ApplicationNOTE

Spectroelectrochemistry – Part 1: Getting started

Purpose of This Note

This application note is part 1 of a series of notes introducing Gamry's spectroelectrochemistry system.

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

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

Introduction

Spectroscopy has a wide field of application, especially in analytical chemistry. Various types of materials can be investigated and classified by studying interactions with electromagnetic radiation.

Spectroelectrochemistry combines two major fields of application. Electrochemical and optical processes can be investigated simultaneously. Combining results from electrical and optical responses allows detailed insights in underlying mechanisms and more precise studies.

Typical application fields for spectroelectrochemistry are bioelectrochemistry, redox polymer processes, and organometallic reactions among others.

For a better understanding, this application note covers first the term spectroscopy, explains its basics, and proceeds to more practical aspects.

The electromagnetic spectrum

In spectroscopy, matter is studied by investigating its interactions with electromagnetic radiation. This form of energy can be described as an electromagnetic wave consisting of a coupled electric wave field $\vec{E}$ and magnetic wave field $\vec{B}$. Figure 1 shows a schematic diagram of an electromagnetic wave.

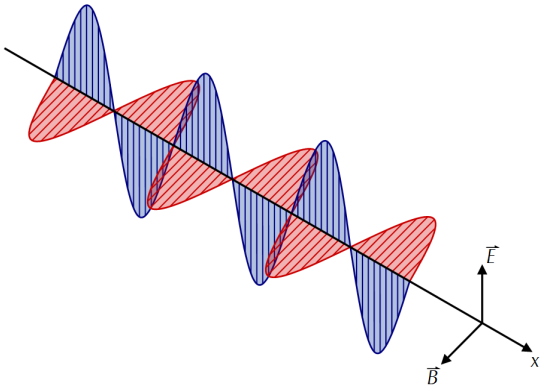


Figure 1 – Electromagnetic wave in propagation direction x consisting of a coupled electric wave field $\vec{E}$ and magnetic wave field $\vec{B}$.

Another important fact about light is its particle nature. When light shines on a metal surface, light particles transfer their energy to electrons which are ejected from the surface.

This phenomenon is called photoelectric effect. It can not be completely described by the light's wave nature. Hence light also has to be treated as flux of light particles, called photons.

The energy E of photons that is needed to eject electrons from the metal surface is inversely proportional to the wavelength λ of the light, see Equation 1.

$$E = h \cdot \nu = h \cdot \frac{c}{\lambda} \qquad \text{Eq 1}$$

ν is the frequency of the electromagnetic wave, h is the Planck constant ($6.626 \cdot 10^{-34}$ J·s), and c is the speed of light (about $300 \cdot 10^{6}$ m·s^{-1}).

Both characteristics of light, its wave and particle nature are called wave-particle duality.

The entire electromagnetic radiation is summarized in the electromagnetic spectrum, see Figure 2. Typically, it is listed by its wavelength or energy and divided into groups.

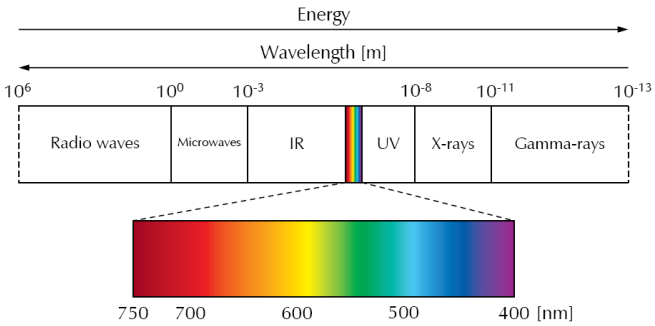


Figure 2 – Diagram of the electromagnetic spectrum.

The most known part of the electromagnetic spectrum is the visible light (Vis). It contains all colors we can see. However, the visible part is only a small portion of the whole spectrum. It ranges from about 400 nm to 750 nm.

Following the spectrum to higher wavelengths and lower energies leads to the Infrared (IR). It ranges from about 750 nm to 1 mm. IR light resembles the heat that is emitted and reflected by an object.

Proceeding to higher wavelengths leads to microwaves (MW). The energy content is further decreasing. Microwaves are used in radar technologies. Radio waves are in the region where wavelengths are ranging from meters to several kilometers. Its most common application field is telecommunication.

The other side of the spectrum exhibits radiation with higher energies and lower wavelengths. Ultraviolet (UV) light ranges from about 400 nm to 10 nm. UV is applicable in sterilization and purification processes among others.

High-energy electromagnetic radiation is classified into X-rays and Gamma-rays. Latter one is emitted by radioactive decay processes, for example on the sun or by nuclear explosions. Radiation with this amount of energy can cause cancer (carcinogenic) and damage the DNA (mutagenic). However, it can be also used for medical examination and cancer treatment.

Absorption spectroscopy

Spectroscopy can be classified into various groups depending how electromagnetic radiation is interacting with matter. Energy can be absorbed, emitted, reflected, or scattered among others. This application note will mainly focus on absorption spectroscopy.

As the name absorption spectroscopy implies, electromagnetic radiation which is focused on matter is absorbed. Depending on the kind of electromagnetic radiation or energy content, molecules and atoms interact with electromagnetic radiation in various ways. Table 1 lists different kinds of interactions between radiated energy and matter on molecular and atomic basis.

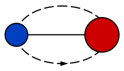
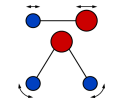
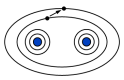
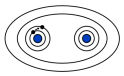
MW	Change of molecule orientation (rotational)	
IR	Change of molecule configuration (vibrational)	
UV-Vis	Change of electron distribution (outer shell)	
X-rays	Change of electron distribution (inner shell)	

Table 1 – Effect of electromagnetic radiation on molecular and atomic basis.

Amount and wavelength range of absorbed energy depend on the molecular structure. Hence every molecular structure yields a spectroscopic fingerprint by measuring radiated energy passing the sample.

Important parameters and equations

The spectrometer's detector converts photo current from light into electric current. The output depends mainly on the intensity of light that passes a sample.

Intensity *I*

When light passes a transparent medium, the intensity I_0 of the incident light drops exponentially. The decay depends on pathlength *d* through matter and its wavelength-dependent absorption coefficient *k*.

$$I = I_0 \cdot e^{-kd} \qquad \text{Eq 2}$$

Transmittance *T*

Transmittance – also called Transmission – is the ratio of light passing a transparent medium to incident light. It is typically represented as a percentage.

$$T = \frac{I}{I_0} \qquad \text{Eq 3}$$

Absorbance *A*

Absorbance (or also called absorption) is – similar to Transmittance – an expression for the amount of energy that is absorbed by a medium. It is the negative logarithm of transmittance *T*.

$$A = -\log\left(\frac{I}{I_0}\right) = -\log(T) \qquad \text{Eq 4}$$

For example, if absorbance has the value three, only one-thousandth of the incident light reaches the detector. In general, best accuracy is achieved with absorbance around one.

Note: In literature, absorbance is sometimes called extinction (attenuance). This term is no longer recommended as it also takes into account effects of luminescence and light scattering.

Integration time τ

The integration time τ defines how long the detector of a spectrometer collects light to record a single spectrum. Depending on the experiment it can range from several milliseconds to seconds.

In general, longer integration times lead to a stronger output signal and reduced signal-to-noise ratio. However, if the integration time is set too long the detector can get saturated. Peaks in a spectrum can be cut off which makes the measurement impractical.

Note: Check the spectrometer's technical specifications before measuring and make pre-tests to find the best integration time for your experiment.

Lambert-Beer-Bouguer law

P. Bouguer, J. H. Lambert, and A. Beer proved that the absorbance is directly proportional to the concentration c of a transparent medium.

$$A = \varepsilon \cdot c \cdot d \qquad \text{Eq 5}$$

ε is the molar decadic absorption coefficient and d is the pathlength of the cuvette.

Due to the fact that absorption spectroscopy is a very sensitive technique, slightest changes in concentration of a sample can be measured.

Spectrum

In absorption spectroscopy, the measured quantity of interest (i.e. absorbance A, transmittance T, or just raw counts) is plotted versus wavelength λ. This plot is called absorbance, transmittance, or raw count spectrum respectively.

Figure 3 shows an example for an absorbance spectrum.

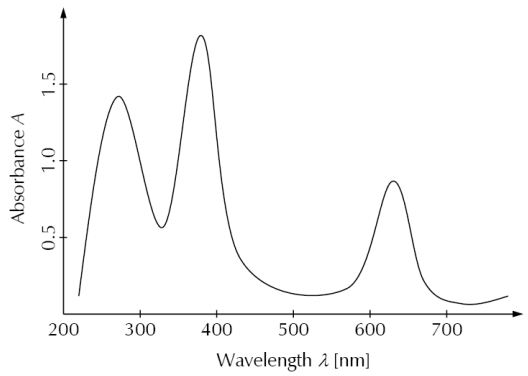


Figure 3 – Example for an absorbance spectrum in the UV-Vis region.

Absorbance peaks are at about 270 nm, 380 nm, and 630 nm.

The wavelength is typically given in nanometers (nm). In IR-spectroscopy, the spectrum's x-axis is mostly given by the inverse of wavelength λ, so-called wavenumber σ. Commonly, it is represented in cm^{-1}.

Setup for spectroelectrochemical experiments

The typical setup for absorption spectroscopy including electrochemical experiments is shown in Figure 4.

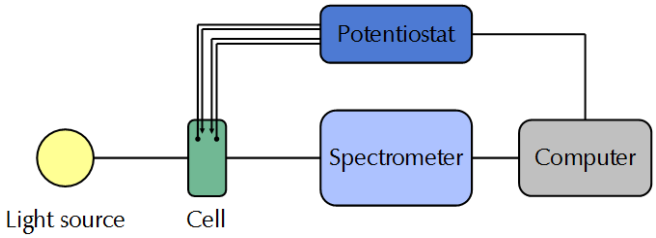


Figure 4 – Diagram of the setup for a spectroelectrochemical experiment. For details, see text.

Light source

A beam of light is focused on the sample via fiber optic bundles. Common light sources include but are not limited to Deuterium, Tungsten, or Halogen lamps, LEDs, and lasers. The light output can have a wide spectral bandwidth or it can cover only narrow spectral regions of several nanometers. Latter one is mostly used for fluorescence measurements where matter is irradiated by a laser and induced fluorescence is measured.

Cell

The sample itself is placed within a cuvette. The wavelength range of light passing the sample is strongly limited by the material of the cuvette. It can be made of plastic for cheaper and disposable cuvettes right up to fused silica quartz glass. Latter ones are more expensive but allow spectroscopy measurements down to lower wavelengths in the UV.

Cuvettes also define the pathlength of the light through the specimen. A typical value for pathlength d is 1 cm. Shorter pathlengths of several millimeters are used at higher analyte concentrations or if only small sample volumes are possible. Longer pathlengths can be used at lower analyte concentrations when the absorbance is in general lower, too (see Equation 5).

In addition, for spectroelectrochemical experiments working, counter, and reference electrode are immersed into the analyte. However, only the working electrode is within the light path. In general fine metal meshes or thin coated glass substrates are used. These materials allow sufficient transmission of light.

Spectrometer
After passing the cell, the beam of light is redirected into the spectrometer through its entry slit. The slit defines how much light enters a spectrometer and strongly determines its optical resolution.

Another important part of a spectrometer is the grating. Its fine structure is also an important factor for the optical resolution. Before passing the grating, the beam of light is a unity of radiated energy with different wavelengths. The grating separates this unity and diffracts light into its monochromatic parts – beams of light with a narrow band of wavelength.

The beam of light is redirected via mirrors within the spectrometer. In the end it reaches the detector which for most modern spectrometers is a CCD (charge coupled device) array. CCDs consist of semiconductors with a photoactive region. The detector is able to convert photo current from light into electric current. The output signal is wavelength-resolved.

Potentiostat
The potentiostat is used to perform electrochemical experiments within the cuvette. On one side it is connected to working, counter, and reference electrode. On the other side it is connected to and controlled by a computer.

Computer
Spectrometer and potentiostat are separately connected to a computer via data interface. Experiments are set and controlled by using special computer software. After finishing an experiment, recorded data are saved on the computer and can be analyzed.

Spectroelectrochemical equipment

The following sections introduce Gamry's system for spectroelectrochemical applications. It enables both spectroscopic and spectroelectrochemical experiments. It is fully compatible with Gamry's potentiostats (PCI4 and newer) and software.

Spectro-115E/115U spectrometer

Gamry Instruments offers two spectroelectrochemistry systems – Spectro-115E and Spectro-115U, see Figure 5. Each system includes one deuterium/tungsten light source, one cell holder, and two fiber optic bundles.

Both spectrometers are equipped with a linear CCD array detector with 2048 elements, a USB 3.0 communication interface, and they support temperature compensation for ultra-low thermal drift. The spectrometers are equipped with a standard SMA 905 fiber coupler.

Figure 5 – Gamry's spectrometer Spectro-115E and Spectro-115U. For details, see text.

Measurements can be performed in the UV, Vis, and near-Infrared (NIR) region. Customizable configurations allow absorbance, transmittance, and reflectance measurements.

The Spectro-115E is suitable for measurements from 350 to 1050 nm and 380 to 750 nm respectively. The Spectro-115U achieves a wavelength range from 200 to 850 nm. To gain best efficiency in the selected wavelength range, both spectrometers are available in different grating configurations.

Please contact us if you need support for customized configurations. For more detailed information about Gamry's spectroelectrochemistry system, visit Gamry's website:
www.gamry.com

BDS100 light source

BDS100 is a deuterium/tungsten light source with a total spectral output from 200 to >1100 nm.

The UV-Vis deuterium lamp (D2) has a spectral output from 200 to 400 nm. The Vis-NIR tungsten halogen lamp (W) reaches a spectral output from 400 to >1100 nm. Both lamps can be individually turned on and off via switches on the back side. In addition, a third switch on the back side serves as safety shutter (S).

The light source is driven by a 12 V power supply which can be connected on the back side. The front side has a standard SMA 905 fiber coupler.

BCH100A cuvette holder

The BCH100A cuvette holder is suitable for standard cuvettes – 12.5 mm x 12.5 mm (outer dimensions). Cuvettes are tightly held by a spring-loaded terminal.

The cuvette holder has as standard feature two ports that go straight through. Both ports are equipped with standard SMA 905 fiber couplers and can be used with any spectrometer and light source supporting this standard connector type.

The upper cuvette aperture can be darkened by a cap which is connected to the cuvette holder.

The cuvette holder is also available with a three-port configuration for Raman spectroscopy. Please contact us if you need more information or visit Gamry's website:
www.gamry.com

FPC fiber optic bundles

Spectrometer, light source, and cuvette holder can be connected among each other by standard SMA 905 fiber optic bundles.

Gamry Instruments offers matching fiber optic bundles in two different lengths – 1.5 m and 15 cm.

The core material of all fiber bundles is UV-grade fused silica with a core diameter of 600 µm which allows measurements in a wavelength range from 190 nm to 1100 nm.

Important note: Do not bend fiber optic bundles too much. You risk breaking the fine cables which makes the optic bundles impractical.

Summary

This note is part 1 of a two-part application note series. It introduces Gamry's spectroelectrochemical system.

It begins with basics of spectroscopy and explains important parameters and terms. In addition, the general setup to perform spectroelectrochemical experiments is shown and the function of each part is discussed.

Finally, Gamry Instruments' spectroelectrochemical equipment is introduced – spectrometer, light source, cuvette holder, and fiber bundles.

Part 2 of this application note series discusses on the basis of examples Gamry's Framework and its experiments. Further, data analysis with the Echem Analyst is explained including its new spectroscopy functions.

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