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?

Last revision: March, 2025

www.palmsens.com

Last document update: March, 2025

Application Note

Contents

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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 provides a step-by-step guide to getting started with a spectroelectrochemistry bundle of a PalmSens potentiostat along with an Avantes spectrometer, ensuring you can successfully record spectroscopic data during an electrochemical experiment.
First, we demonstrate how to obtain a single-wavelength transmittance signal during a Cyclic Voltammetry (CV) experiment. The experiment illustrates the reduction and oxidation of Methyl Viologen by measuring both the electric current and the transmittance changes in the solution within the electrochemical cell.
Next, we show how to acquire full spectral data, also enabling the construction of a 3D plot that visualizes spectral changes over the course of the CV experiment.

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.

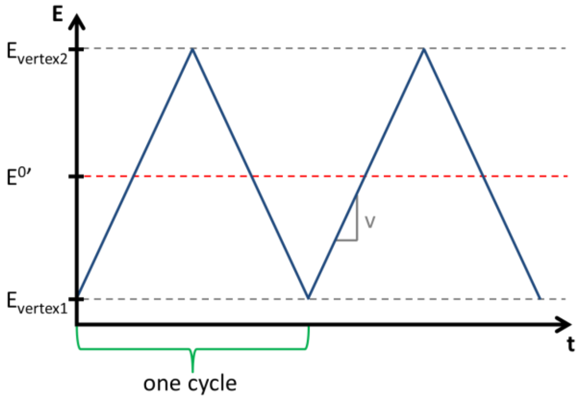


Figure 1 Potential vs time during cyclic voltammetry with indicated vertex potentials (E_{vertex}), the formal potential of the investigated species ($E^{0'}$), and scan rate (v)

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.

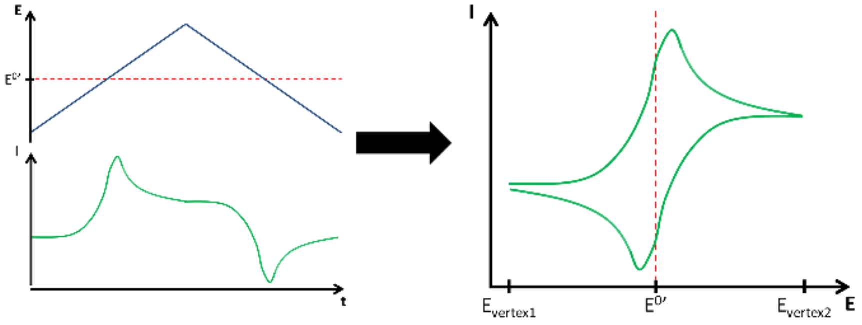


Figure 2 E and I vs t curves in a voltammetric experiment (left) and the resulting voltammogram (I vs E curve)

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 Experimental Section and Result Examples

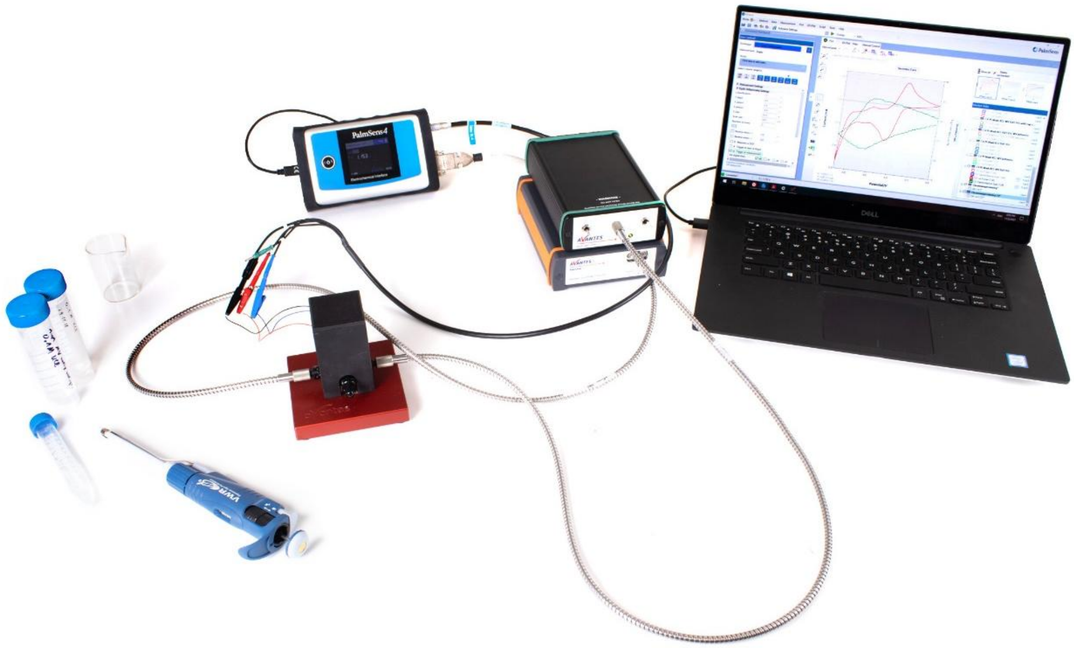


Figure 3: Spectroelectrochemistry setup

This section provides a detailed description of the experimental setup, step-by-step procedures, and examples of results obtained from spectroelectrochemical experiments. It covers the necessary instrumentation, software configurations, and key parameters to ensure accurate and reproducible measurements. The results illustrate how electrochemical and spectroscopic data complement each other, providing deeper insights into redox reactions.
The Spectroelectrochemical experiments require the following equipment:

Potentiostat	PalmSens4, EmStat4X or Nexus
Electrochemical Cell	ItalSens K300 with wires soldered to the electrodes
Special Cable	Custom cable to connect a PalmSens potentiostat via the auxiliary DSUB15 port to an Avantes spectrometer via the DSUB26 port
Spectrometer	AvaSpec-ULS2048CL-EVO or Varius series
Light source	AvaLight-DHc
Fibers	2xd FC-UVIR600-1
Cuvette holder	CUV-UV/VIS
Laptop	Windows 11 with Microsoft Excel, PSTrace and AvaSoft
Miscellaneous chemistry	Pipettes, vials, glassware, wash bottle, etc.

The experiment has a wavelength window of interest between 380 and 780 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

- $KCl_{(aq)}$ 0.1 mol/L
- $KCl_{(aq)}$ 3 mol/L (filling solution for Reference Electrode)
- 1 mmol/L Methyl Viologen (MV^{2+}) in KCl 0.1 mol/L (aqueous)

2.2 Safety Notice

Methyl viologen dichloride hydrate is acutely toxic if ingested, harmful if inhaled, and can cause skin irritation. This application note is intended for use by trained chemists or related professionals who are familiar with handling hazardous substances. If you lack experience with such chemicals, seek assistance from a qualified professional before proceeding.

PalmSens BV assumes no responsibility for accidents, injuries, or damage resulting from the improper handling or misuse of chemicals. Users are responsible for ensuring safe laboratory practices and compliance with local safety regulations.

2.2.1 Methyl Viologen

Methyl Viologen (MV) is also known as paraquat. It was widely 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 4).

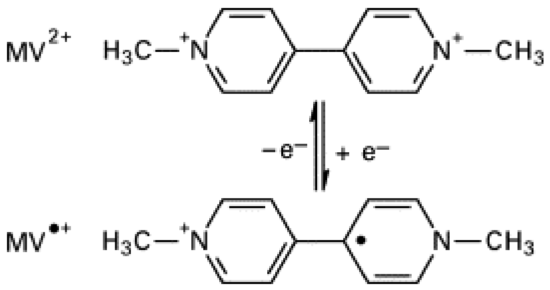


Figure 4: Redox reaction of the Methyl Viologen $MV^{2+} \leftrightarrow MV^{+}$

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 visible spectrum. Thus MV^{+} can be produced by electrochemical methods while being detected by UV/Vis spectroscopy. This kind of spectroelectrochemical measurement could be applied to measure the kinetics of the oxidation, for example.

2.3 Common Software Settings

This section outlines the essential software configurations required for conducting this spectroelectrochemical experiment.

- The potentiostat is controlled by PSTrace 5.12. It is available to download at myps.palmsens.com.
- The spectrometer is controlled by AvaSoft 8.16.1.0. It is available to download at Avantes.com.
- Later versions can be compatible, until further notice.

2.3.1 AvaSoft Settings

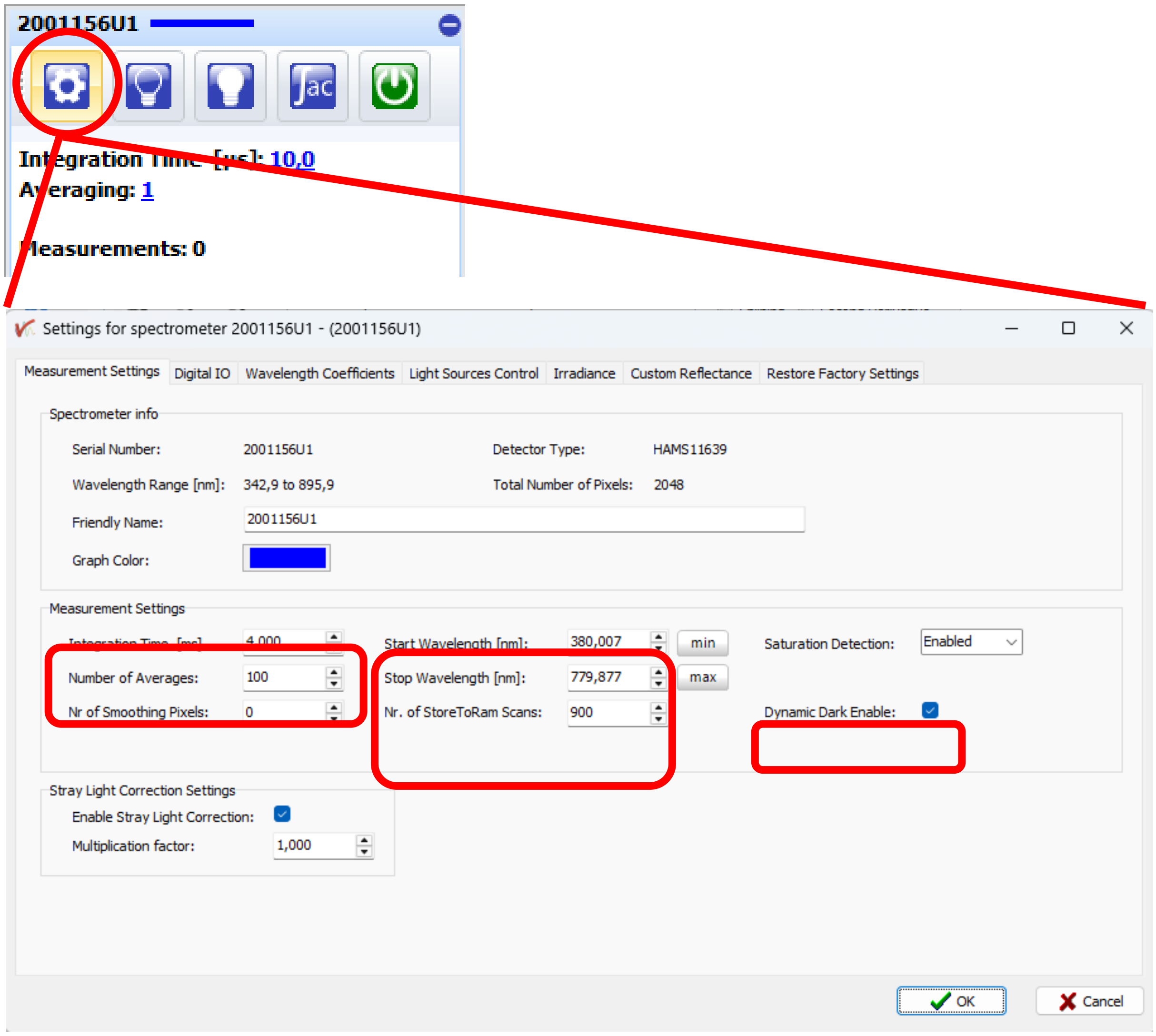
2.3.1.1 Setting Up Spectrometer Parameters in AvaSoft

To set up AvaSoft, start by connecting your spectrometer. Avantes EVO and Varius models do not require an external power supply, as they can be powered directly via a USB port. The light source does not require a communication connection for this experiment—simply connect it to the provided DC power adapter to power it on. For light sources with multiple lamps, consider that only the Halogen (H) lamp is needed.

For your convenience, **turn on your light source as soon as possible**, as it requires a pre-warming period to stabilize its output.

After connecting the spectrometer, you need to configure a few parameters. Click on the **gear icon** on the left side of the screen to access the spectrometer settings and adjust the following (see Figure 5):

- **Integration Time**: Set to **4 ms**. This value is optimized for a 1 cm cuvette containing a transparent aqueous solution but may need adjustments depending on the optical path.
- **Number of Averages**: Set to **100**. A higher number reduces noise but decreases the number of acquired data points. With the 4 ms integration time, this results in one spectrum every 400 ms.
- **Start Wavelength**: Set to **380 nm**.
- **Stop Wavelength**: Set to **780 nm**. This defines the wavelength window, ensuring that only relevant data is acquired, avoiding unnecessary information.
- **Number of StoreToRam Scans**: Set to **900**. This parameter is used for 3D plots. With the selected settings, this means 900 scans × 400 ms per scan, resulting in a total duration of 360 s (6 minutes)—matching the duration of a full CV experiment.
- **Dynamic Dark Enable**: **Checked**. This optimizes the dark spectrum for better measurement accuracy, especially regarding temperature variation. Refer to the Avantes manual for further information.
- If you are unsure about the other settings, go to the tab *Restore Factory Settings* and proceed to reset everything and start over.



2001156U1
Integration Time [µs]: 10,0
Averaging: 1
Measurements: 0

Settings for spectrometer 2001156U1 - (2001156U1)

Spectrometer info

Serial Number: 2001156U1
Detector Type: HAMS11639
Wavelength Range [nm]: 342,9 to 895,9
Total Number of Pixels: 2048
Friendly Name: 2001156U1
Graph Color: 🟦

Measurement Settings

Integration Time [ms]: 4,000
Number of Averages: 100
Nr of Smoothing Pixels: 0
Start Wavelength [nm]: 380,007
Stop Wavelength [nm]: 779,877
Nr. of StoreToRam Scans: 900
Saturation Detection: Enabled
Dynamic Dark Enable: ☑

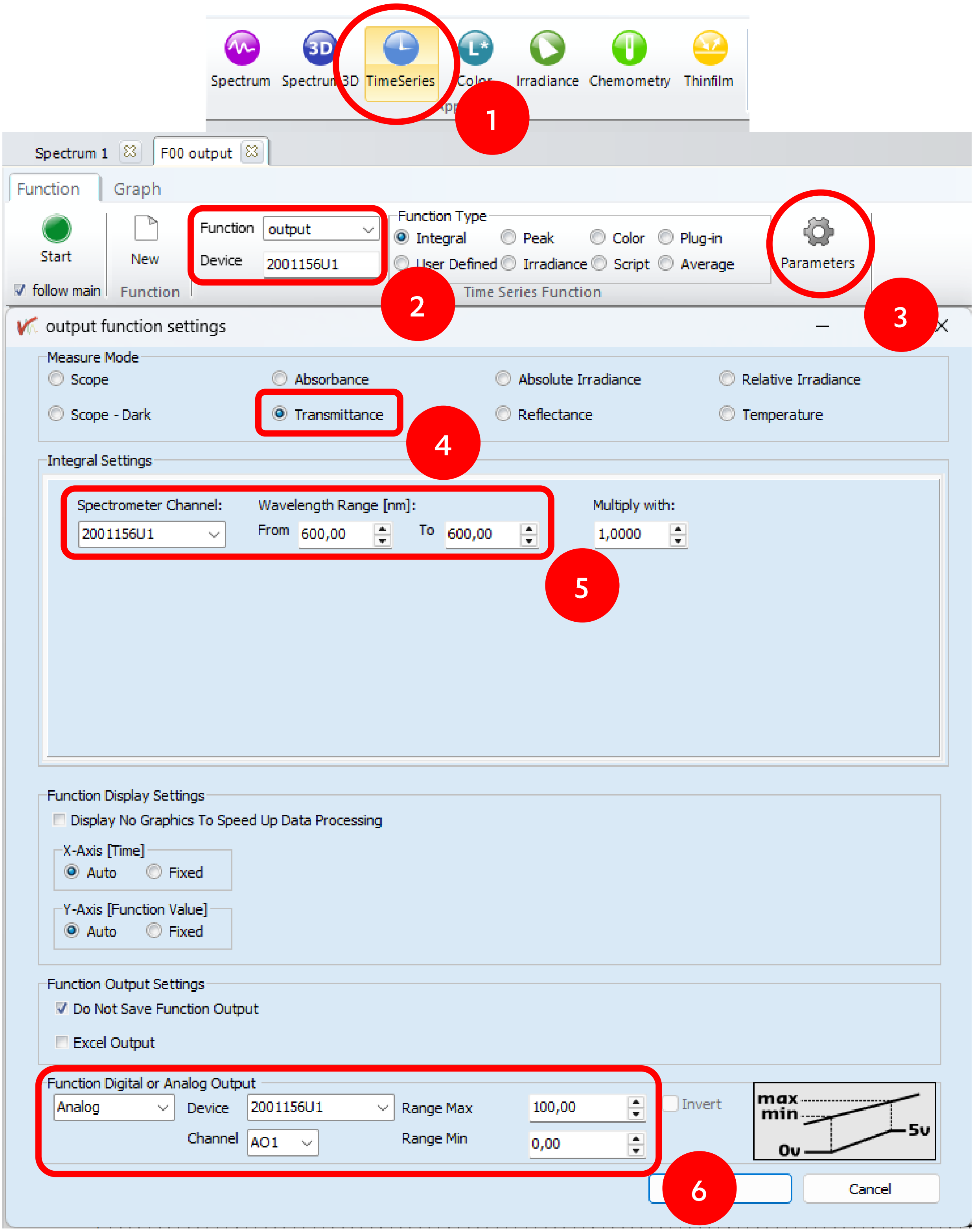
Stray Light Correction Settings

Enable Stray Light Correction: ☑
Multiplication factor: 1,000

Figure 5: Optimal settings for the Avantes spectrometer when used with the ItalSens K300 and a transparent aqueous solution as sample.

2.3.1.2 Set transmittance at 600 nm 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 voltage signal, using the *TimeSeries*. In the *TimeSeries* tab you can define an output function. In Figure 6 the parameters for the output function used for this experiment are shown. Once you have finished the settings click on *OK*. The *Spectrometer Channel* field will display the name of your connected spectrometer (its serial number by default).



Function: output
Device: 2001156U1

Function Type: ● Integral ○ Peak ○ Color ○ Plug-in ○ User Defined ○ Irradiance ○ Script ○ Average

output function settings

Measure Mode: ○ Scope ○ Absorbance ○ Absolute Irradiance ○ Relative Irradiance ○ Scope - Dark ● Transmittance ○ Reflectance ○ Temperature

Integral Settings
Spectrometer Channel: 2001156U1
Wavelength Range [nm]: From 600,00 To 600,00
Multiply with: 1,0000

Function Display Settings
☐ Display No Graphics To Speed Up Data Processing
X-Axis [Time]: ● Auto ○ Fixed
Y-Axis [Function Value]: ● Auto ○ Fixed

Function Output Settings
☑ Do Not Save Function Output
☐ Excel Output

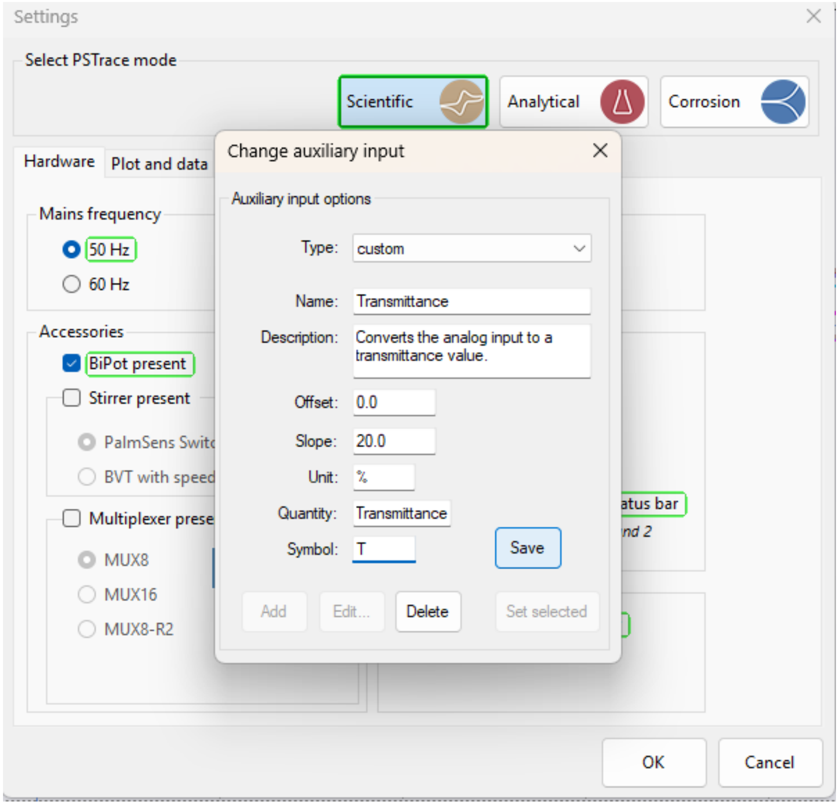
Function Digital or Analog Output
Analog
Device: 2001156U1
Channel: AO1
Range Max: 100,00
Range Min: 0,00
☐ Invert

Figure 6: Setting to output the analog signal of spectrometer as the measured transmittance at 600 nm, where 5 V is 100 % transmittance.

The spectrometer continuously outputs a transmittance signal as an analog voltage during continuous measurements. Since the spectrometer passively measures the spectral signal in real time, triggering is not required for this process. However, in specific modes such as *StoreToRam*, the transmittance signal will not be output.

2.3.2 PSTrace Settings

A PalmSens potentiostat equipped with auxiliary port continuously read a voltage signal coming from pin 3 *vs.* pin 14 (ground) of the AUX port. Refer to the PSTrace manual for details about the auxiliary port pin-out.
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 input 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 7 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. It is not necessary for spectroelectrochemical experiments.



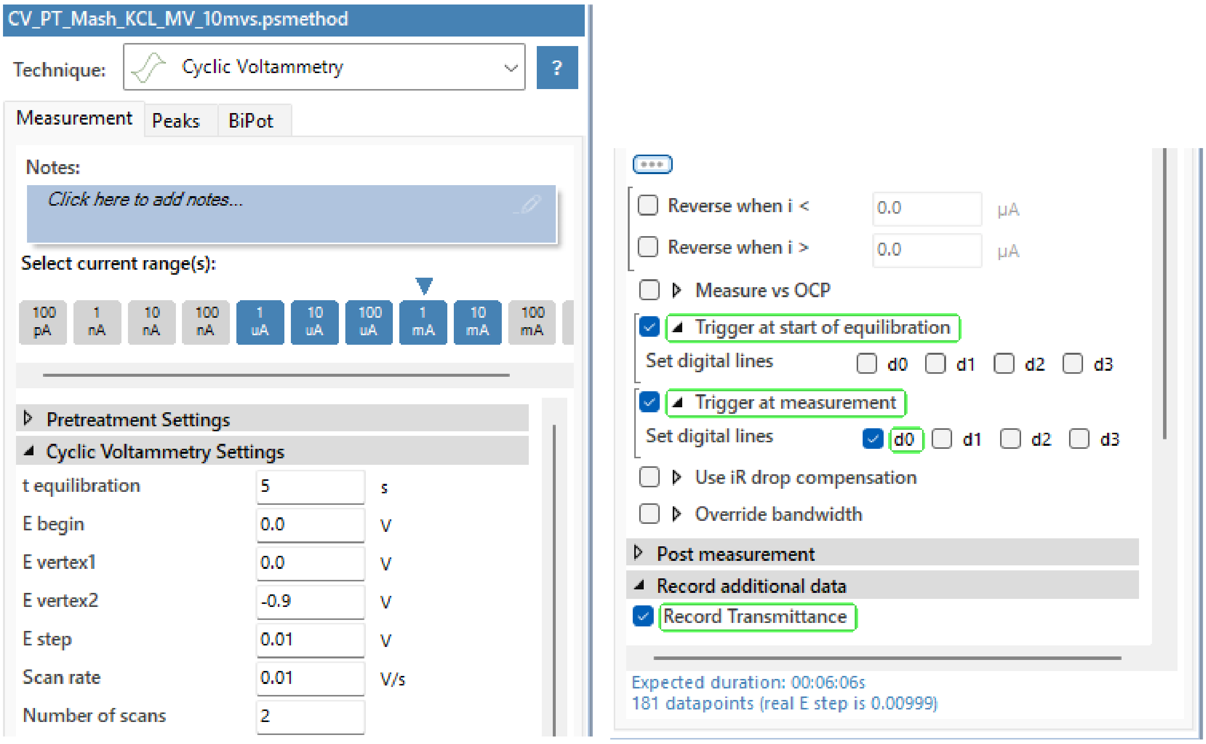
● 50 Hz
☑ BiPot present

Type: custom
Name: Transmittance
Description: Converts the analog input to a transmittance value.
Offset: 0.0
Slope: 20.0
Unit: %
Quantity: Transmittance
Symbol: T

Figure 7: How to create a custom transmittance input from the analog voltage 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.

In this application note, the oxidation and reduction of Methyl Viologen is conducted through Cyclic Voltammetry (CV). The method editor is the section of PSTrace where you set your technique's parameters (in the left side of the main window). You can set the parameters according to Figure 8 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*. To record the Aux. input during the measurement, check in the method editor the box *Record Aux. input* in the segment *Record additional data.* If you changed the name in the *Auxiliary input options* that name will replace *Aux. input*, e.g. *Transmittance* (see Figure 8).



CV_PT_Mash_KCL_MV_10mvs.psmethod

Technique: Cyclic Voltammetry

Notes:
Click here to add notes...

Select current range(s):
100 pA, 1 nA, 10 nA, 100 nA, 1 uA, 10 uA, 100 uA, 1 mA, 10 mA, 100 mA

Pretreatment Settings

Cyclic Voltammetry Settings

t equilibration	5	s
E begin	0.0	V
E vertex1	0.0	V
E vertex2	-0.9	V
E step	0.01	V
Scan rate	0.01	V/s
Number of scans	2	

☐ Reverse when i < 0.0 µA
☐ Reverse when i > 0.0 µA
☐ Measure vs OCP
☑ Trigger at start of equilibration
Set digital lines ☐ d0 ☐ d1 ☐ d2 ☐ d3
☑ Trigger at measurement
Set digital lines ☑ d0 ☐ d1 ☐ d2 ☐ d3
☐ Use iR drop compensation
☐ Override bandwidth
Post measurement
Record additional data
☑ Record Transmittance

Expected duration: 00:06:06s
181 datapoints (real E step is 0.00999)

Figure 8: PSTrace CV settings for spectroelectrochemical experiments with Methyl Viologen in KCl.

To synchronize the start of the CV and the start of recording the spectra, a trigger must be sent to the spectrometer.

To ensure the digital lines are all low when we start, click on the …-button in the method editor and check *Trigger at start of equilibration* and none of the digital line checkboxes. To send the trigger at the start of the CV check *Trigger at measurement* as well as *d0* (see Figure 8). This presetting is necessary because the EmStat4X and Nexus instruments maintain the last digital output signal after a measurement is completed. While the spectrometer requires a transition from OFF (0) to ON (1) to initiate spectrum acquisition. To ensure this signal change occurs, an intermediate step was included with the digital d0 output set to position 0 before proceeding with the main measurement.

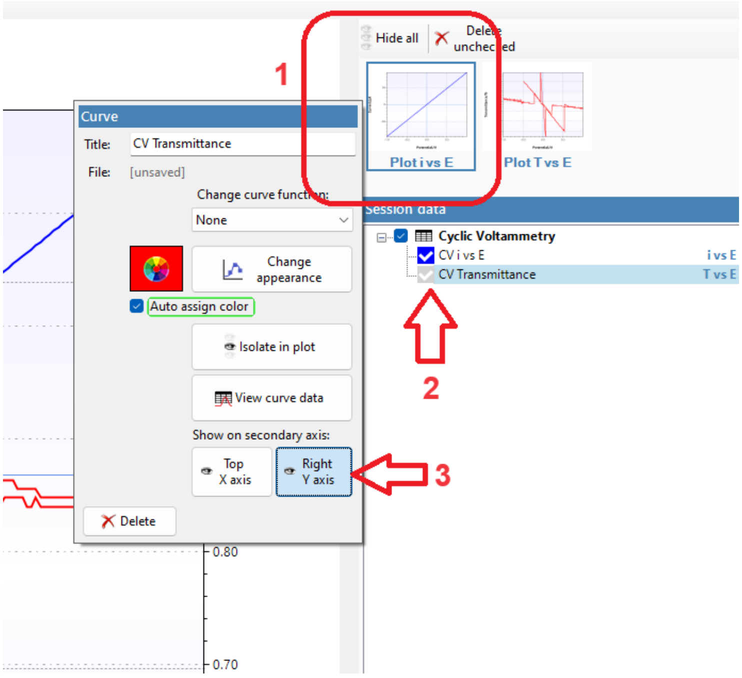
This step is necessary only for the 3D-plotting experiment, but it will not affect the single-wavelength spectroelectrochemical experiment.

2.3.2.1 Current and Transmittance in the same Plot

Following these steps will enable the secondary Y axis, allowing you to visualize the auxiliary data (transmittance) alongside the CV plot.

You can enable a secondary Y axis in a CV plot by following these steps:

- Ensure that the regular Cyclic Voltammetry (CV) plot, i.e. I vs E, is displayed on your screen.
- Click on the *Transmittance* curve or which name you have chosen for *Aux input*. This option will initially appear inactive (gray) since it belongs to a graph with different axes.
- To display this data as a secondary Y axis on the CV plot, simply click on *Right Y axis*.



Curve

Title: CV Transmittance

File: [unsaved]

Change curve function: None

Figure 9: The analog input can be plotted on the Y-axis by pressing "Right Y-axis".

2.4 Getting Started with the Spectrometer

2.4.1 Sample Connections

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 3. See Figure 3 for a view of the complete setup.

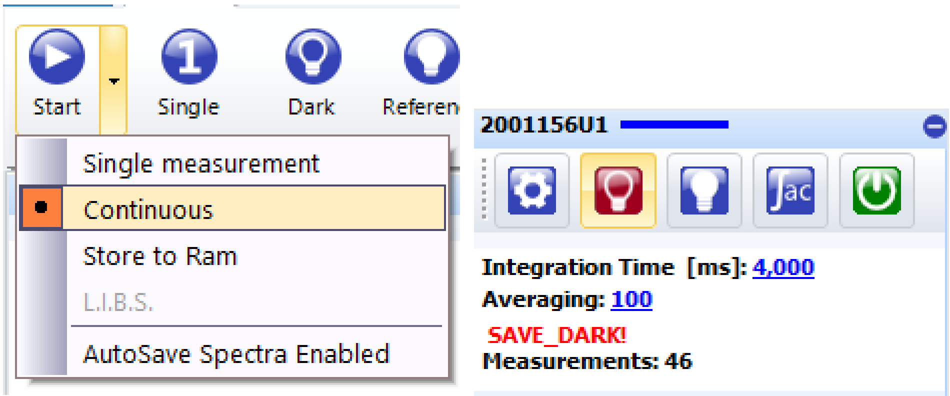
Check the cuvette (electrochemical cell) and electrodes before starting the experiment:

- Reference Electrode (RE): Ensure the body is completely filled with solution and free from air bubbles. If bubbles are present, gently tap the electrode to dislodge them and, if necessary, refill with 3 M KCl.
  - During storage, keep the RE bulb immersed in 3 M KCl.
  - If the porous frit appears dry, immerse it in the filling solution and allow it to soak for at least 1 hour to fully rehydrate.
- Counter Electrode (CE) and Working Electrode (WE):
  - Ensure the platinum wire CE and platinum mesh WE do not touch each other.
  - If needed, carefully adjust their positions using tweezers to prevent contact.

2.4.2 Dark Measurement

Turn on the spectrometer and turn off the light source. Make sure to cover the electrochemical cell completely to prevent any stray light from affecting the measurement. This step is essential for recording an accurate dark measurement, which will be stored in the spectrometer and automatically subtracted from future measurements. In AvaSoft, follow the steps:

- Disable Triggering – If triggering was enabled, make sure to disable it before proceeding.
- Click *Start* and *Continuous* (see Figure 10, left).
- One or two pop-ups about the dark measurement may appear. Click on *OK* to proceed.
- Store the dark measurement by clicking on the empty lamp button (red lamp in Figure 10).



Integration Time [ms]: 4,000
Averaging: 100
SAVE_DARK!
Measurements: 46

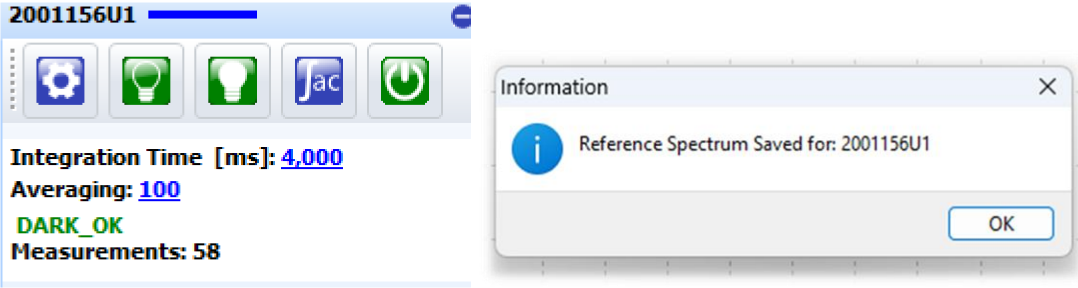
Figure 10: How to save a dark measurement.

After completing the dark measurement, a pop-up notification will confirm that the dark measurement has been recorded successfully. Additionally, the left lamp icon in AvaSoft will turn green, indicating that the dark measurement has been stored.

Finally, switch on the light source.

2.4.3 Reference measurement

Fill the cuvette of the electrochemical cell with the KCl 0.1 M solution. Insert the three electrodes into the cap and put the cap on the cuvette.
Turn on the light source, wait 10 minutes (if it was not warmed up before) and perform a reference measurement by clicking on the second bulb from the left (filled lightbulb) in AvaSoft, as depicted in Figure 11. 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). Disable triggering before saving a reference measurement and enable triggering after saving a reference management.


2001156U1

Integration Time [ms]: 4,000
Averaging: 100
DARK_OK
Measurements: 58

Information

Reference Spectrum Saved for: 2001156U1

Figure 11: How to save a Reference Spectrum.

2.4.3.1 Optimizing the Integration Time to avoid Clipping

Clipping reduces your accuracy at the wavelength where it is clipping. A clipped spectrum can be easily identified by the presence of flattened peaks. Clipping can be avoided by reducing the integration time.
To find a suitable integration time and averaging for your experiment, set the spectrometer to continuous mode (see Figure 12 left). Choose as measurement mode *S* (scope mode) (see Figure 12 right) and press *Start*. You will see the result of the measurement as in Figure 13. If your measurement at a certain wavelength is touching the maximum number of counts (65.536), the result is clipping. Set the integration time to a value where no clipping is visible in the spectrometer measurement.
Unfortunately, after changing the integration time, the dark and reference measurements have to be remeasured.

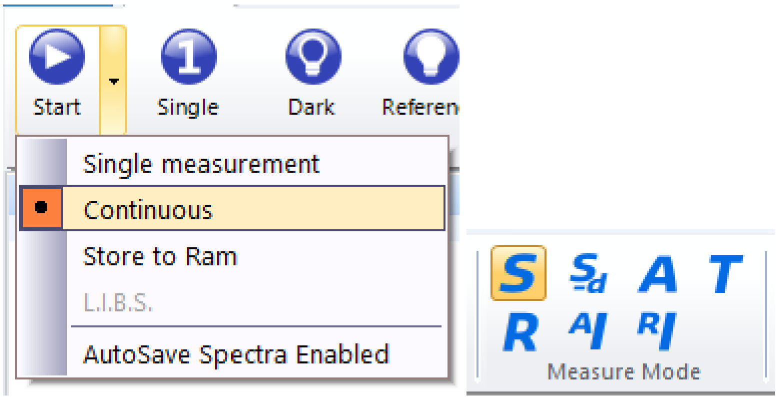


Figure 12: Start a measurement in Continuous mode in AvaSoft (left). Scope mode selected (right).

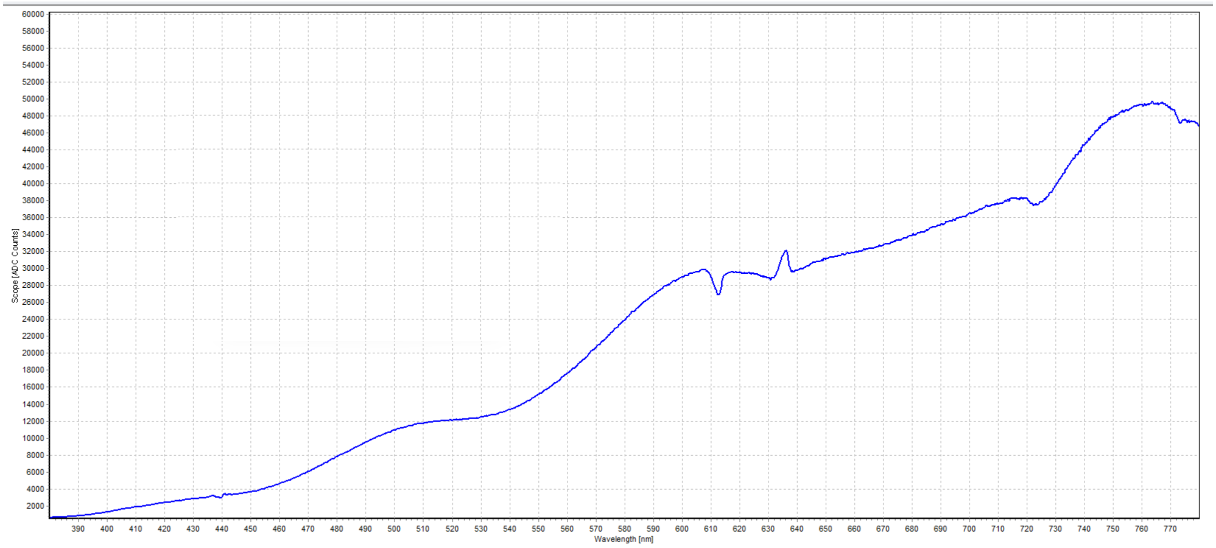


Figure 13: Example of a Scope blank (KCl_{aq}) spectrum.

If you have already started experiments using an MV solution in KCl, you can use the same solution to take a reference spectrum. The presence of MV^{2+} will not significantly affect the spectrum unless a negative potential is applied, leading to the formation of MV^{+} species. After MV^{+} is generated, allowing the solution to rest for a while or applying an anodic potential will help restore it to a blank-like reference spectrum state.

2.5 Single-Wavelength Transmittance Data Along with a Cyclic Voltammogram

In this section, we describe how to record a Cyclic Voltammetry (CV) experiment while simultaneously measuring transmittance at a single wavelength. This is the most straightforward spectroelectrochemical experiment, making it an ideal starting point.

To conduct this experiment, it is essential to identify a wavelength at which either the oxidized or reduced form of the analyte exhibits strong absorption. Such a wavelength can be found in literature, spectral databases, or determined experimentally.

In this experiment, the MV^{+} cation absorbs light at 600 nm, which lies in the yellow region of the spectrum. When this wavelength is removed from white light, the solution appears blue. In contrast, MV^{2+} is colorless and does not absorb at 600 nm. We determined this wavelength by recording spectra of MV^{2+} and of the MV^{+} cation, the latter generated by applying -0.7 V. More details are available in Section 2.6.

2.5.1 Performing the experiment

First, the cuvette is filled with 1 mM MV in 0.1 M KCl.

Open PSTrace and connect your potentiostat. Select from the list of techniques *Cyclic Voltammetry* and set the parameters according to Table 1 or load the method 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*.

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

In AvaSoft, double-check the output transmittance setting as described in Section 2.3.1 and then click *Start* - *Continuous*. In PSTrace, click *Run* to start the CV.

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 scan rate of 0.01 V/s allows the MV^{2+} reduction to take place.

2.5.2 Results

Figure 14 presents a typical CV result for MV in KCl. A noticeable decrease in transmittance begins around -700 mV, corresponding to the reduction of MV^{2+} to MV^{+}, which is also reflected as a small peak in the CV curve. As the potential sweeps back from -0.7 V to 0 V, transmittance increases again, indicating the oxidation of MV^{+} back to MV^{2+}.

By combining electrochemical and spectroelectrochemical data, a deeper understanding of redox processes can be achieved, providing additional insights into the reaction mechanisms.

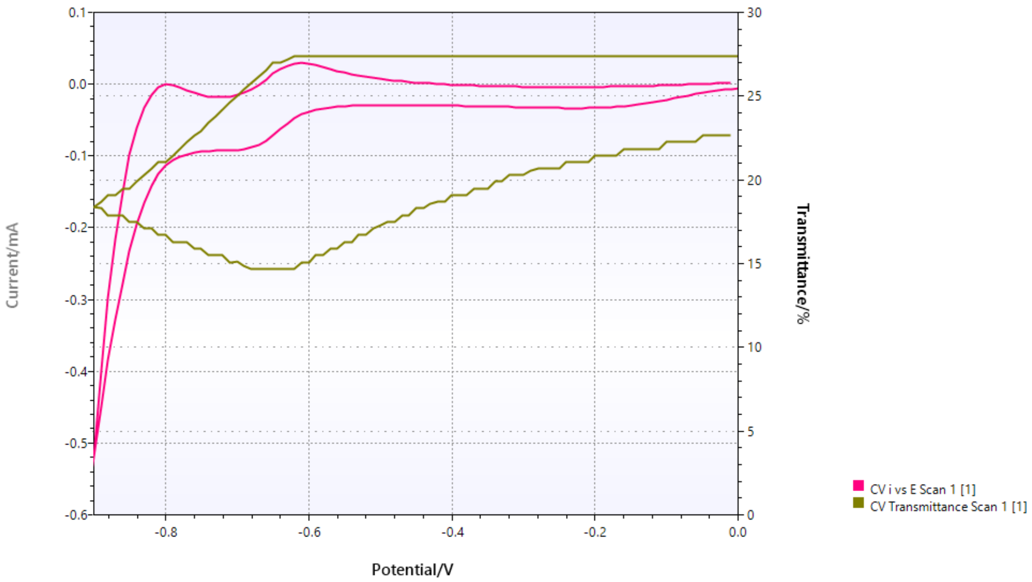


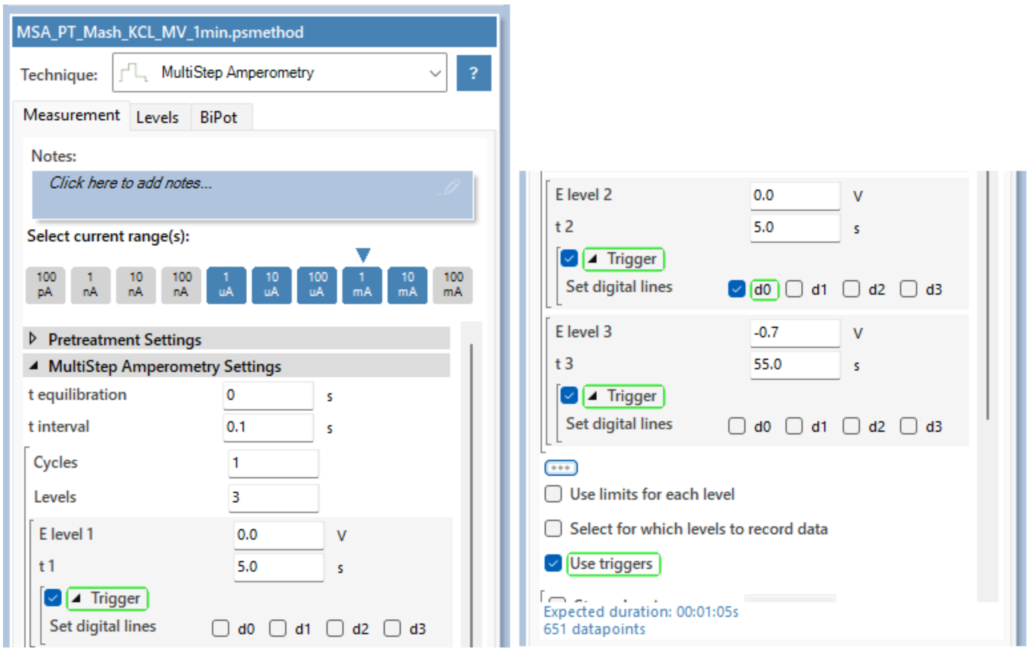
Figure 14: Example of resulted CV scan (pink, scan rate 0.01 V/s) of 1 mM MV solution in 0.1 M KCl. The transmittance in percentage (ecru) while performing the scan is plotted as a second Y-axis.

2.6 Recording Full Spectra During a Chronoamperometry Experiment

This section outlines how to record full spectral data during a constant potential (Chronoamperometry) experiment. In this experiment, a full spectrum is captured every 10 s during a 2-level constant voltage experiment lasting 60 s, resulting in seven full spectra (including the initial measurement at t = 0).

2.6.1 Step 1: Configure MultiStep Amperometry in PSTrace

Set up *MultiStep Amperometry* in PSTrace as shown in Figure 15.
In this experiment, we utilized the *MultiStep Amperometry* technique, which allows for executing chronoamperometry with multiple steps. This approach was chosen to establish a baseline spectrum at a potential where no MV^+ is formed. Additionally, the potential for the baseline spectrum was segmented into two steps to first set all digital lines to low, so in the following step the spectrometer is triggered. This preset is necessary because the EmStat4X and Nexus instruments maintain the last digital output signal after a measurement is completed. While the spectrometer requires a transition from OFF (0) to ON (1) to initiate spectrum acquisition. To ensure this signal change occurs, an intermediate step was included with the digital D0 output set to position 0 before proceeding with the main measurement.



Technique: MultiStep Amperometry

Notes:

Select current range(s):

t equilibration 0 s

t interval 0.1 s

Cycles 1

Levels 3

E level 1 0.0 V

t 1 5.0 s

☑ Trigger

Set digital lines ☐ d0 ☐ d1 ☐ d2 ☐ d3

E level 2 0.0 V

t 2 5.0 s

☑ Trigger

Set digital lines ☑ d0 ☐ d1 ☐ d2 ☐ d3

E level 3 -0.7 V

t 3 55.0 s

☑ Trigger

Set digital lines ☐ d0 ☐ d1 ☐ d2 ☐ d3

☐ Use limits for each level

☐ Select for which levels to record data

☑ Use triggers

Expected duration: 00:01:05s

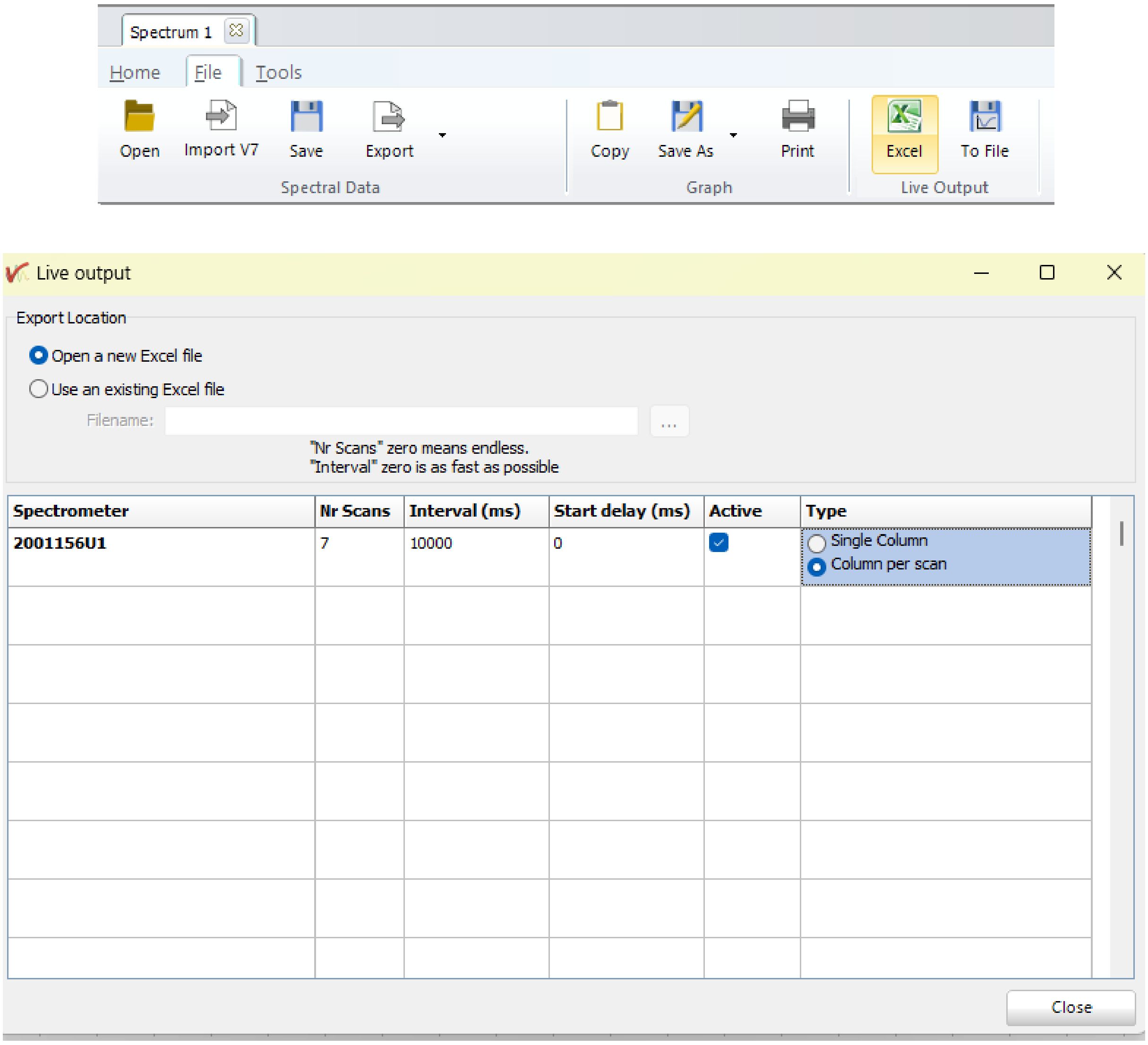
651 datapoints

Figure 15: PSTrace MultiStep Amperometry settings for spectroelectrochemical experiments

2.6.2 Step 2: Configure AvaSoft for Data Export

In AvaSoft, set the *Live data* output to be exported as an *Excel* file. In the *Live Output* window, apply the following settings (also in Figure 16):

- Nr Scans: 7
- Interval (ms): 10000
- Start delay (ms): 0
- Active: Checked
- Type: Column per scan



Export Location

● Open a new Excel file

○ Use an existing Excel file

Filename:

"Nr Scans" zero means endless.
"Interval" zero is as fast as possible

Spectrometer	Nr Scans	Interval (ms)	Start delay (ms)	Active	Type
2001156U1	7	10000	0	☑	○ Single Column ● Column per scan

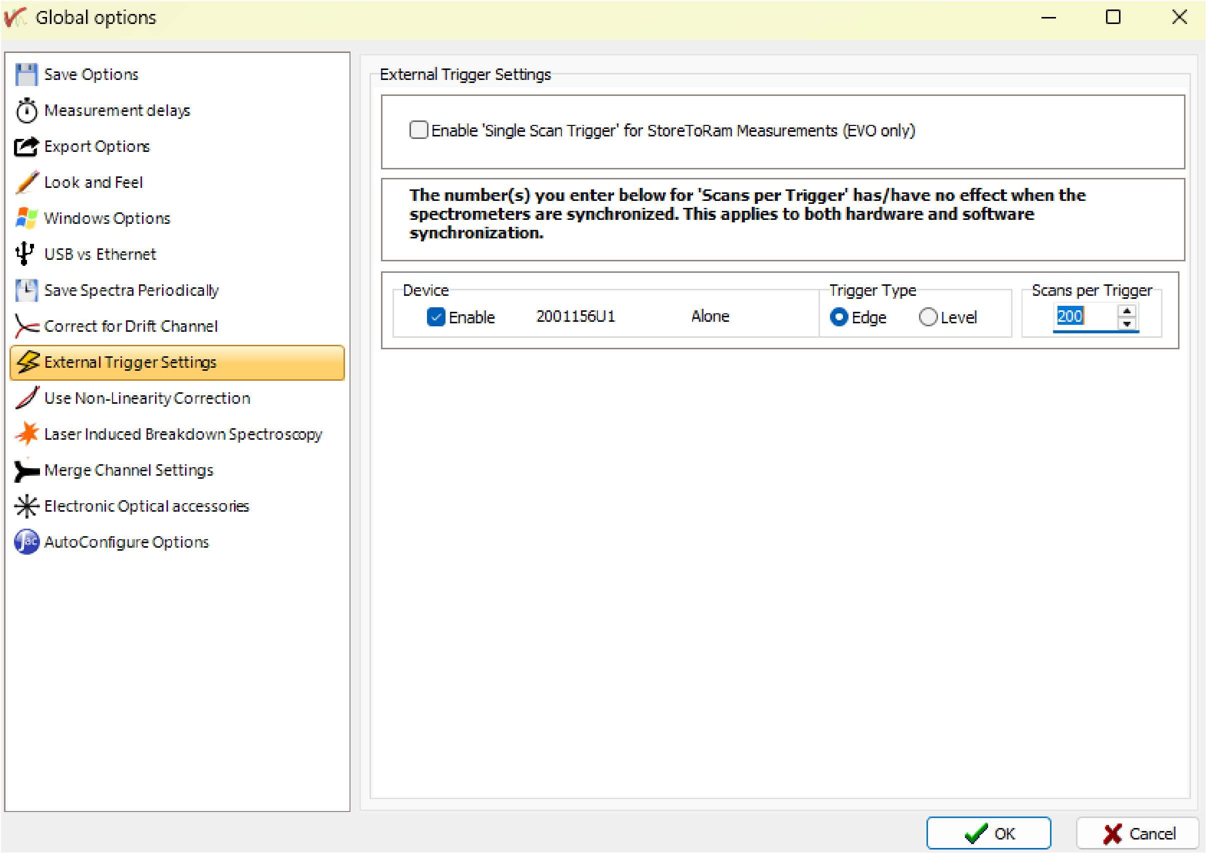
Figure 16: Live Export settings for recurrent full spectrum recording.

2.6.3 Step 3: Configure External Trigger Settings

Navigate to the *External Trigger Settings* in AvaSoft and configure:

- Enable: Checked
- Scans per Trigger: 200 (see Figure 17)

> **When the trigger is enabled, the spectrometer cannot output an analog signal simultaneously. If a Time Series window is open when enabling the trigger, close it to prevent error pop-ups.**



External Trigger Settings

☐ Enable 'Single Scan Trigger' for StoreToRam Measurements (EVO only)

The number(s) you enter below for 'Scans per Trigger' has/have no effect when the spectrometers are synchronized. This applies to both hardware and software synchronization.

Device			Trigger Type		Scans per Trigger
☑ Enable	2001156U1	Alone	● Edge	○ Level	200

Figure 17: AvaSoft trigger settings for the Chronoamperometry experiment

2.6.4 Step 4: Start the Experiment

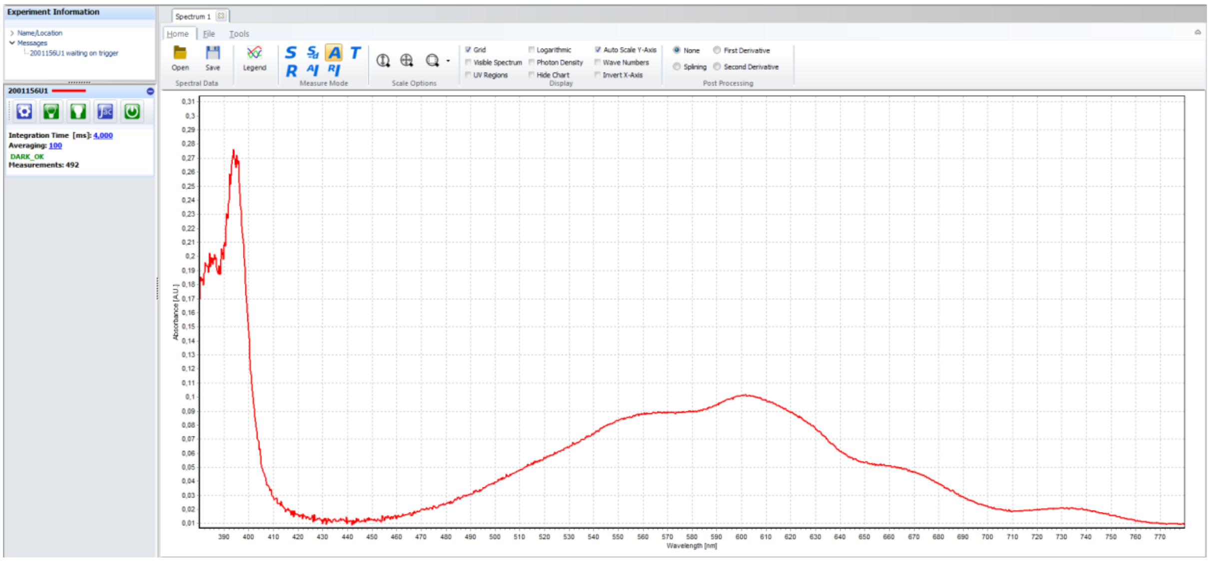
In AvaSoft, double check that you selected the absorbance (icon letter *A*) in the *Spectrum* window. Then click *Start* - *Continuous*. In PSTrace, click *Run* to initiate the *MultiStep Amperometry* experiment. An Excel file will open, and a column with spectral data will be added recurrently.

2.6.5 Results

During the chronoamperometry experiment, the spectral data displayed in AvaSoft updates continuously, with the spectrum refreshing every 400 ms. A few seconds after the experiment begins, you will see live how the spectrum changes and how it is recorded in real time, as shown in Figure 18.

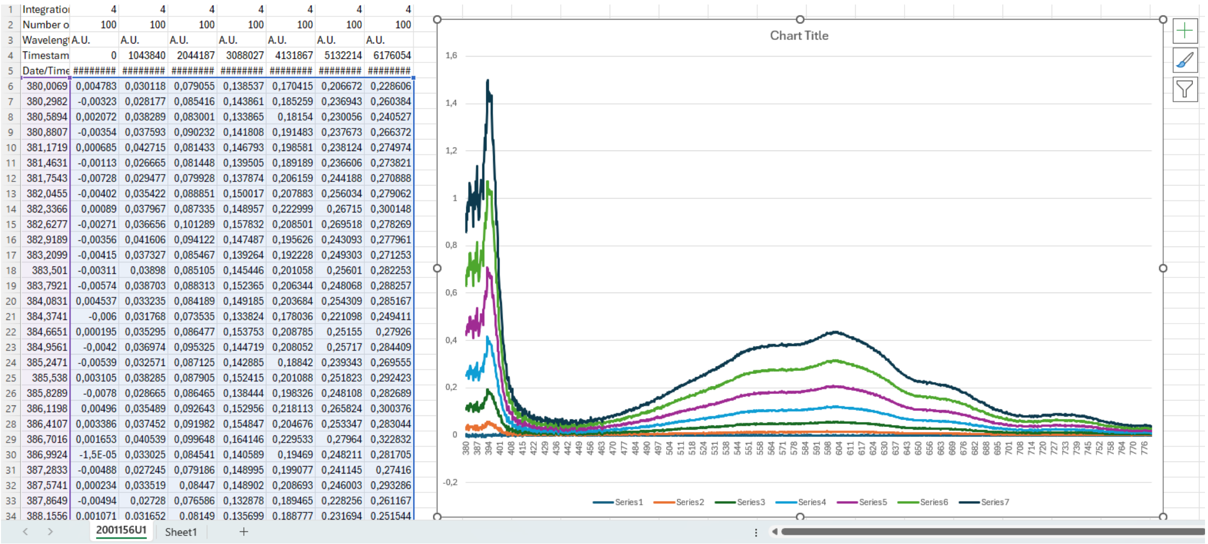
Once the chronoamperometry is completed, the exported Excel file will contain seven columns of spectral data, each representing a full spectrum recorded at ten-second intervals throughout the experiment. By plotting this data in Excel or any other spreadsheet software, it is possible to visualize how the spectra evolve over time.

As shown in Figure 19, the absorbance bands associated with MV gradually increase as the experiment progresses. This indicates the continuous formation of MV^{+}, which leads to a higher concentration of the reduced species over time. The spectral changes observed in the data provide valuable insights into the electrochemical process and its dynamics.



Integration Time [ms]: 4,000
Averaging: 100
DARK_OK
Measurements: 492

Figure 18: Example of Absorbance Spectrum live view during a Chronoamperometry in MV.



1	Integratio	4	4	4	4	4	4	4
2	Number o	100	100	100	100	100	100	100
3	Wavelengt	A.U.	A.U.	A.U.	A.U.	A.U.	A.U.	A.U.
4	Timestam	0	1043840	2044187	3088027	4131867	5132214	6176054
5	Date/Time	########	########	########	########	########	########	########
6	380,0069	0,004783	0,030118	0,079055	0,138537	0,170415	0,206672	0,228606
7	380,2982	-0,00323	0,028177	0,085416	0,143861	0,185259	0,236943	0,260384
8	380,5894	0,002072	0,038289	0,083001	0,133865	0,18154	0,230056	0,240527
9	380,8807	-0,00354	0,037593	0,090232	0,141808	0,191483	0,237673	0,266372
10	381,1719	0,000685	0,042715	0,081433	0,146793	0,198581	0,238124	0,274974
11	381,4631	-0,00113	0,026665	0,081448	0,139505	0,189189	0,236606	0,273821
12	381,7543	-0,00728	0,029477	0,079928	0,137874	0,206159	0,244188	0,270888
13	382,0455	-0,00402	0,035422	0,088851	0,150017	0,207883	0,256034	0,279062
14	382,3366	0,00089	0,037967	0,087335	0,148957	0,222999	0,26715	0,300148
15	382,6277	-0,00271	0,036656	0,101289	0,157832	0,208501	0,269518	0,278269
16	382,9189	-0,00356	0,041606	0,094122	0,147487	0,195626	0,243093	0,277961
17	383,2099	-0,00415	0,037327	0,085467	0,139264	0,192228	0,249303	0,271253
18	383,501	-0,00311	0,03898	0,085105	0,145446	0,201058	0,25601	0,282253
19	383,7921	-0,00574	0,038703	0,088313	0,152365	0,206344	0,248068	0,288257
20	384,0831	0,004537	0,033235	0,084189	0,149185	0,203684	0,254309	0,285167
21	384,3741	-0,006	0,031768	0,073535	0,133824	0,178036	0,221098	0,249411
22	384,6651	0,000195	0,035295	0,086477	0,153753	0,208785	0,25155	0,27926
23	384,9561	-0,0042	0,036974	0,095325	0,144719	0,208052	0,25717	0,284409
24	385,2471	-0,00539	0,032571	0,087125	0,142885	0,18842	0,239343	0,269555
25	385,538	0,003105	0,038285	0,087905	0,152415	0,201088	0,251823	0,292423
26	385,8289	-0,0078	0,028665	0,086465	0,138444	0,198326	0,248108	0,282689
27	386,1198	0,00496	0,035489	0,092643	0,152956	0,218113	0,265824	0,300376
28	386,4107	0,003386	0,037452	0,091982	0,154847	0,204676	0,253347	0,283044
29	386,7016	0,001653	0,040539	0,099648	0,164146	0,229533	0,27964	0,322832
30	386,9924	-1,5E-05	0,033025	0,084541	0,140589	0,19469	0,248211	0,281705
31	387,2833	-0,00488	0,027245	0,079186	0,148995	0,199077	0,241145	0,27416
32	387,5741	0,000234	0,033519	0,08447	0,148902	0,208693	0,246003	0,293286
33	387,8649	-0,00494	0,02728	0,076586	0,132878	0,189465	0,228256	0,261167
34	388,1556	0,001071	0,031652	0,08149	0,135699	0,188777	0,231694	0,251544

Figure 19: Example of Exported Absorbance Spectra during a Chronoamperometry in MV and a plotted graph in Excel

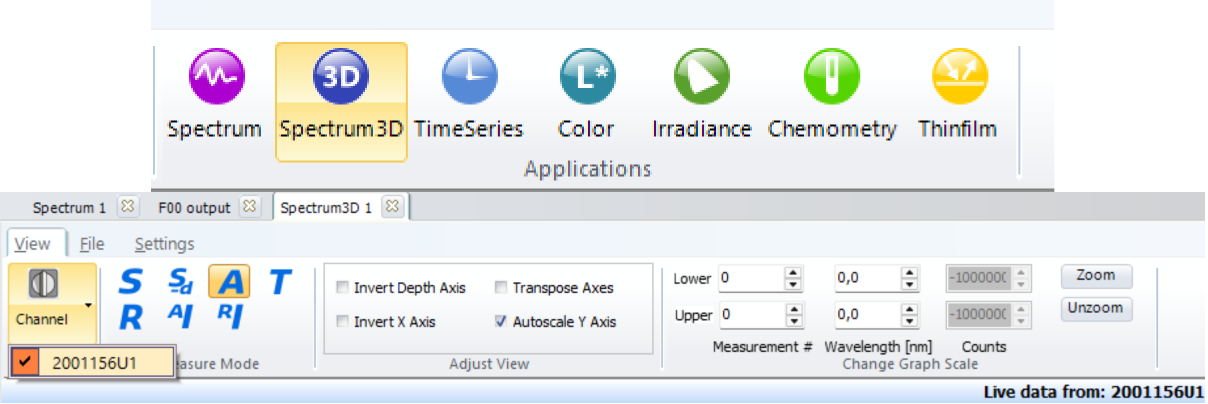
Avantes spectrometers provide high-speed data acquisition, making them well-suited for capturing spectroscopic data during rapid reactions. In this example, the averaged spectra acquired over 400 ms was sufficient to observe the process. However, for investigations of faster transitions, it is possible to obtain a full spectrum in just a few milliseconds. Conversely, increasing the number of spectra used for averaging can help reduce noise and improving data quality.

2.7 3D Graph of full Spectra

With the described instruments and software, it is possible to record full UV/Vis spectra at multiple points during a CV experiment. This results in both a CV curve and a corresponding set of spectra. For better visualization, the data is typically represented in a 3D plot, with wavelength on one axis, absorbance in the Z axis and either time or potential or sequence number on the third axis.

2.7.1 Step 1: Configure AvaSoft for 3D Spectrum Collection

Open AvaSoft and click on the *3D Spectrum* icon. This will open a new tab for collecting 3D spectral data. Ensure that the spectrometer is selected as the active channel (see Figure 20).



☑ 2001156U1

☐ Invert Depth Axis ☐ Transpose Axes
☐ Invert X Axis ☑ Autoscale Y Axis

Lower 0 0,0 -100000(
Upper 0 0,0 -100000(

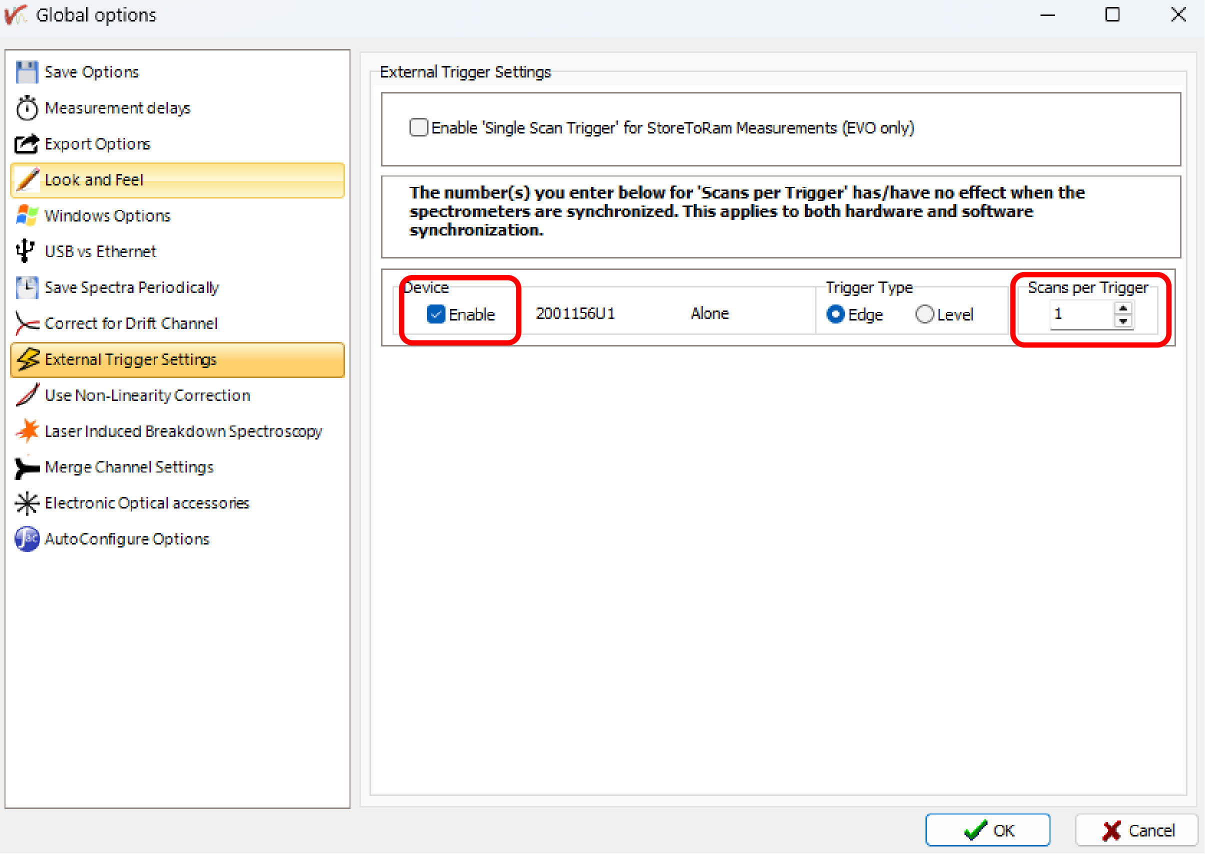
Live data from: 2001156U1

Figure 20: Setting the spectrometer to record 3D series spectral dataset.

2.7.2 Step 2: Set the External Trigger

Open *Options* and choose the *External Trigger Settings* and set *Scans per Trigger* to 1. This setting ensures that each scan corresponds to a full spectral series, containing the number of spectra defined in the *StoreToRam* setting (see Figure 21).

When the trigger is enabled, the spectrometer cannot output an analog signal simultaneously. If a Time Series window is open when enabling the trigger, close it to prevent error pop-ups.



External Trigger Settings

☐ Enable 'Single Scan Trigger' for StoreToRam Measurements (EVO only)

The number(s) you enter below for 'Scans per Trigger' has/have no effect when the spectrometers are synchronized. This applies to both hardware and software synchronization.

Device			Trigger Type		Scans per Trigger
☑ Enable	2001156U1	Alone	● Edge	○ Level	1

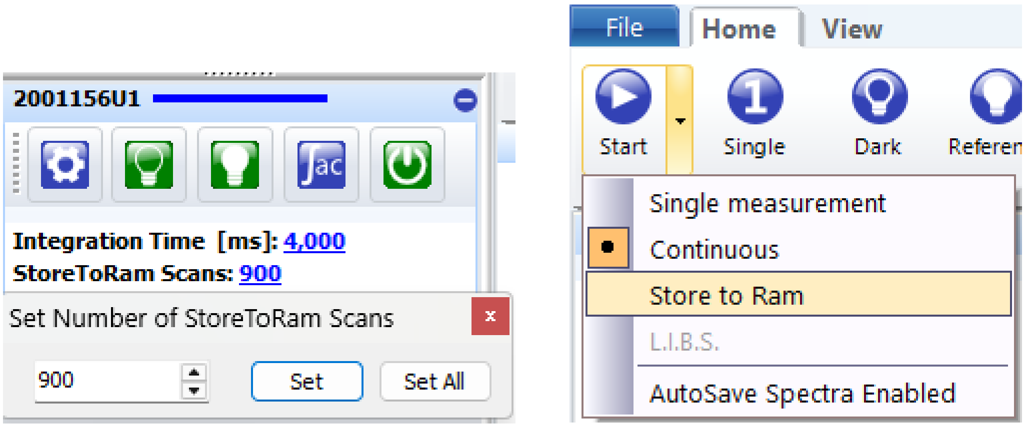
Figure 21: External Trigger Settings for a 3D spectrum experiment.

2.7.3 Step 3: Adjust the StoreToRam Setting

Verify that the *StoreToRam* number is set to 900 (see Figure 22 left). With a 400 ms integration time, this results in 360 seconds of total acquisition time, aligning with the duration of two CV cycles.

2.7.4 Step 4: Start the 3D Spectral Acquisition

Click *Start* - *Store to Ram* in AvaSoft (see Figure 22 right). This sets the device to wait for the trigger, and you will see an indicative message in the left AvaSoft window. Once the trigger is detected, the spectrometer begins data collection. However, the 3D spectral data will only become available after the full acquisition is completed.



Integration Time [ms]: 4,000
StoreToRam Scans: 900
900

Figure 22: Setting the Number of 'StoreToRam' scans (left) and starting the 3D spectrum experiment (right).

A 3D series works only with the *StoreToRam* option, to ensure that the spectral data will not suffer constraints due to a limited USB data throughput. Due to this data buffering, 3D data appears only after the end of a full series.

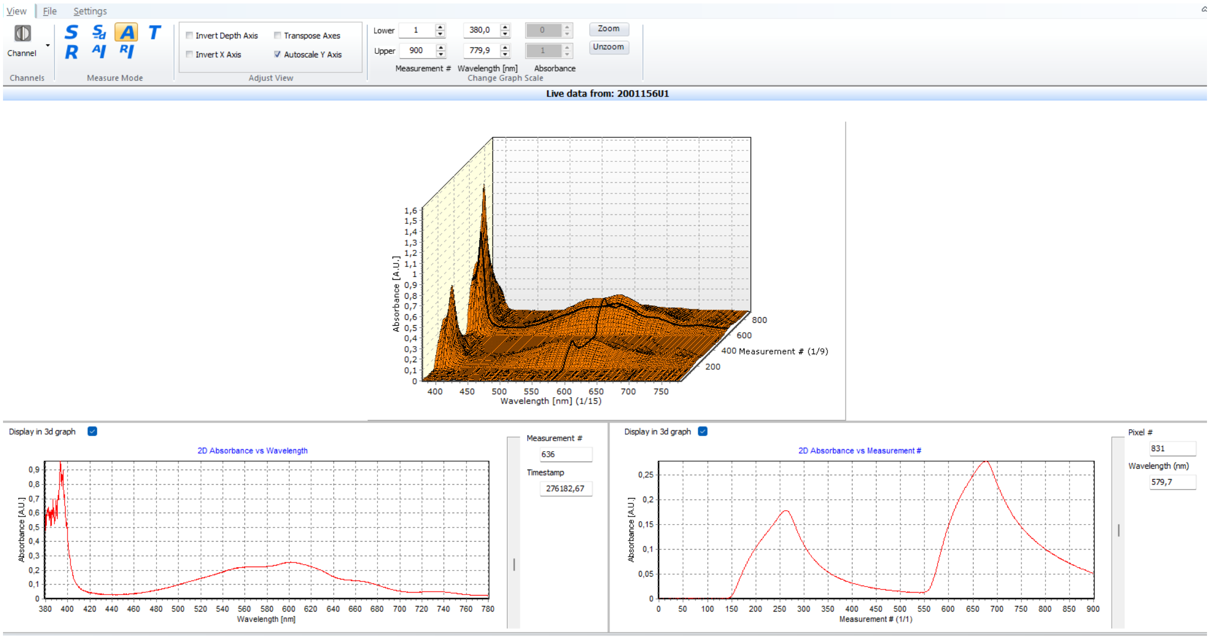
We suggest trying a short series (e.g., 10 scans, so 4 s) without triggering to familiarize yourself with the StoreToRam mode. You can do this without any electrochemical experiment running; it is simply to observe how the 3D data acquisition process works.

2.7.5 Step 5: Configure and Start the CV in PSTrace

Go to PSTrace and configure the potentiostat to perform a Cyclic Voltammetry experiment, as described in Section 2.3.2 or Figure 8. Uncheck the option *Record Aux. input* in the segment *Record additional data*, as this signal will be absent in this mode. Click *Run* to begin the experiment.
The spectrometer will store the spectral data internally and retrieve it after the experiment ends.

2.7.6 Results

After the CV experiment is completed, the AvaSoft window will display the 3D plot. The CV results will appear as expected, similar to the pink curve shown in Figure 14 of Section 2.5.2. Nevertheless, note that the analog signal corresponding to the transmittance data will not be exported. If you had previously left the option to *Record Aux. input* checked in the *Record additional data* section of PSTrace, disregard any data obtained through the auxiliary port.
A typical 3D plot is shown in Figure 24. At the bottom of the 3D plot, you can scroll through the 2D plots and select specific scans for review. By checking the option *Display in 3D graph* the corresponding 2D scan will appear as a black line over the 3D plot for better visualization.



☐ Invert Depth Axis ☐ Transpose Axes
☐ Invert X Axis ☑ Autoscale Y Axis

	Measurement #	Wavelength [nm]	Absorbance
Lower	1	380,0	0
Upper	900	779,9	1

Display in 3d graph ☑

Measurement # 636

Timestamp 276182,67

Display in 3d graph ☑

Pixel # 831

Wavelength (nm) 579,7

Figure 23: Typical 3D spectrum plot obtained during a CV with Methyl Viologen in KCl.

To save or export the data, navigate to the *File* tab in AvaSoft. For further details on data handling and export options, refer to the AvaSoft manual.

The results presented in this application note are for demonstrational purposes only. Actual responses may vary depending on experimental conditions and setup, particularly the light source used.

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, EmStat4X or Nexus
2.	Electrochemical Cell	ItalSens K300 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 a complete bundle:

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 Spectroelectrochemistry Kit

4 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, EmStat4X or Nexus 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 of the cable used to connect a PalmSens potentiostat via the AUX port to an Avantes spectrometer.

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

The cable to connect the spectrometer to the potentiostat is included in the Spectroelectrochemistry Extension and the Spectroelectrochemistry Starter Kit

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Please contact us at **info@palmsens.com** or go to our website to get in touch with a distributor in your region.

Please do not hesitate to contact PalmSens for more details: info@palmsens.com

For support with Avantes products, contact: support@avantes.com

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