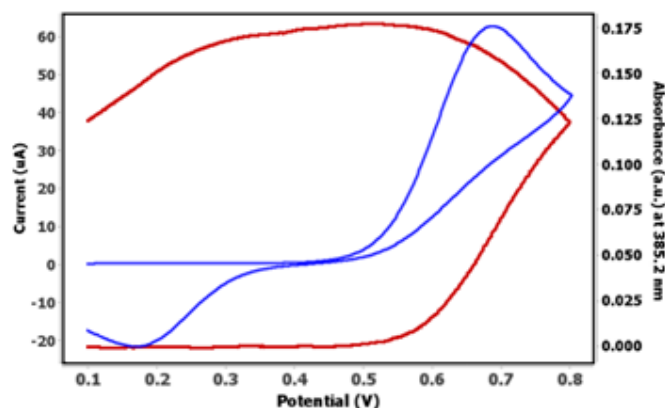

Figure 5. Comparison of cyclic voltammogram (blue line) and the voltabsorptiogram at 385.2 nm (red line) in the workspace.

As explained above, DropView SPELEC software not only allows monitoring the absorbance at one wavelength with the potential, but also allows calculating the derivative signal and representing it. In order to do this, among the options available after using "Spectra vs EC" function, "Derivative" option is selected and Fig. 6 is obtained. As time-resolved or operando spectroelectrochemsitry records a huge number of spectra during the electrochemical reaction, derivative signal can be calculated, offering interesting results as will be explained.
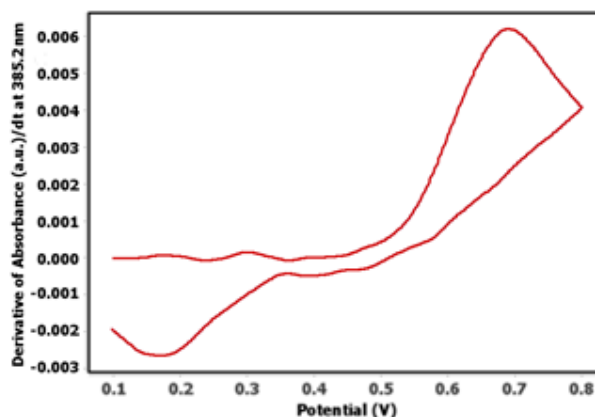

Figure 6. Derivative of the absorbance at 385.2 nm with potential (derived voltabsorptiogram at 385.2 nm).

Once the derived voltabsorptiogram is represented, different options are available, for example, it can be filtered if the signal is noisy or be sent to the workspace. Derived voltabsorptiogram at 385.2 nm shows two peak, one anodic related to the oxidation of adrenaline to adrenoquinone, and the cathodic one associated with the reduction of adrenoquinone to adrenaline. These two peaks are close similar to those observed in the cyclic voltamperogram. They can be compared sending both signals to the workspace (Fig. 7).
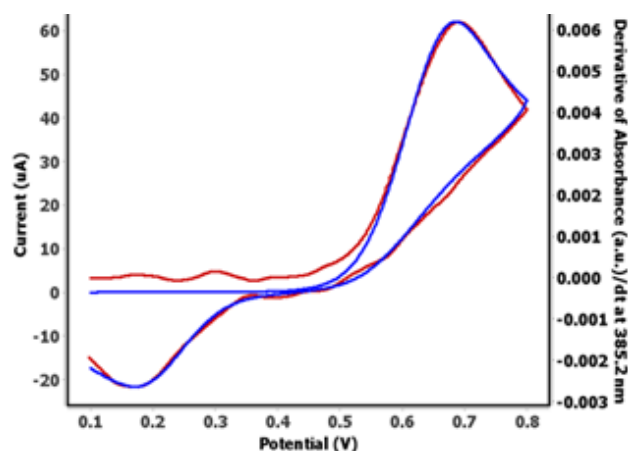

Figure 7. Comparison of the cyclic voltammogram (blue line) and the derived voltabsorptiogram at 385.2 nm (red line) in the workspace.

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As Fig. 7 displays, derivative signal at 385.2 nm and cyclic voltammogram are close similar. While electrochemical signal considers faradic and a non-faradic processes, the optical signal discriminates between faradaic and non-faradaic processes and only faradic processes are considered in this response. Thus, although the electrochemical and spectroscopic techniques are two different techniques, the information obtained in a UV-VIS spectroelectrochemical experiment demonstrates that both information are perfectly correlated.

"Spectra peak height vs EC"

"Spectra vs EC" tool can be also used for Raman spectroelectrochemistry experiment in a similar way that explained in the previous section for UV-VIS experiment. Apart from this tool, additional functions as "Spectra peak height vs EC" are implemented in DropView SPELEC software.

In order to show the usefulness of this tool, Raman spectroelectrochemistry experiment was performed. It consists of the electrochemical activation of the metal surface of the screen-printed electrode and the detection by surface-enhanced Raman scattering (SERS) effect of one analyte present in solution. Raman experiment was performed using a silver screen-printed electrode, DRP-C013, with 0.5 mM tris(bipyridine)ruthenium(II) chloride (Rubpy) in 0.1 M KCl solution, scanning the potential between +0.30 V and -0.40 V at 10 mV/s.

As in the previous experiment, two different signals are simultaneously recorded, electrochemical profile and Raman spectra. Cyclic voltammogram (Fig. 8a) shows two electrochemical processes, one reduction peak at -0.27 V and one oxidation peak at +0.21 V. Taking into account that Rubpy is not electrochemically active at this range of potentials, both processes are only related to the reduction and oxidation of silver surface.

Simultaneously, Raman spectra were recorded during the whole electrochemical experiment (Fig. 8b). As the experiment lasts only 28 seconds and integration time of 50 ms was used, 560 spectra were recorded. Raman spectra show the characteristic bands of Rubpy, each of them associated with particular vibrational modes. Although the spectra recorded in this experiment has a weak background signal, it is very common that the baseline changes during Raman spectroelectrochemistry experiments. For that reason, baseline correction can be done using the different tools included in DropView SPELEC for this purpose.
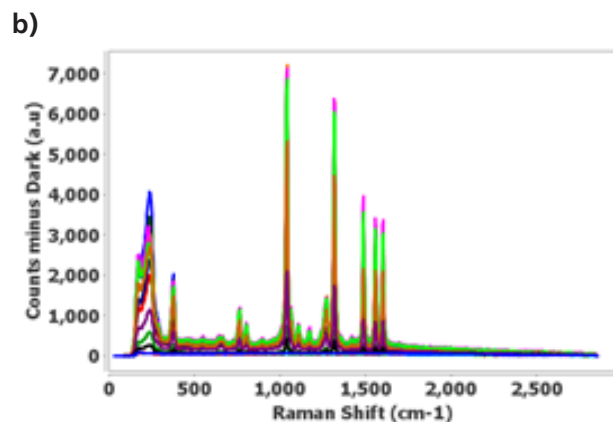
b)

Figure 8. (a) Cyclic voltammogram and (b) Raman spectra recorded in 0.15 mM Rubpy in 0.1 M KCl scanning the potential from +0.30 to -0.40 V and back to +0.30 V at 50 mV/s scan rate.

The most intense Raman band at 1041 cm-1 is selected to explain the "Spectra peak height vs EC". Selection of this tool is done following the route: Menu bar > Experiment > "Spectra peak" > "Spectra peak height vs EC". Then, Raman Shift value, 1041.8 cm-1, is introduced. As "Spectra peak height vs EC" tool automatically subtracts the baseline to obtain only the value that corresponds to the Raman band, "Autobaseline" tool is not required. Additionally, smoothing can be applied if a noisy signal is obtained. After performing these steps, the representation shown in blue line in Fig. 9 is obtained, showing the evolution of Raman intensity at 1041 cm-1 with potential. This figure as well as the EC curve are sent to workspace for comparison purposes (Fig. 9).
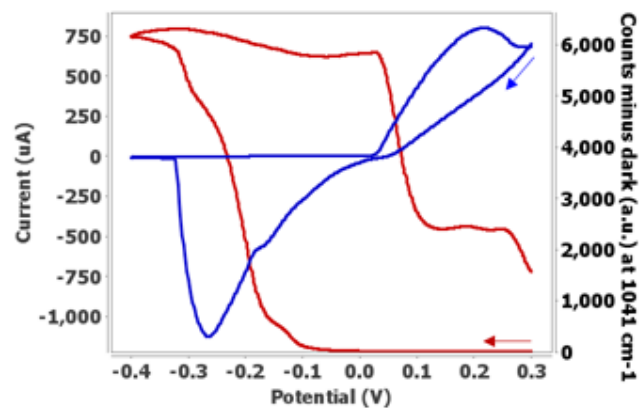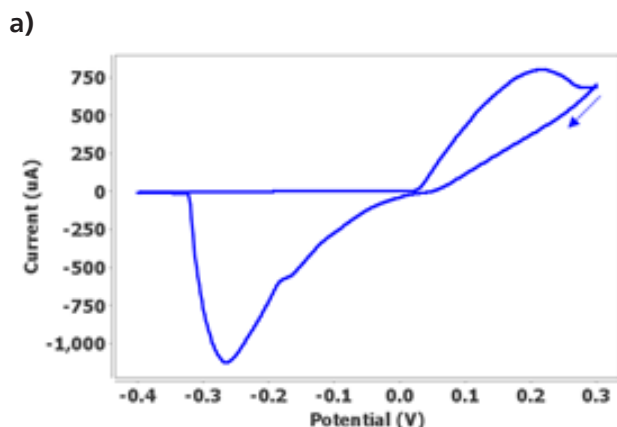

Figure 9. Comparison of the cyclic voltammetry (red line) and evolution of Raman intensity 1041 cm-1(blue line) with potential in the workspace.

a)

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Evolution of Raman intensity shows that, initially, the presence of Rubpy is not detected as the metallic substrate does not show SERS effect. Once SERS substrate is electrochemically generated by reduction of silver surface (cathodic peak at -0.27 in Fig. 9), Raman intensity increases from -0.10 V up to -0.40 V. In the backward scan, intensity remains approximately constant from -0.40 V to +0.03 V. At more positive potentials, Raman intensity decreases due to the oxidation of silver surface takes place. Hence, "Spectra peak height vs EC" tool provides an interesting representation to understand the different processes produced on the electrode surface and allows us to correlate electrochemical and spectroscopic responses.

CONCLUSIONS

DropView SPELEC is a dedicated software not only to perform spectroelectrochemistry, but also for data treatment and analysis. Two interesting tools, "Spectra vs EC" and "Spectra peak height vs EC" are explained in this Application Note, showing that they allows the whole understanding of the electrochemical processes produced on the electrode surface. Furthermore, time-resolved or operando spectroelectrochemistry uses short integration times, and in that way, it enables the calculation of derivative signal. Comparison of electrochemical and optical responses demonstrates that these techniques are fully related.

AUTHORS

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Method: Electrochemistry, Spectroelectrochemistry

Industry: R&D

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