PSAN410-Spectroelectrochemistry

Get more insight into electrochemistry by adding a spectrometer to your potentiostat

The platinum mash changes color by applying a voltage.
What if you could measure the change with a spectrometer?

PalmSens
Compact Electrochemical Interfaces

Last revision: July 5, 2023

www.palmsens.com

Last document update: July 5, 2023

Application Note

1 Introduction

Scientific methods can deliver a lot of information about your molecule, solution, or reaction, however, a single method will only provide a limited amount of information based on a single interaction, for example, light absorption, oxidation at an electrode, change of mobility, or movement of mass in an electric field.
For this reason, scientists try to create hyphenated techniques that allow observing the same system at the same time with multiple techniques. In protein analysis, the combination of liquid chromatography with electron spray-based mass spectroscopy allows the identification of even complex proteins.
Another popular hyphenated technique is spectroelectrochemistry, where electrochemical reactions or products are characterized by electrochemical methods, e.g., cyclic voltammetry (CV), and spectroscopy, e.g. UV-VIS. Electrochemical and optical instruments have in the last decades become more compact and more economical. The information both techniques deliver is complementary as well. For example, an unstable product of electrochemical oxidation can be detected by spectroscopy before it decays.
In this application note first some basic concepts will be introduced before the experiment with a focus on the used equipment and how to operate it will be described. If you want to start with spectroelectrochemistry yourself, you can find at the end a link to our spectroelectrochemical kit, which will get you started quickly.

1.1 Goal

This application note helps you to get started with spectroelectrochemistry and clearly shows what components you need to successfully record a UV-VIS spectrum during CV.

The experiment in this application note shows that a change in potential causes reduction and oxidation of methyl viologen not only by measuring the electric current but also by measuring the change in the transmittance and absorbance of the solution in a cell.

1.2 Potentiostat

An electronic device that controls the potential (or voltage) difference between two electrodes and measures the current between them is called a potentiostat. A three-electrode setup, comprising a working electrode, reference electrode, and counter electrode, is very common. The potential is applied between the working electrode and the reference electrode, while the current is measured between the working electrode and counter electrode. This way the potential of the working electrode is known, while a current is flowing.
The electrodes can be very small like micro-electrodes in a conductive solution or large coated metal coupons in an acidic environment. A potentiostat can be used in the fields of electrochemistry and biochemistry, but also sensor development and battery research.

For more information about a potentiostat, please visit:
https://www.palmsens.com/knowledgebase-article/potentiostat/

1.3 Spectrometer

Optical spectroscopy is a technique that is used to measure light intensity in the ultraviolet (UV), visible (VIS), near-infrared (NIR), and infrared (IR) range of the electromagnetic spectrum. Spectroscopic measurements are used in many different applications, such as color measurement, characterization, or concentration determination of chemical components.

For more information about how a Spectrometer works, please visit:

https://www.avantes.com/support/theoretical-background/introduction-to-spectrometers/

1.4 Cyclic Voltammetry

Cyclic Voltammetry is an electrochemical technique, applied by a potentiostat. During a cyclic voltammogram, the potential is controlled, and the current is measured. The potential is linear increasing or decreasing. The change of the potential per time is the scan rate v. As can be seen from the mathematical definition (see Equation 1) this is the slope of the linear potential.

$$v = \frac{\partial E}{\partial t}$$

Equation 1

At the start, the potential is usually in a region where no electrochemical reaction is occurring. The linear sweep of the potential is usually chosen in such a way that the potential crosses the formal potential of the investigated species (see Figure 1). After reaching a set potential, the slope of the linear potential is inverted, that is a decreasing becomes an increasing potential and vice versa. This potential is called the vertex potential. One cycle is finished when the potential reaches the starting potential again.

It is possible to repeat this process several times. The intention behind multiple cycles is often to observe the stability of a system. Modern software usually offers the option to choose two vertex potentials and a start potential, that is the potential sweeps between the two vertex potentials and starts at a potential between these two.

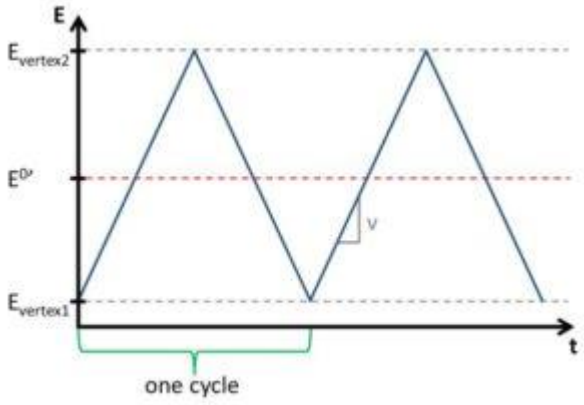

Figure 1: Potential vs time during cyclic voltammetry with indicated vertex potentials (E_{vertex}), the formal potential of the investigated species (E0'), and scan rate (v)

To directly read the potentials corresponding to the peak, usually a voltammogram, a curve of I vs E, is plotted. This way many important parameters can be determined faster than by plotting the E vs t and I vs t on top of each other as in Figure 2. The I vs E curves are very compact and have characteristic shapes. Symmetry is visible more easily. Very symmetric curves are hints to reversible systems, where both species have the same diffusion coefficient.

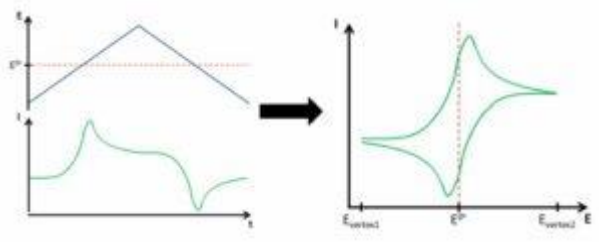

Figure 2: E and I vs t curves in a voltammetric experiment (left) and the resulting voltammogram (I vs E curve)

For more information about Cyclic Voltammetry, please visit:
https://www.palmsens.com/knowledgebase-article/cyclic-voltammetry-introduction/

1.5 Transmittance

To create a UV/VIS spectrum of an object, solution, or gas the light reflected by the sample or transmitted by the sample can be utilized.
If the object or material you want to measure is more transparent, for instance, a filter, glass, or fluid, the amount of reflected light is too low to perform a reflection measurement. For (mostly) transparent materials, transmission spectroscopy is the best choice, since it measures the light that passes through the material I_{trans} in comparison to the emitted light I_0, instead of light reflecting from it. The ratio is known as transmittance T:

$$T = \frac{I_{trans}}{I_0}$$

Equation 2

For more information, please visit:
https://www.avantes.com/applications/measurement-techniques/transmission/

1.6 Absorbance

The absorbance A (also called optical density) of a material is a logarithmic ratio of the light falling upon a material I_0, to the light transmitted through a material I_{trans}:

$$A = \log_{10} \frac{I_0}{I_{trans}}$$

Equation 3

UV/VIS absorbance measurements encompass a wide variety of chemical and biochemical applications which involve many areas of research and industrial end uses. UV/VIS absorbance can be applied qualitatively and quantitatively in spectroscopic measurement applications ranging from blood parameters to chemical concentrations in process and reaction monitoring.

For more information, please visit:
https://www.avantes.com/applications/measurement-techniques/absorbance/

2 Equipment

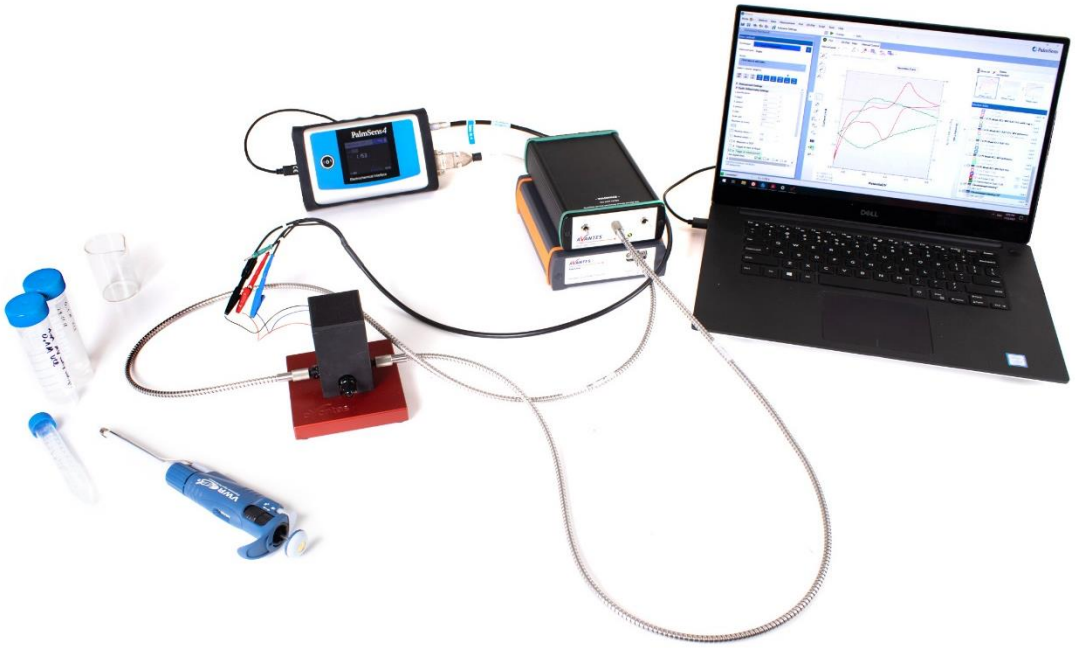

Figure 3: Spectroelectrochemistry setup.

The following equipment was used

1.	Potentiostat	PalmSens4
2.	Electrochemical Cell	ItalSens K003 with wires soldered to the electrodes
3.	Cable	Custom cable to connect the potentiostat and the spectrometer
4.	Spectrometer	AvaSpec-ULS2048CL-evo
5.	Light source	AvaLight-DHc
6.	Fibers	2xd FC-UVIR600-1
7.	Cuvette holder	CUV-UV/VIS
8.	Laptop	With PSTrace and Avasoft

The experiment has a window of interest between 200 and 650 nm with great interest around 600 nm. The light source and the spectrometer are required to generate and measure a spectrum in this window.

2.1 Solutions and Chemicals

- 0.1 M KCl
- 1 mmol/L methyl viologen (MV^{2+}) in 0.1 M KCl

2.2 Software Setup and Settings

- The potentiostat was controlled by PSTrace 5.9. It is available for download at My.palmsens.com.
- The spectrometer was controlled by Avasoft 8.11. It is available for download at Avantes.com.

2.2.1 PSTrace settings

To send a trigger signal from PSTrace:

1. Enable AUX input, so the analog input can be used to receive information from the spectrometer
2. Set CV settings, to perform the measurement
3. Check the box to send a trigger from digital output D0 at the start of a measurement

Before enabling the Aux. input, you have the option to name and convert the AUX inputs voltage into a linear correlating signal. To do that open the top menu *Tools – General settings…* Click on Change aux, which opens the *Auxiliary output options*. Click on *Add* and configure the aux input as you like. The Offset and Slope are the y-axes intersection and slope of the linear function to convert the voltage into a signal. During this experiment, the settings visible in Figure 4 were applied. Click on Save to add the setting to your dropdown list for the Aux. input. The *Calibrate* button in the general settings allows you to perform a 2-point calibration for your auxiliary input.
If you check the box *Show AUX idle reading in status bar*, your AUX signal will be visible at the bottom of the PSTrace window, even when no measurement is running.

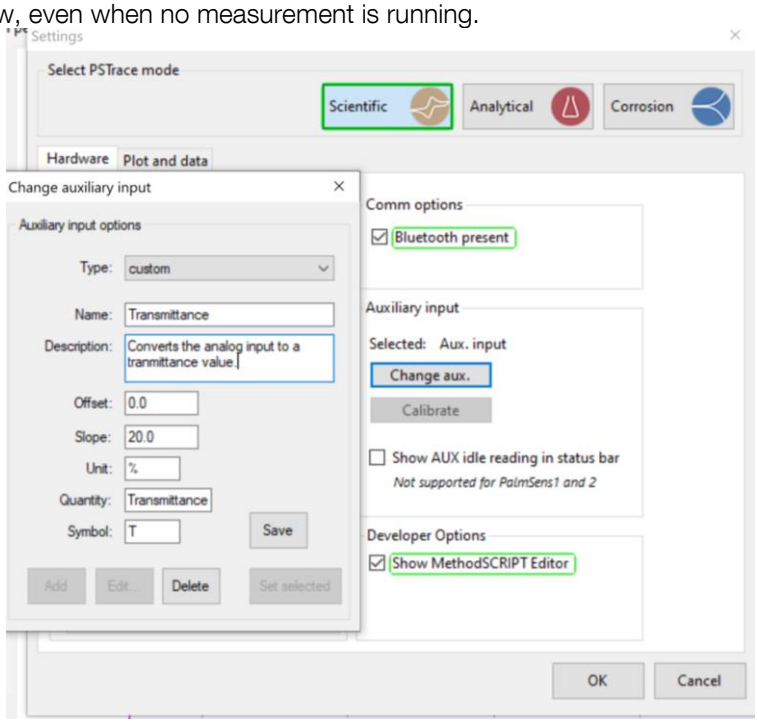

Figure 4: Create a custom transmittance input from the analog input. Set 20% of transmittance per volt, 5V will be converted 100% transmittance.

To record the Aux. input during the measurement, check in the method editor the box Record Aux. input in the segment *Record additional data* (see Figure 6). The method editor is the section of PSTrace where you set your techniques parameters

In this application note, the oxidation and reduction of methyl viologen should be triggered, so Cyclic Voltammetry (CV) is used as a technique. You can set the parameters according to Figure 5 or load the PSmethod file "*CV_PT_Mash_KCL_MV_10mvs.psmethod*". You can download an example method file at Palmsens.com/spectro and load it by choosing in the top menu *Method – Load*. As an alternative, you can set the parameters manually using Figure 5.

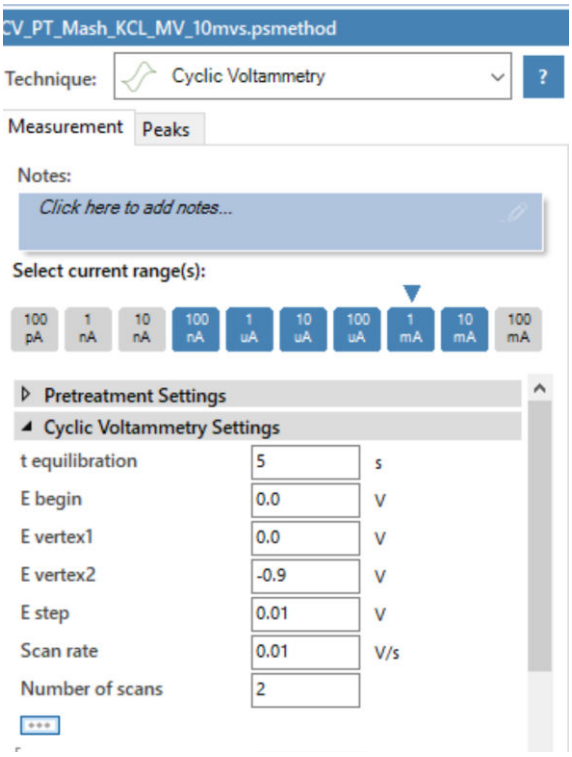

Figure 5: PSTrace CV settings

To synchronize the start of the CV and the start of recording the spectra a trigger must be sent to the spectrometer. Click on the …-button in the method editor and check *Trigger at measurement* as well as *d0* (see Figure 6).

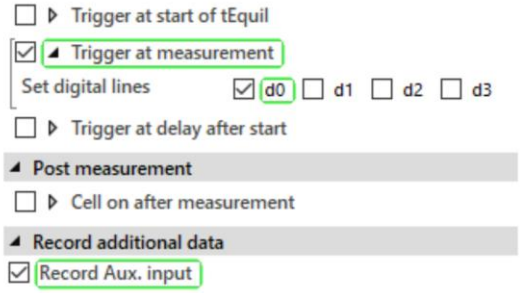

Figure 6: PSTrace trigger and AUX input settings.

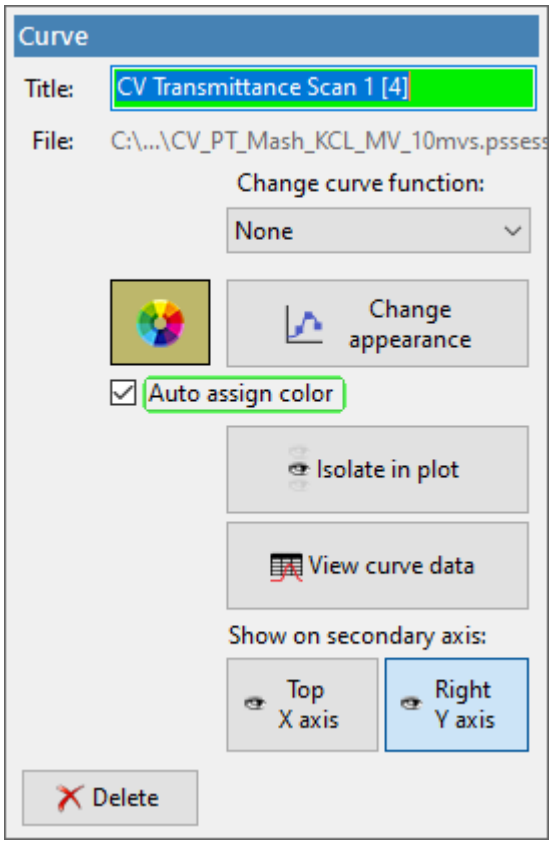

Figure 7: The analog input can be plotted on the Y-axis by pressing "Right Y-axis".

2.2.2 Avasoft settings

Setting the integration time and averaging to starting values

To set up Avasoft, you first need to connect your instrument. You will have to set two parameters on the left side of the main screen:

- Set the integration time to 4000, by clicking on the number after “integration time”.
- Set the Averaging to 10, so you will reduce the noise in your measurement. Click on the number after “averaging”.

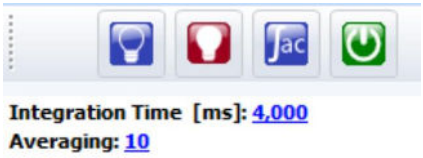

Figure 8: The integration time is set such, that the spectrometer almost clips. The result is averaged with 10 measurements to reduce noise.

Optimizing the integration time to avoid clipping

To set the integration time and averaging set your spectrometer to continuous mode, see Figure 9 and press start. You will see the result of the measurement as in Figure 10. If your measurement at a certain wavelength is touching the maximum amount of counts (65.536), the result is clipping. Clipping reduces your accuracy at the wavelength where it is clipping. Clipping can be avoided by reducing the integration time. Set it such, that there is no clipping visible in the spectrometer measurement.

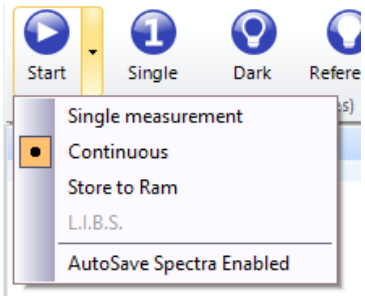

Figure 9: Set continuous mode in Avasoft

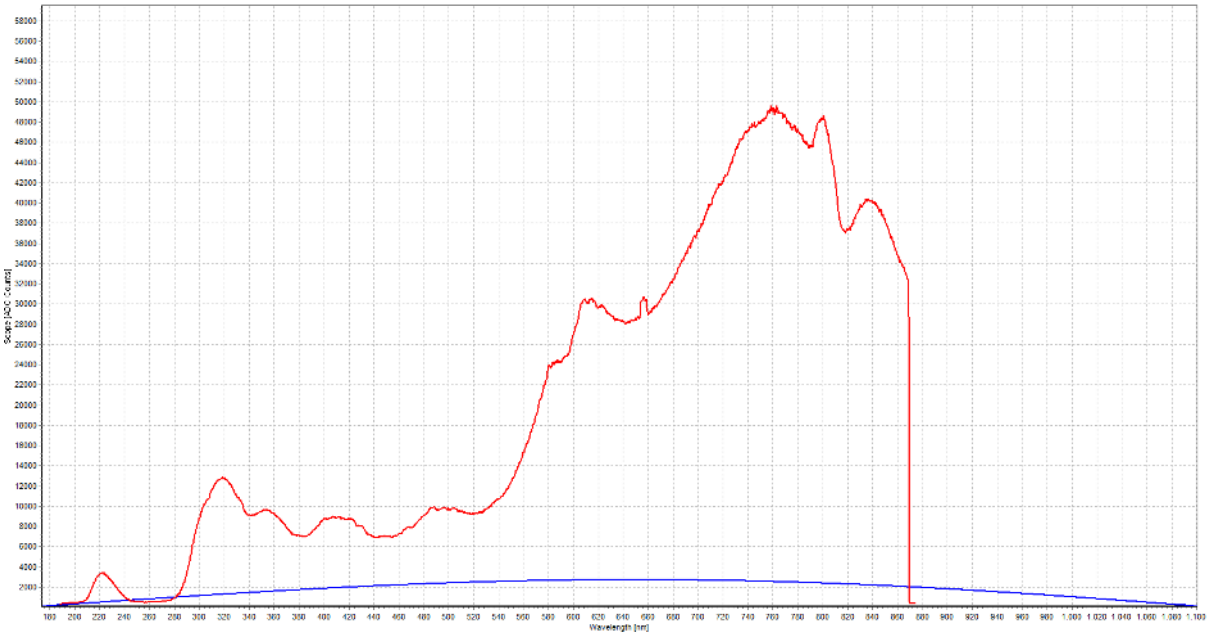

Figure 10: example of a spectrometer measurement.

Set External trigger

Next up is setting the external trigger, so the potentiostat can trigger the spectrometer. The external trigger can be enabled in the Global options, see Figure 11. If you enable the external trigger, the potentiostat can trigger the spectrometer. When a measurement is started the spectrometer will wait until it receives the trigger and then start recording.

You can also define how many scans are performed when the trigger is received. In this application, the spectrometers scan should last the whole CV. Each scan takes in the current setup 4 ms * 10 = 40 ms. If your total measurement takes for example 6 minutes, you will need 6*60/(40x0.001) = 9.000 scans per trigger. Please note: Don't change the trigger settings during a scan, to avoid unexpected results from the software.

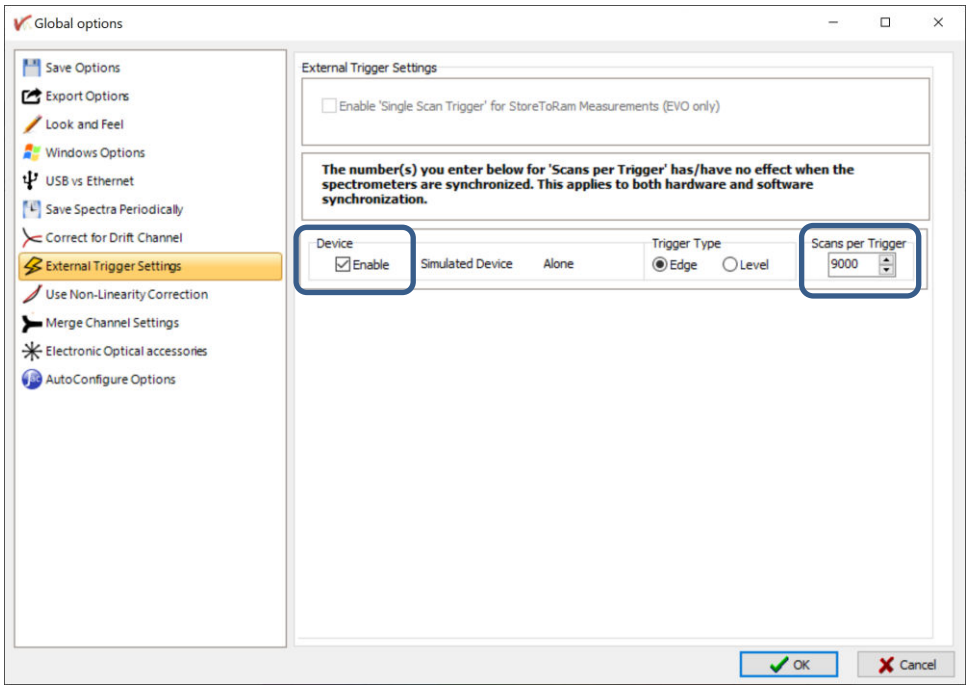

Figure 11: Global options

Set transmittance at 600nm at analog output port of spectrometer

To measure the transmittance in PSTrace, we need a signal that converts 100% transmittance at 600 nm to an analog signal of 5 V. Avasoft can convert the transmittance to an analog signal, using the Timeseries. In Avasoft create an output function which is an integral, and as parameters the values indicated in Figure 12.

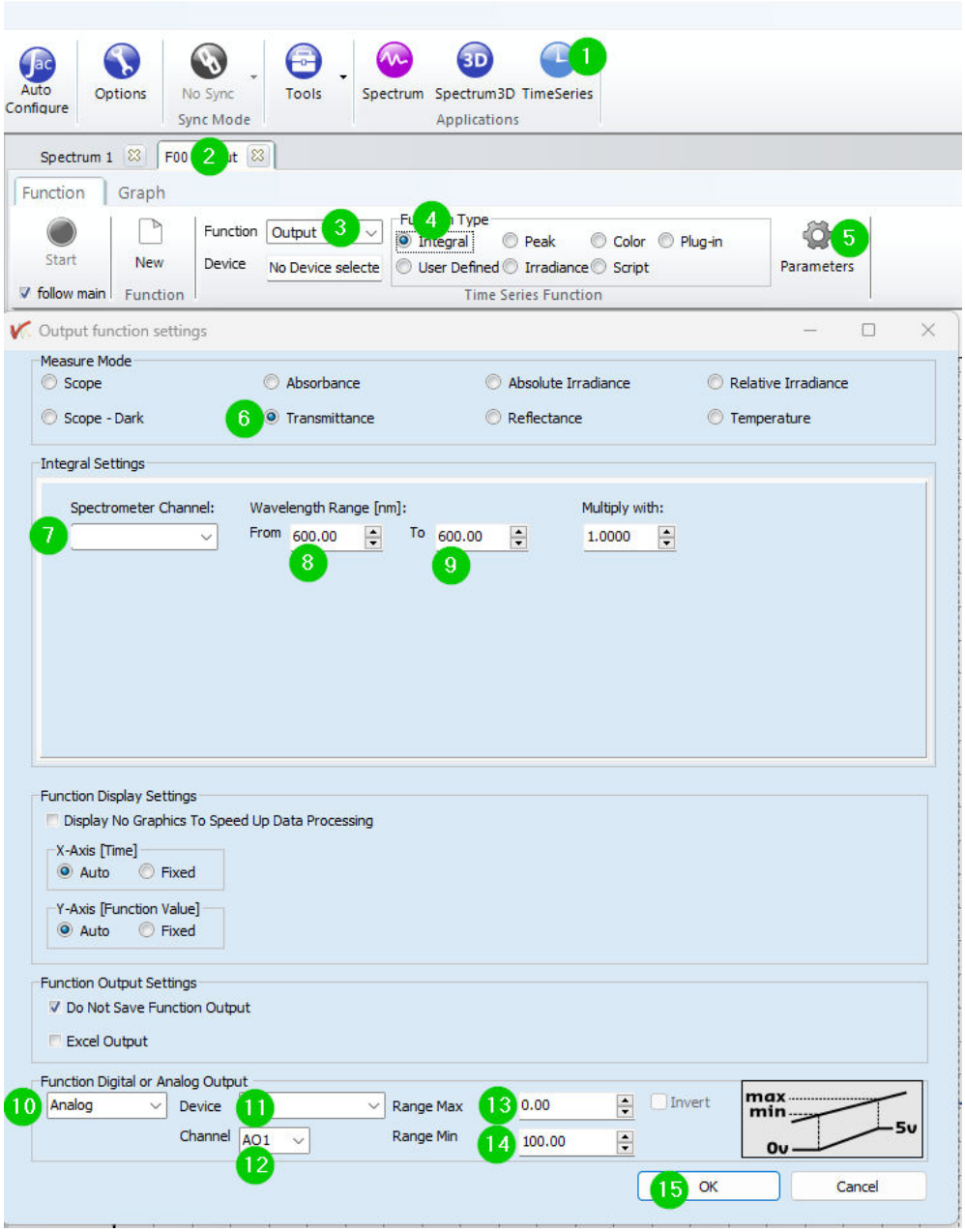

Figure 12: Set analog output of spectrometer, as the transmittance at 600 nm, where 5 V is 100% transmittance.

2.3 Hazards

Methyl viologen dichloride hydrate has acute oral toxicity and is toxic by inhalation and irritation to the skin.

2.3.1 Methyl Viologen

Methyl Viologen (MV) is also known as paraquat. It is used as a herbicide, but due to its toxicity for humans and scientific studies showing links between methyl viologen and Parkinson's disease it has lost popularity. Methyl viologen's toxicity is based on its RedOX chemistry. The reduction of the colorless ion MV^{2+} leads to the blue radical ion MV^{+} (see Figure 13).

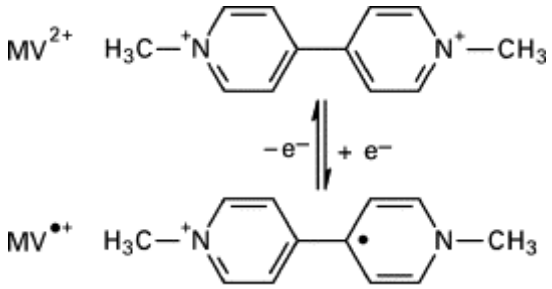

Figure 13: MV^{2+} ↔ MV^{+}

This oxidation can be triggered electrochemically at a platinum electrode. As mentioned above MV^{2+} is colorless while MV^{+} is blue and accordingly is absorbing in the visual spectrum. Thus MV^{+} can be produced by electrochemical methods while being detected by UV/VIS spectroscopy. These spectroelectrochemical measurements could be applied to measure the kinetics of the oxidation, for example.

2.4 Performing the Measurement

2.4.1 Setup

First connect the light source to the electrochemical cell using the optic fiber, the cell to the spectrometer with another optic fiber, and the spectrometer to the potentiostat using the cable mentioned in Appendix 0. See Figure 3 for a view of the complete setup.

2.4.2 Dark measurement

Turn on the spectrometer and turn off the light source. Make sure to cover the electrochemical cell and perform a dark measurement. This will be stored in the spectrometer and subtracted from future measurements. In Avasoft you can perform a dark measurement by running a single measurement, and then pressing the "save dark measurement" button, as depicted in Figure 14.

Figure 14: Icon to save a dark measurement.

2.4.3 Reference measurement KCl

Fill the cuvette of the electrochemical cell with the KCl solution. Insert the three electrodes into the cap and put the cap on the cuvette. The platinum wire CE and the platinum mesh working electrode must not touch. Turn on the light source, wait 10 minutes and perform a reference measurement by clicking on the red bulb

in Avasoft, as depicted in Figure 15. This measurement defines the I_0 for the setup and thus is needed to calculate the Absorbance and Transmittance (see Equation 2 and Equation 3).

Figure 15: icon to perform a reference measurement.

2.4.4 Cyclic Voltammogram and Transmission of Methyl Viologen

In this segment, we will describe how to record a CV while recording the transmittance for a single frequency. This requires the knowledge of a suitable wavelength where ideally either the oxidized or the reduced form of the characterized species is absorbing.
Such a wavelength can be found in literature as well as databases or it must be determined by measurements. The latter is described for methyl viologen in appendix 4.1.
MV^+ will absorb light with 600 nm, which is in the yellow spectrum. Removing 600 nm from a white spectrum, let the light appear blue. MV^{2+} is colorless and does not absorb at 600 nm. We have determined the wavelength for the MV measurement by measuring a spectrum of the MV^{2+} and a spectrum when -0.85 V was applied to produce MV^+. More details are available in appendix 4.1.
The cuvette is filled with 1 mM MV in 0.1 M KCl.
Open PSTrace and connect the PalmSens4. Select from the list of techniques Cyclic Voltammetry and set the parameters according to Table 1.

Table 1 Parameters for CV

t equilibration	5
E begin	0 V
E vertex 1	0 V
E vertex 2	-0.9 V
E step	0.01 V
Scan rate	0.01 V/s
Number of Scans	1

Open the additional options by clicking the …-button. Check the box for *Trigger at measurement* and *d0* as described in chapter 2.2.1.
After you set the spectrometer to start the measurement at a trigger (see chapter 2.2.2) press the run button in PSTrace.

Scan rate
The scan rate influences greatly the measurement duration. Choosing a high scan rate will decrease your measurement time, but it might give the reaction insufficient time to complete. A step size of 0.01 V/s allows the MV^{2+} reduction to take place.

2.4.5 3D Graph of full Spectrums

With the described instruments and software, it is also possible to record at multiple points of a CV a full UV/VIS spectrum. The result of such a measurement is a CV and a series of spectra. Usually, these are

plotted in a 3D plot vs wavelength and time or potential on the other axis. More information is available in appendix 4.2.

2.5 Results

Figure 16 shows the result of the measurement described in chapter 2.4.4. A decrease of transmittance is visible starting at around -700 mV, which is a result of the MV^{2+} reduction to MV^{+} and is also visible in the CV as a small peak. From -0.7 V to 0 V the transmittance increases again because MV^{+} is oxidized.

Combining electrochemistry and spectroelectrochemistry results in more insights and a better understanding into the oxidation and reduction processes.

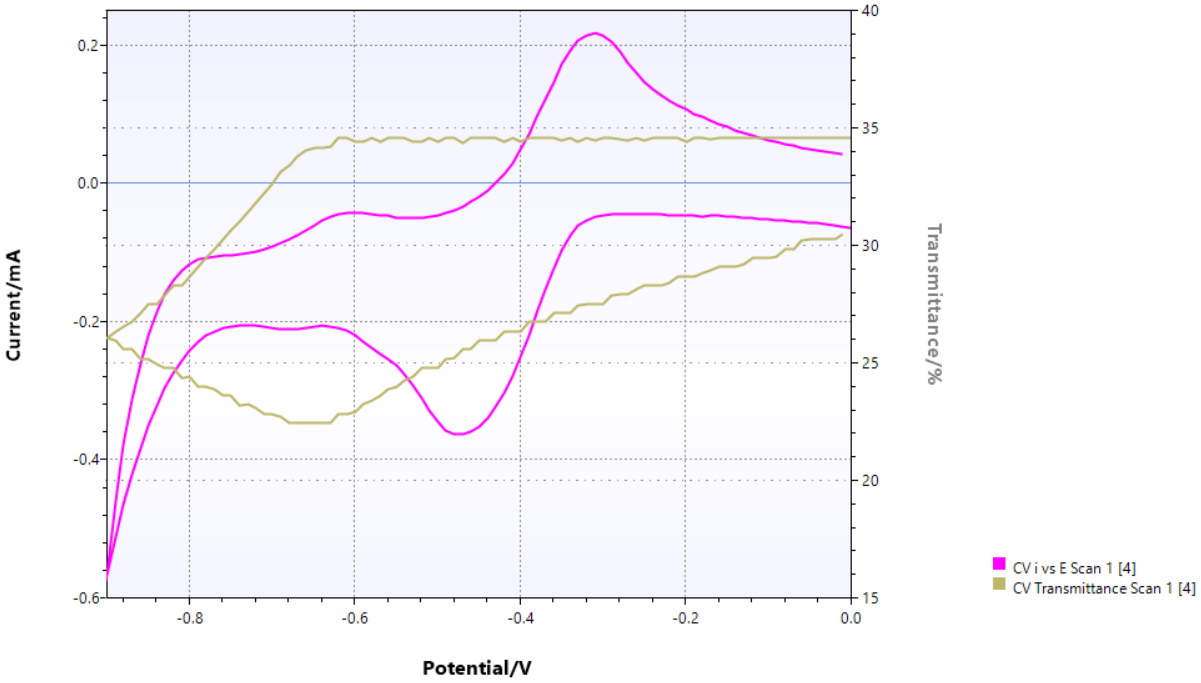

Figure 16: Shown is one CV scan (pink, scan rate 0.01 V/s) of 1 mM MV solution in 0.1 M KCl. The transmittance in percentage (ecru) while performing the scan is plotted on the second Y-axis.

3 Order Spectroelectrochemistry Starter Kit

If you are interested in performing Spectro-electrochemistry using PalmSens instruments, please contact us for the Starter kit.

The Starter kit includes:

1. Potentiostat — PalmSens4
2. Electrochemical Cell — ItalSens K003 with wires soldered to the electrodes
3. Cable — Custom cable to connect the potentiostat and the spectrometer

We have partnered with Avantes to offer you:

4. Spectrometer — AvaSpec-ULS2048CL-evo
5. Light source — AvaLight-DHc
6. Fibers — 2xd FC-UVIR600-1
7. Cuvette holder — CUV-UV/VIS

Or visit Palmsens.com/spectro

Visit Palmsens.com/spectro for the starter kit

4 Appendix

4.1 Full UV/VIS Spectrum of MV^{2+} and MV^{+}

4.1.1 Absorbance measurement during chronoamperometry

Under the influence of a voltage, MV will absorb 600 nm, which is in the yellow spectrum. Removing 600 nm from a white spectrum, makes the MV appear blue. For more details see chapter 2.3.1. PSTrace can set a voltage on the cell using the technique chronoamperometry, see *Figure 17*.

1. First, record the spectrum using Avasoft without applying any potential. This is the spectrum of MV^{2+}.
2. Set the voltage to -0.85 V and record a spectrum after 30 seconds.
3. Wait 30 more seconds and record a third spectrum.

The last two spectra include MV^{+} in an increasing concentration. The visible changes are due to the different absorption of MV^{2+} and MV^{+}.

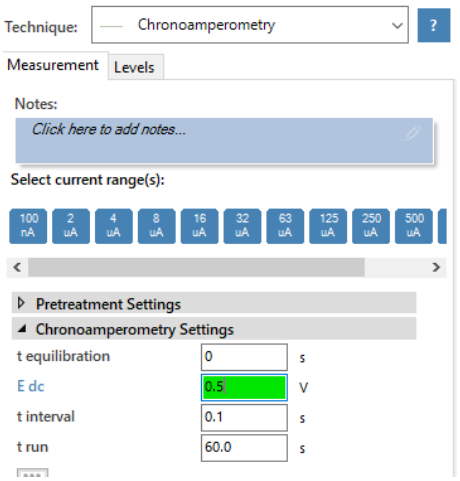

Figure 17: Set chronoamperometry 0.5 V in PSTrace.

Figure 18 shows the three spectra recorded according to the procedure described above. Around 390 and 600 nm, the absorbance is increasing, while at 200 nm the absorbance is decreasing with increasing MV^{+} concentration.

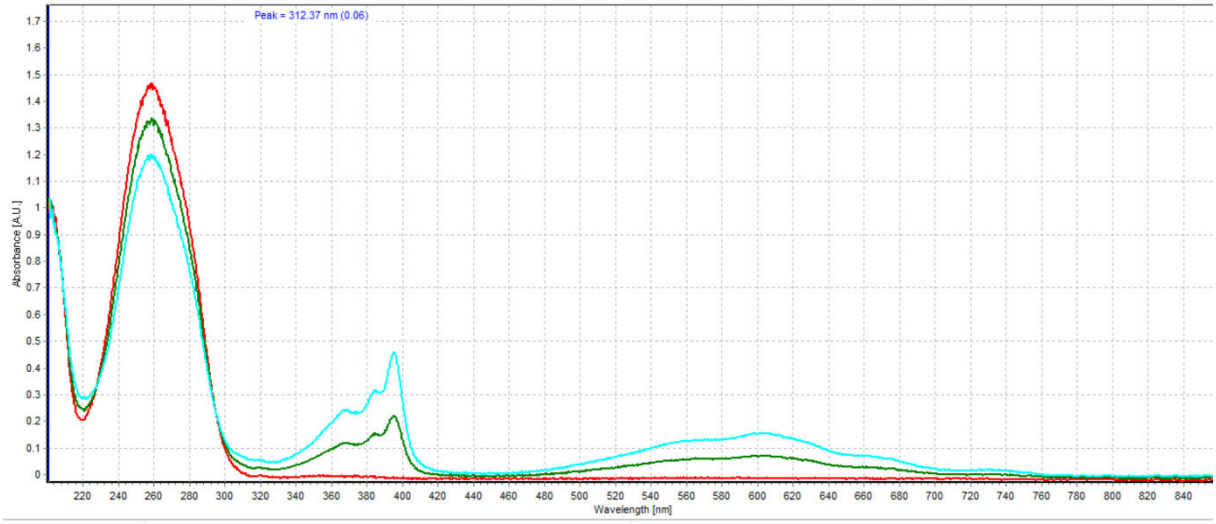

Figure 18: Spectra of methyl viologen without potential control (MV2+, red) and at -0.85 V for 30 seconds (MV^{+}, green), and 60 seconds (MV^{+}, turquoise).

4.2 2D transmittance and 3D absorption graph

In Figure 19 two cycles of a CV as described in chapters 2.4.4 and 2.5 are shown. During these CVs, not only the transmission of a single wavelength but full spectra were recorded every 4 s. The spectra were plotted versus a running number, which correlated with the measurement time and thus the applied potential (see Figure 20). An increased absorbance at around 390 nm and 600 nm can be observed two times, showing a clear correlation with the two CV scans. Figure 21 shows how to create a 3D figure of recorded spectra.

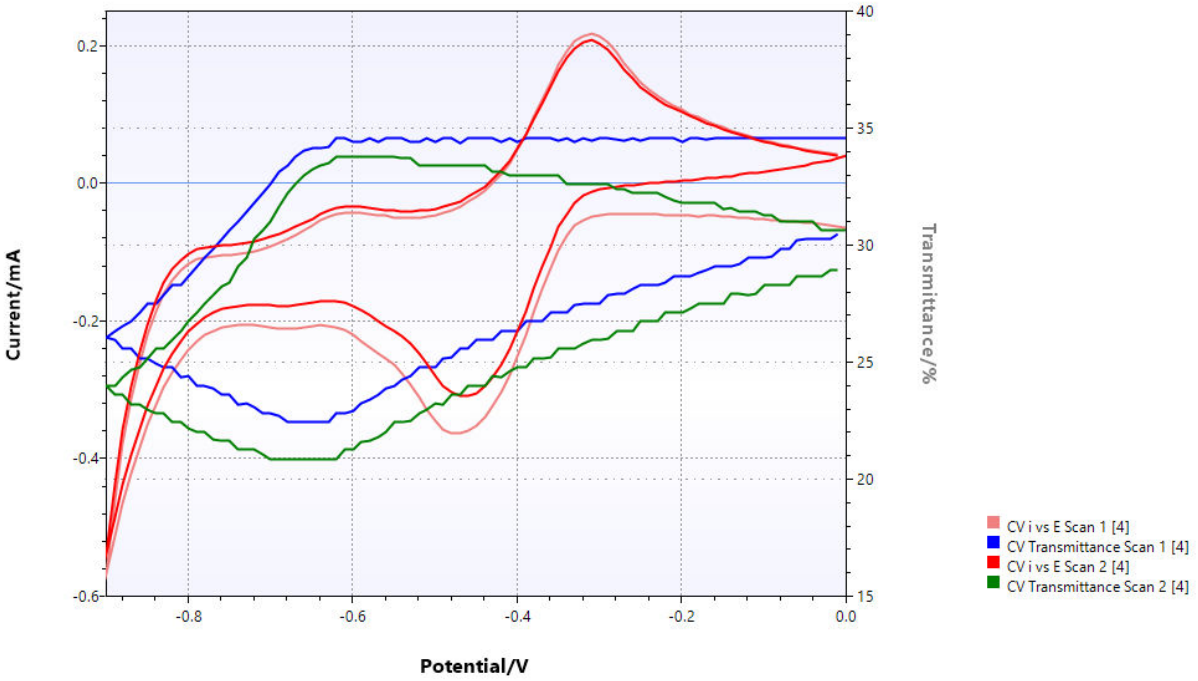

Figure 19: Two CV scans (red, pink) with a scan rate of 0.01 V/s of 1 mM MV in 0.1 m KCl. This graph shows the transmittance in percentage (blue and green) while performing the scan.

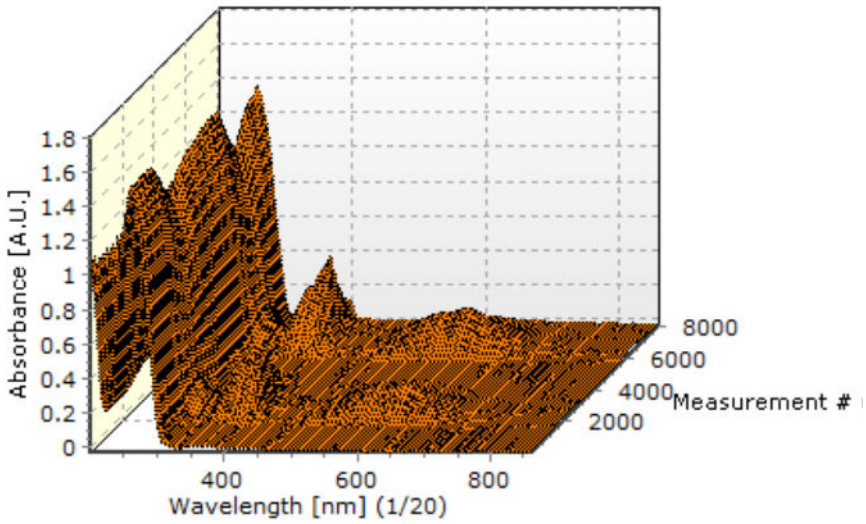

Figure 20:Full UV/VIS spectra recording during CVs from Figure 19

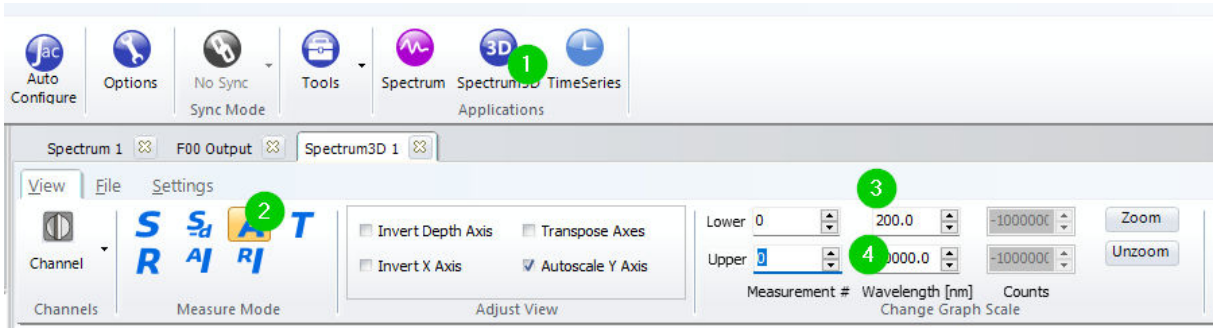

Figure 21: Set 3D spectrum in Avasoft

5 Appendix: Cable to connect the Spectrometer to the Potentiostat

The Spectroelectrochemistry Starter Kit includes a custom-made cable for the connection between the potentiostat's auxiliary port and the spectrometer's auxiliary port. This connection enables two features:

1. The PalmSens4 potentiostat can trigger the Avantes spectrometer.
2. The spectrometer can return any result via the analog output to the analog input of the potentiostat.

PSTrace allows setting a digital output to *high* at the start of a measurement. This allows triggering of the spectrometer via the Avasoft software. Avasoft allows for custom results to be applied as a potential on its analog output, which can be directly fed to PSTrace. This way PSTrace can conveniently show both the results of the spectrometer and the potentiostat in one window.

Table 2: pin connection per function.

Function	Pin PalmSens4 AUX port DSUB15	Pin Avantes AUX port DSUB26
GND	10	1
Trigger	1	6
GND	14	14
Analog signal	3	17

Cable included

The cable to connect the spectrometer to the potentiostat is included in the PalmSens spectroelectrochemistry package