Spectroelectrochemical measurements

Summary

Spectroelectrochemistry is an experimental method that combines an electrochemical measurement coupled to an *in-situ* spectroscopical measurement. The spectroscopical measurement can be performed either in transmittance or in absorbance. The light is used to probe the immediate vicinity of the working electrode located in the cell. The spectroscopic measurement provides useful complementary information during an electrochemical measurement. It can be used to identify reaction intermediates or product structures, during an electrochemical measurement.

Configuration

AUT204.S - Autolab PGSTAT204

The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.

AUT302N.S - Autolab PGSTAT302N

This high end, high current potentiostat/galvanostat, with a compliance voltage of 30 V and a bandwidth of 1 MHz, combined with our FRA32M module, is specially designed for electrochemical impedance spectroscopy.The PGSTAT302N is the successor of the popular PGSTAT30. The maximum current is 2 A, the current range can be extended to 20 A with the BOOSTER20A, the current resolution is 30 fA at a current range of 10 nA.

AUT.SPECT.UA.S - Autolab Spectrophotometer UA

The Autolab Spectrophotometer UA is a compact device for applications in the UV/VIS/NIR wavelenght range (from 200 nm to 1100 nm). This instrument is designed to work in combination with all Autolab potentiostat/galvanostat instruments and is supported by the NOVA software.The spectrophotometer can be manually controlled or can be synchronized with electrochemical measurements. This ensures accurate timing during the measurements and allows a direct correlation between the electrochemical and spectroscopic data.

AUT.SPECT.UB.S - Autolab Spectrophotometer UB

The Autolab Spectrophotometer UB is a compact device for applications in the UV/VIS wavelenght range (from 200 nm to 850 nm). This instrument is designed to work in combination with all Autolab potentiostat/galvanostat instruments and is supported by the NOVA software. The spectrophotometer can be manually controlled or can be synchronized with electrochemical measurements. This ensures accurate timing during the measurements and allows a direct correlation between the electrochemical and spectroscopic data.

AUT.UVIR.KIT.S - Autolab spectrophotometer kit UV/VIS/NIR

The Autolab spectrophotometer kit UV/VIS/NIR consist of: UA spectrophotometer, light source, fiber cables and two type of DIO trigger cables

AUT.UVVIS.KIT.S - Autolab spectrophotometer kit UV/VIS

The Autolab spectrophotometer kit UV/VIS consist of: UB spectrophotometer, light source, fiber cables and two type of DIO trigger cables.

NOVA - Advanced software for electrochemical research

NOVA is the package designed to control all the Autolab instruments with USB interface.Designed by electrochemists for electrochemists and integrating over two decades of user experience and the latest .NET software technology, NOVA brings more power and more flexibility to your Autolab potentiostat/galvanostat.NOVA offers the following unique features:Powerful and flexible procedure editor; Clear overview of relevant real-time data; Powerful data analysis and plotting tools; Integrated control for external devices like Metrohm Liquid Handling devices;

Choice of spectrophotometer

Figure 1. The Autolab spectrophotometer.

For this application note, the Autolab spectrophotometer was used (see **Figure 1**). This device is directly integrated in the NOVA software and can be controlled during an electrochemical measurement.

The spectrophotometer is controlled through a USB interface by NOVA. The spectrophotometer can acquire one spectrum in the specified range each time the Autolab sends a TTL pulse to the spectrophotometer, using a dedicated cable.

The measurements described in the application note are performed in transmission mode.

The spectrophotometer is connected to a cuvette holder using optical fibers. The cuvette holder is connected to an Autolab light source. This light source covers a range from 200 nm to 2500 nm. The light source can be connected to the Autolab using a dedicated cable, allowing the shutter of the light source to be operated remotely by using a TTL pulse.

Experimental conditions

The electrochemical cuvette is fitted with a Pt mesh working electrode and a Pt counter electrode. The reference electrode is a small Ag/AgCl 3 M KCl electrode that can be fitted in the lid of the cuvette. The optical path is 1 mm.

The cuvette is filled with a few mL of a 0.05 M potassium ferrocyanide ($K_4[Fe(CN)_6]$) solution. This solution is pale yellow in color. When the potassium ferrocyanide is oxidized in potassium ferricyanide ($K_3[Fe(CN)_6]$), the solution changes to orange. This electron transfer reaction can therefore be followed by visible light spectroscopy.

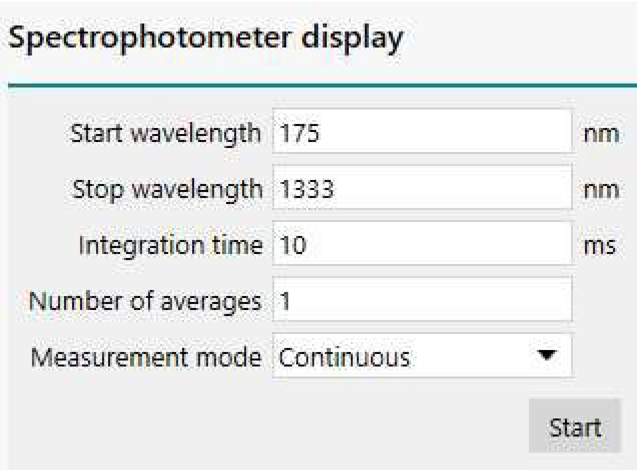

Figure 2. Software settings used to control the spectrophotometer.

The measurement range of the spectrophotometer is defined in the software, see **Figure 2**.

The electrochemical measurements were performed using the linear sweep voltammetry. During the electrochemical measurement, a trigger is sent to the spectrophotometer every 10 points. For every 10 data points in the electrochemical measurement, one spectrum is acquired, using the settings defined in the software (see **Figure 2**).

At the beginning of the measurement, two additional measurements are taken in order to determine the dark spectrum (blue line in **Figure 3**) and the reference spectrum (red line in **Figure 3**).

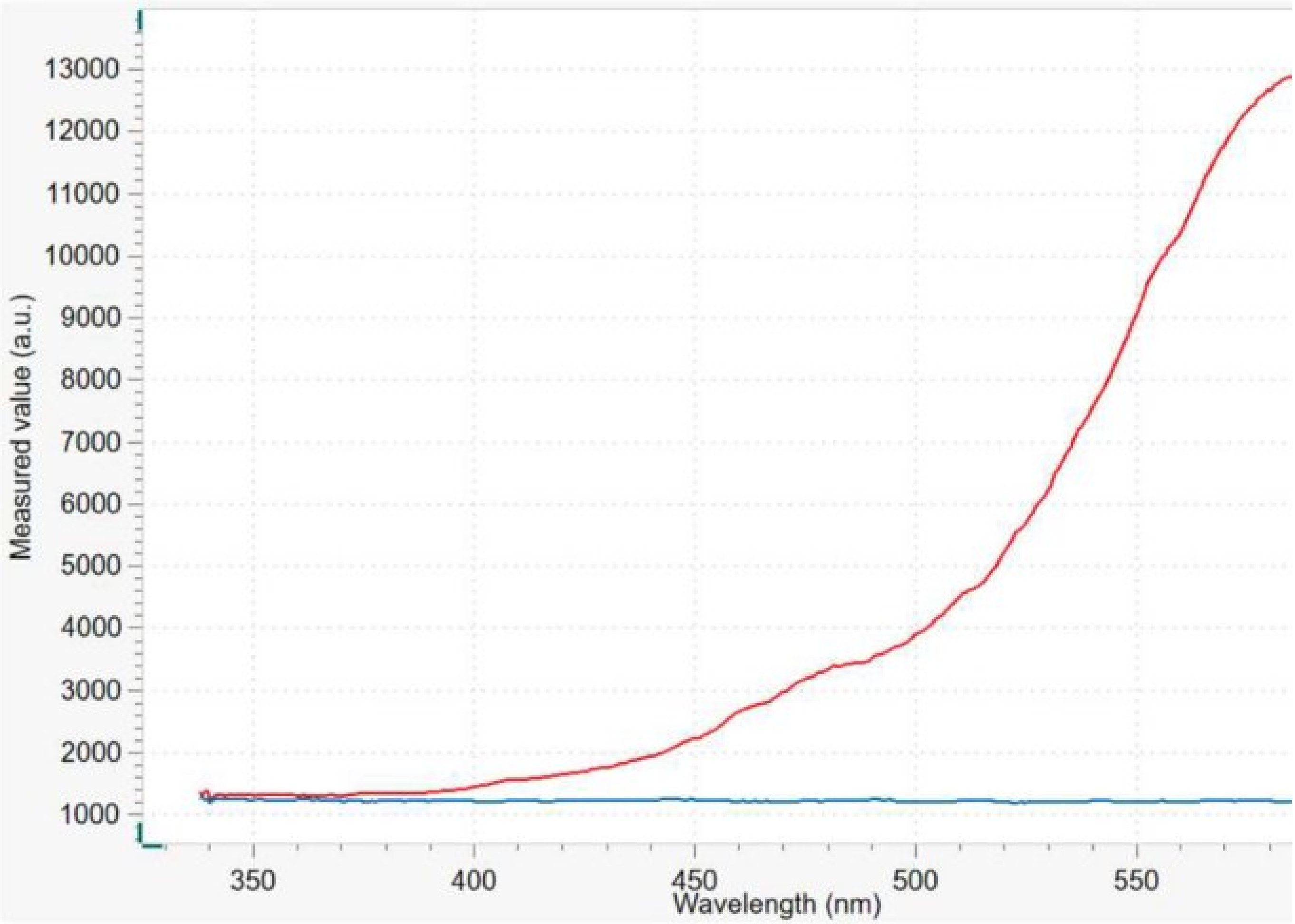

Figure 3. Dark spectrum (blue line) and reference spectrum (red line) recorded at the beginning of the measurement.

A single dark and reference spectrum is recorded for the whole experiment. These spectra are recorded at the start potential of the linear sweep voltammetry measurement.

Experimental results

Figure 4 shows a typical linear sweep voltammetry recorded for the ferrocyanide/ferricyanide system.

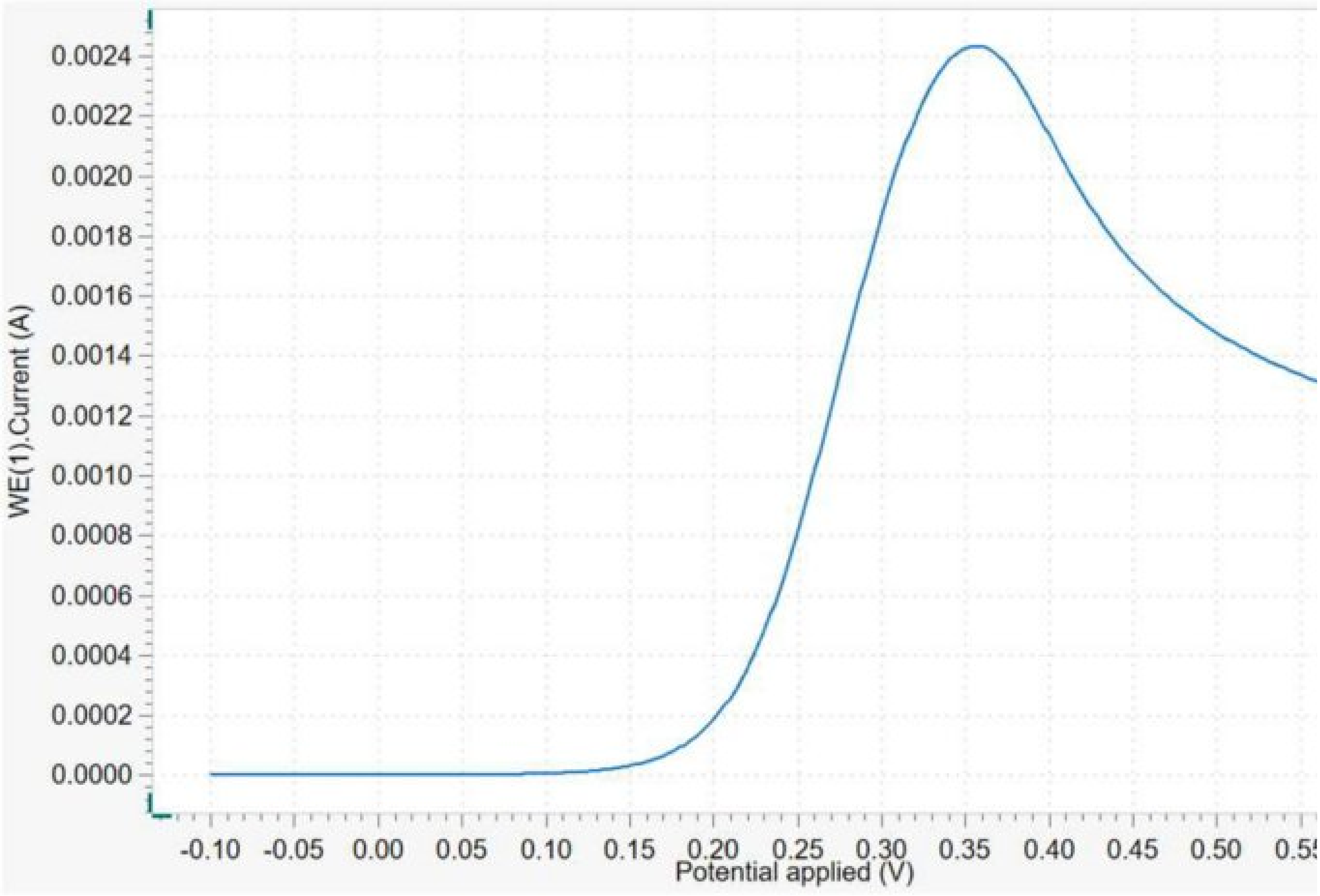

Figure 4. Typical linear sweep voltammogram for the oxidation of ferrocyanide.

At the end of the linear sweep voltammetry measurement, the spectroscopic data is recovered from the spectrophotometer and correlated to the electrochemical data. The measured intensity is converted into absorbance *A*, using the following Equation:

$$A = -\log\left(\frac{I - I_{Dark}}{I_{Reference} - I_{Dark}}\right) \qquad 1$$

Where (. .) is the measured intensity, $_{Dark}$ (. .) is the measured dark intensity and $_{Reference}$ (. .) is the measured reference intensity.

Figure 5 shows an overlay of spectra recorded during the positive going potential scan. The spectra show an increase in absorbance at 425 nm, corresponding to the formation of the oxidized form of ferrocyanide.

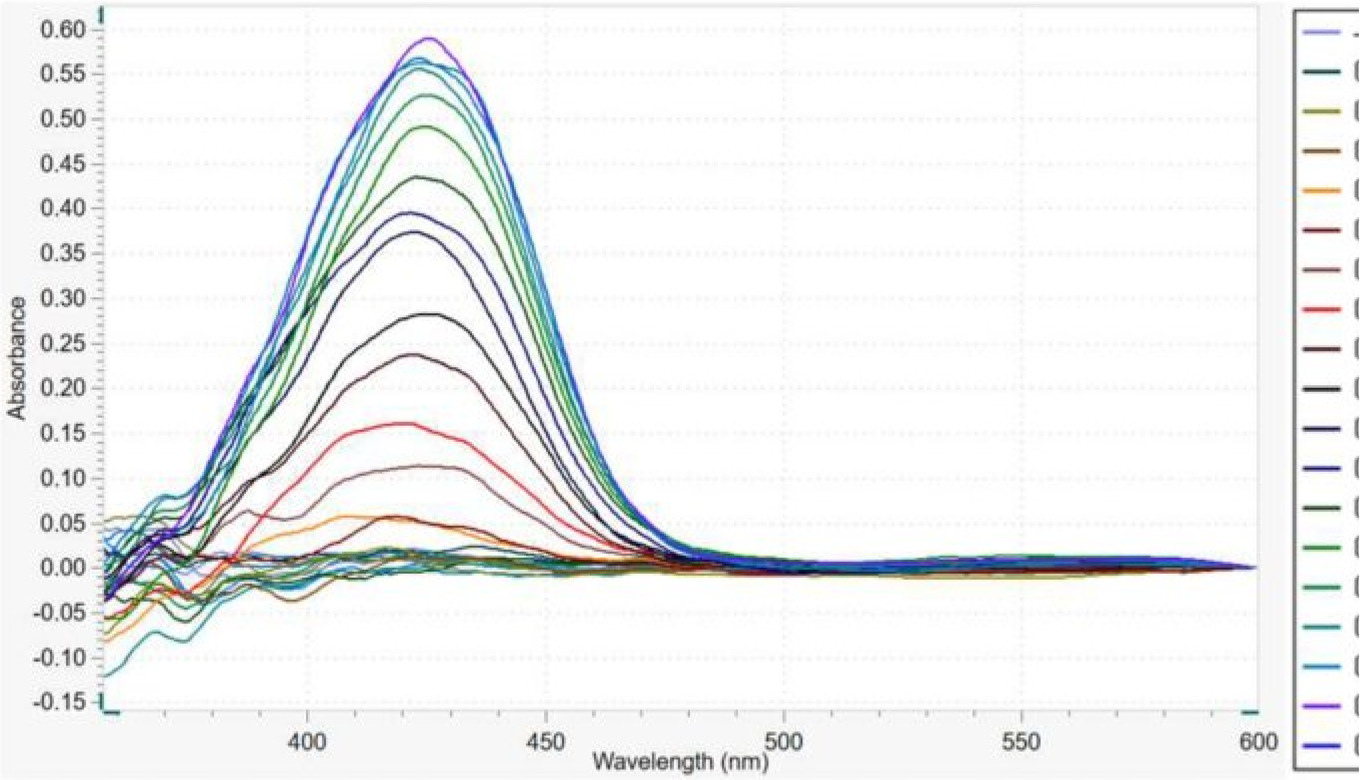

Figure 5. Overlay of spectra recorded between 360 nm and 600 nm for increasing potential values.

The increase in absorbance at 425 nm is consistent with the yellow shift observed during the oxidation of the Fe(II) to Fe(III) complex.

Conclusions

The Autolab NOVA software provides direct integration of Autolab spectrophotometers and light sources. Combined with a suitable electrochemical cuvette, the combination of these instruments together with any Autolab potentiostat/galvanostat provides the means to perform any spectroelectrochemical measurement from one convenient software.

The spectroscopic data obtained during the measurement can be directly correlated to the electrochemical data, thus providing the means to create 3D plots combining the spectroscopic data with the electrochemical data.

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