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Spectroelectrochemistry with Low-cost Instruments

A. Habekost*

University of Education Ludwigsburg, Ludwigsburg, Germany
*Corresponding author: A.Habekost@t-online.de

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Abstract Processes at electrodes can be monitored simultaneously electrochemically and spectroscopically. In electrochemical science, expensive equipment is needed to study these spectroelectrochemical processes. Because of the high price of these instruments, they are often not used in university education. Several experiments of three chemiluminescence systems with low-cost instruments are presented and partly compared with the expensive setups

Keywords: *electrogenerated chemiluminescence, low-cost spectroelectrochemistry*

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1. Introduction

Spectroelectrochemistry has become a standard technique for studying redox reactions at electrodes associated with changes in spectroscopic properties. [1-5]

There are now several commercial systems that can synchronously detect electrochemical redox reactions associated with changes in optical, chemiluminescence and Raman properties (SPELEC®, SPECTOECL® and SPELECRAMAN®, all from Metrohm/DropSens). The main advantages of these systems are compactness and sophisticated software. The disadvantage is the high price.

In this paper, we present experiments with low-cost instruments. The results are partly compared with those of high-priced instruments.

Three university experiments on electrogenerated chemiluminescence and on optical spectroelectrochemistry have already been presented by the author in this journal. [6-8] For this purpose, potentiostats, photodiodes and fiber spectrometers are used, the costs of which far exceed school budget.

Typically, cyclic voltammograms are used for the electrochemical characterisation of redox systems. [9] A potentiostat moves back and forth over a set voltage range, measuring the current between the working- and counter-electrodes in a three-electrode setup. The voltage is measured with respect to a reference electrode. The electrochemical reactions take place within the set voltage range. This results in positive current peaks for oxidation and negative current peaks for reduction reactions.

Simultaneously with the change in potential, the change in absorption or luminescence of the substance is measured in spectroelectrochemistry. In addition, instead of an optical change, a vibrational change during the redox processes can be detected by means of IR or (surface-enhanced) Raman spectroscopy. [10]

2. Experiments

This article will present experiments with a total cost of about 1000 Euro. The Rodeostat, an open-source potentiostat from IORodeo (price 250 USD) as well as the photomultiplier R 4632 with the power supply socket C 6270 from Hamamatsu (price approx. 100 USD) and for spectral resolution, the USB-VIS-OEM minispectrometer (http://www.khs-instruments.com / Products/ Spectrometer/ spectrometer.html, about 300 USD) were used.

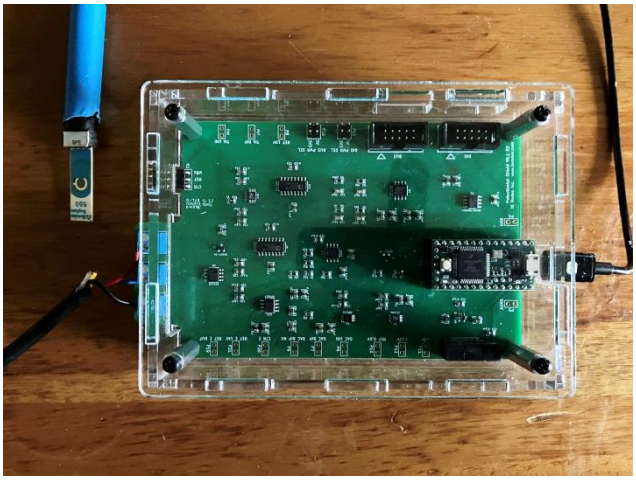


Figure 1. Rodeostat potentiostat with Screen-printed electrode (SPE, left) and USB connection (right).

The Rodeostat potentiostat (Figure 1) can be used to perform various electrochemical procedures, such as chronoamperometry, linear sweep as well as cyclic voltammetry. The included software is based on the open-source Arduino software (IDE) that programs the Teensy, a development board with numerous features.

To operate the Rodeostat, the program "serialport-bridge"

must first be loaded (https://github.com/iorodeo/serialport-bridge/releases/tag/ v0.1.1). This program controls the connection USB - serial port. Then the user software (http://stuff.iorodeo.com/apps/rodeostat/) is loaded (https://blog.iorodeo.com/rodeostat-software/) and the Rodeostat is connected to the serialport-bridge. After selecting the port number, the serial port is opened. Now, the potentiostat parameters can be set (maximum current flow, initial and reverse potential, sampling rate, scan rate). The current-voltage values can be exported to EXCEL. But even users who have no experience with Arduino can use the Rodeostat without any problems.

Figure 2. Photomultiplier with socket (right) and housing (left).

For the operation of the photomultiplier (Figure 2) two standard DC voltage sources are still necessary, once +15 V (fixed) as well as 0-5 V (variable). The registration of the light intensity dependent output voltage of the photomultiplier is done with a conventional data acquisition system (UT 8802 Benchtop-multimeter, digital, Reichelt electronics, Germany). All of these devices can be found in any equipment collection. The graphical evaluation can be done by EXCEL.

In the experiments presented here, we used so-called screen-printed electrodes (SPE), consisting of three electrodes, the working, reference and counter electrodes on a ceramic substrat. SPEs are available with numerous electrode materials. We used a platinum SPE (DRP 550) from Metrohm/DropSens with Pt as working and counter electrode and a silver pseudo reference electrode. The electrodes cost 3 Euro per piece.

2.1. ECL with Commercial ECL-potentiostat

Figure 3 shows an expensive commercial setup with the potentiostat-photodiode (ECL-Stat, Metrohm/DropSens). For spectral resolution a fiber spectrometer (AvaSpec, Avantes) is used instead of the photodiode (see below, 2.5).

Figure 4 shows the (derived) spectral and CV measurements for the well-studied $[Ru(bpy)_3]^{2+}$ / proline system (proline as coreagent) [11], Figure 5 for lucigenine / H_2O_2 taken with ECL-Stat. Black: CV, red: derived ECL intensity.

The role of H_2O_2 as the coreagent of lucigenine to produce ECL is described in detail in Reshetnyak et. Al. [12]

Figure 3. Experimental setup used. Potentiostat and ECL cell with photodiode

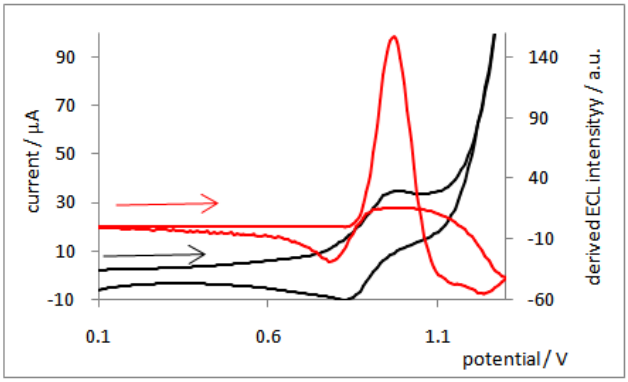


Figure 4. CV-ECL of $[Ru(bpy)_3]^{2+}$ / proline. Black: CV, red: derived ECL, DRP 550 (Pt), scan rate: 0.01 V/s. The arrows indicate the scan direction

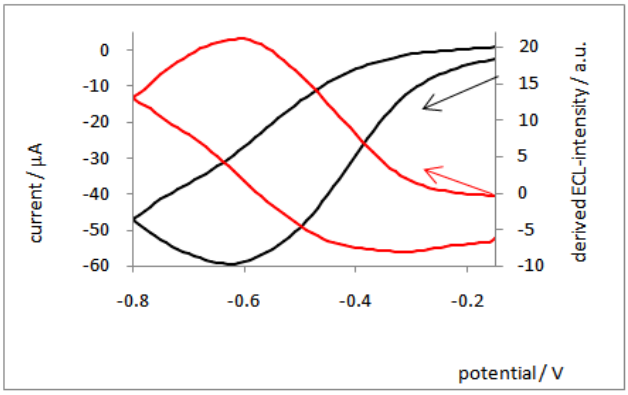


Figure 5. CV-ECL of lucigenine / H_2O_2. Black: CV, red: derived ECL. DRP 550 (Pt). Scan rate: 0.01 V/s.. The arrows indicate the scan direction.

2.2. ECL with Rodeostat and Photomultiplier

Figure 6 shows the complete low-cost setup: The Rodeostat potentiostat (P) circles the potential between the start, turn and end potentials, the photomultiplier (F) detects the light intensity, the output of the photomultiplier is connected to the digital voltmeter (V, with USB output), the pulse generator (UTG 962E from UNI-T, 100 USD, G) is connected to the SPE and produces a sawtooth or a pulsed signal as an alternative to

the potentiostat. The output of the photomultiplier (power supply PS 1 and PS 2) is also connected to the input pin of the Raspberry Pi (R), which is triggered by the negative edge of the photomultiplier signal and sends pulses to the peristaltic pump (S) which pumps the solution after each voltage pulse. The Python program to control the stepping motor can be found in the supporting information.

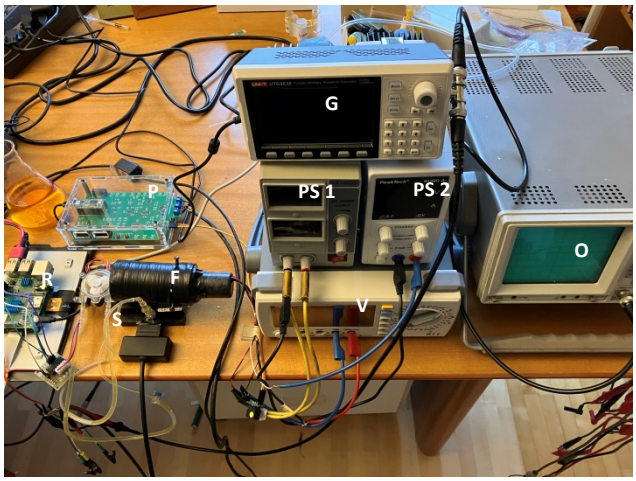


Figure 6. Experimental setup with Rodeostat potentiostat (P), Raspberry Pi (R), peristaltic pump with stepping motor and controller (28BYJ-48 – ULN2003A, S), photomultiplier with flow cell (F), pulse generator (G) power supplies for photomultiplier (P1, P2), voltmeter with USB port (V), control oscilloscope (O)

Figure 7 shows a screenshot of the CV signal recorded by Rodeostat (left) and the ECL intensity of the photomultiplier during the potential scan (right). Both signals can be transferred to EXCEL.

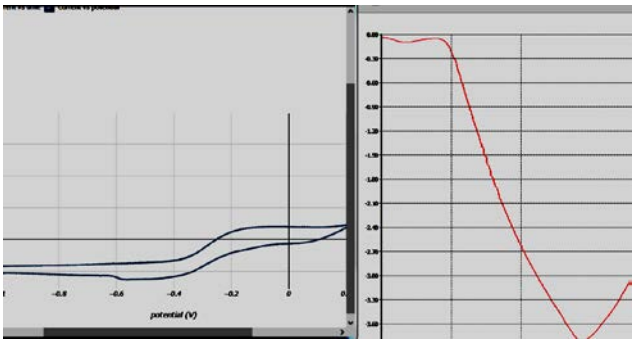


Figure 7. Screen shot of CV with Rodeostat (left) and ECL signal with photomultiplier signal (right)

Figure 8 shows the difference in CV of $[Ru(bpy)_3]^{2+}$ with and without proline. In the presence of proline the anodic peak increases, implying that the electron transfer is followed by a chemical reaction of proline with $[Ru(bpy)_3]^{3+}$ to regenerate (more) $[Ru(bpy)_3]^{2+}$ on the electrode surface. In contrast, the reduction peak decreases because the concentration of $[Ru(bpy)_3]^{3+}$ is lowered) and therefore only a low quantity of $[Ru(bpy)_3]^{3+}$ can be reduced to $[Ru(bpy)_3]^{2+}$

Figure 9 shows the result of the same electrochemical system as in Figure 4: The results are identical, the resolution comparable.

The analogous results are shown in Figure 10 for the sstem lucigenin / $_{H2O2}$, compare with Figure 5.

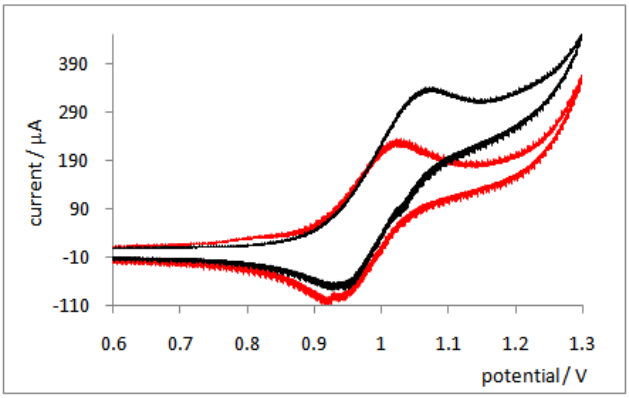


Figure 8. CV of $[Ru(bpy)_3]^{2+}$ with (black) and without proline (red)

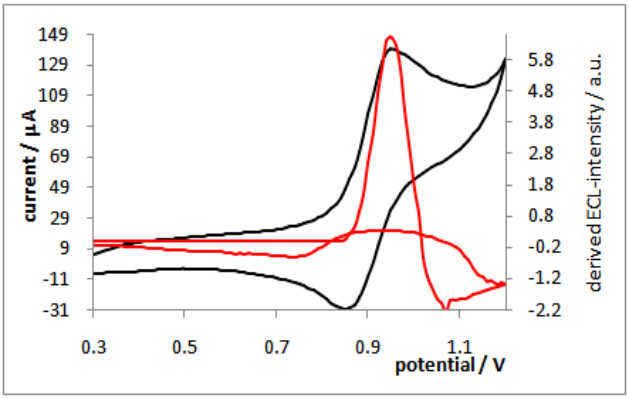


Figure 9. CV-ECL CV-EC $[Ru(bpy)_3]^{2+}$ / proline. Black: CV, red: derived ECL, DRP 550 (Pt), scan rate: 0.01 V/s. Integral ECL-intensity with photomultiplier

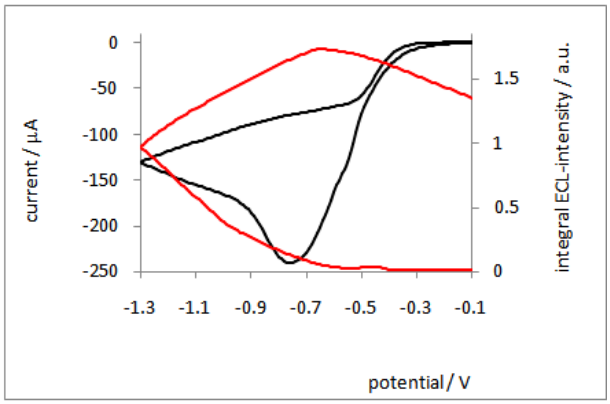


Figure 10. CV-ECL of lucigenine / H_2O_2. Black: CV, red: ECL. DRP 550 (Pt). Scan rate: 0.01 V/s. Integral ECL-intensity recorded with photomultiplier

2.3. Pulsed Excitation and Solution Pumping

Figure 11 shows the flow cell for batch injection of luminol / $_{H2O2}$. On the right is the flow cell (TLFCL-REFLECELL from Metrohm/DropSens) with connections for tubes containing the solution, the peristaltic pump with stepper motor controlled by Raspberry Pi (left). Neyes et al. measured the energy transfer of luminol / $_{H2O2}$ to fluorescein using the same thin-film cell but the expensive SPELEC system [13]. They found a linear relationship between H_2O_2 concentration and ECL signal up to 10 mmol.

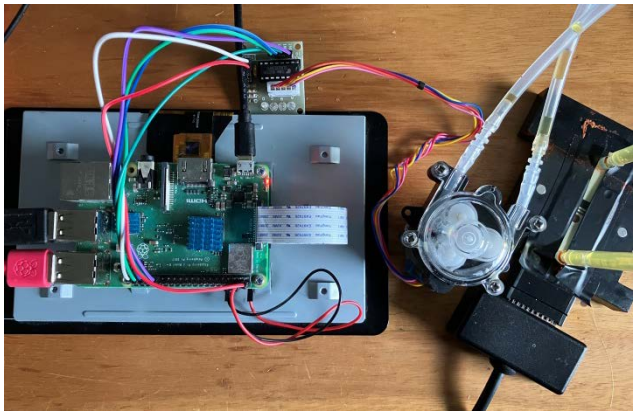


Figure 11. Experimental set up for controlling the peristaltic pump. From left to right: Raspberry Pi 3 with ULN 2003 (stepping moror control), stepping motor with peristaltic pump (G 528 DC 12V, 20 USD) and thin film cell (without photomultiplier)

The injection must not be continuous, as the electrochemically excited luminol will drift away and the ECL intensity will decrease. Otherwise, the solution must be refreshed, as shown in Figure 12: After different times (A-F), the solution was removed and the ECL intensity increased.

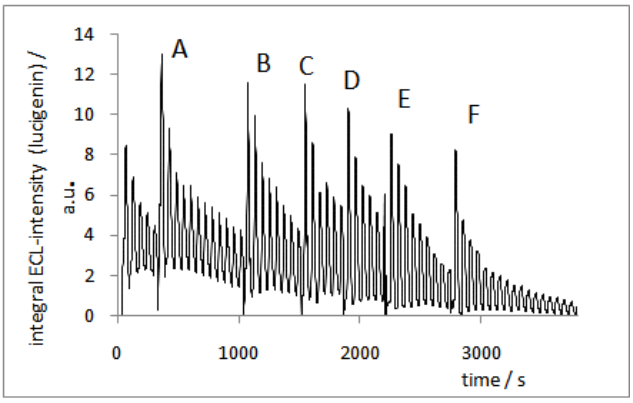


Figure 12. ECL-pulses. The solution was rinsed at A-F

If the solution is rinsed with the peristaltic pump / stepping motor after each ECL-excitation voltage pulse (produced by the pulse generator), the ECL-intensity remains nearly constant (Figure 13).

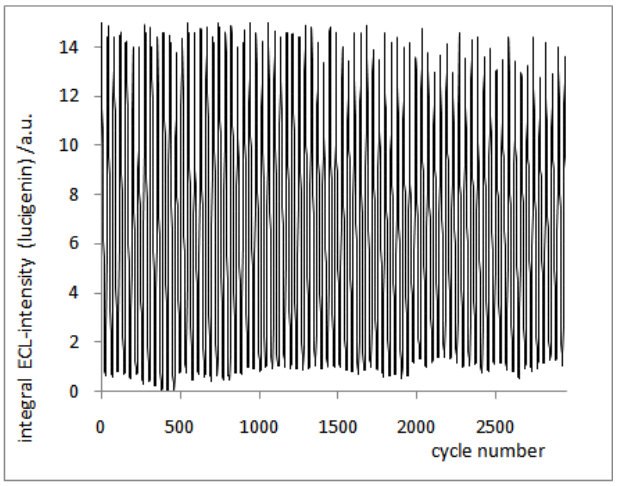


Figure 13. ECL-light pulses with pulsed flowing solution

For quantitative analysis different $_{H2O2}$ concentrations in the range between 1 and 12 µmol show an almost linear behavior, see Figure 14 (note that it is not the task of this paper to investigate measurements to detect the limit of detection of $_{H2O2}$ in order to compare the results with other techniques).

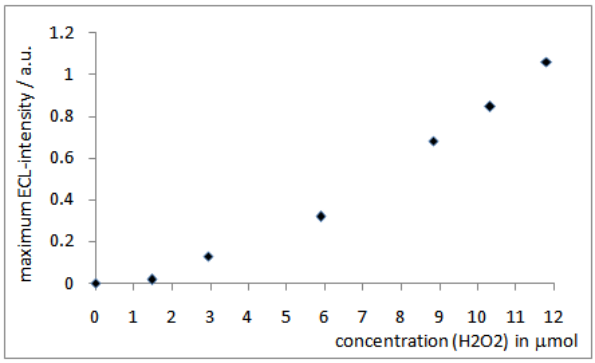


Figure 14. ECL-intensity of lucigenin (1 µmol) as a function of H_2O_2 concentration

2.4. Injection of $_{H2O2}$ Into Luminol Solution

A miniaturized flow injection of H_2O_2 into a luminol solution based on ECL shows Figure 15.

Figure 15. Injection of H_2O_2 with a Hamilton syringe (25 µL) into a continuous fresh luminol solution. Left: peristaltic pump, top: storage vessel for the luminol solution and waste bin

The ECL intensity of the same amount of H_2O_2 (2 µL) is almost constant (Figure 16).

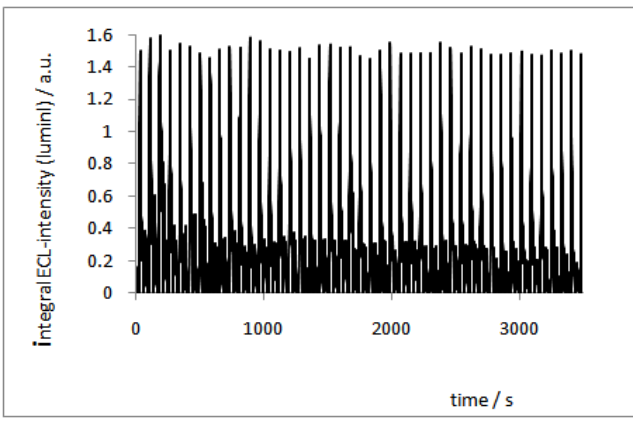


Figure 16. ECL-light pulses of luminol and H_2O_2 with pulse generator and photomultiplier: 0 V to + 0.4 V

2.5. ECL with Microspectrometer

The photomultiplier can only detect the integral ECL intensity. For spectral resolution, a dispersive element must be used. Figure 17, top, shows an expensive fiber spectrometer (Avantes AvaSpec ULS CL-EVO) with a potentiostat and a home-made SPE cell. Figure 17, below, shows a low cost version of a CCD spectrometer.

Figure 17 Top: Potentiostat with fiber spectrometer and home-made cell with collecting lens, bifurcal fiber and adapter for SPE. Bottom: Minispectrometer from KHS instruments. Right: CCD part

The spectrally resolved ECL of luminol / $_{H2O2}$ with the microspectrometer shows an acceptable signal with a signal-to-noise ratio (S:N) of about 20:1 (Figure 18). Averaging can increase the S:N (red line). The ECL was generated by a voltage source at + 0.4 V.

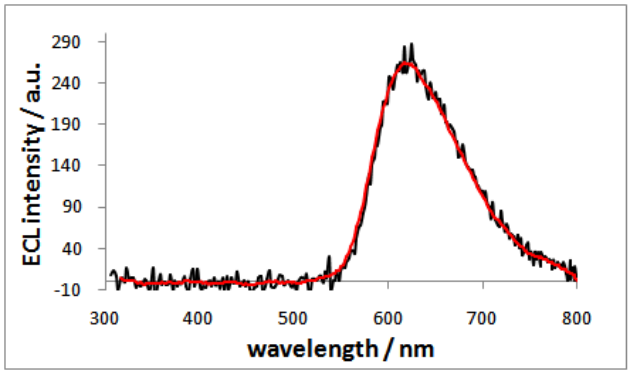
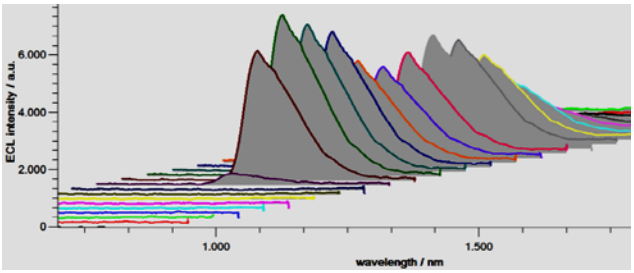


Figure 18. ECL-spectrum of $[Ru(bpy)_3]^{2+}$ / proline with microspectrometer at 0.4.V. Black: raw data, red: Averaging over 10 points

Spectrally resolved potential-dependent ECL is shown in Figure 19 with the fiber spectrometer (top) and the microspectrometer (bottom) between 0 V and 1.3 V and in reverse. The integration times were 10 s for both methods. The difference between the two ECL voltammetry instruments is quite small.



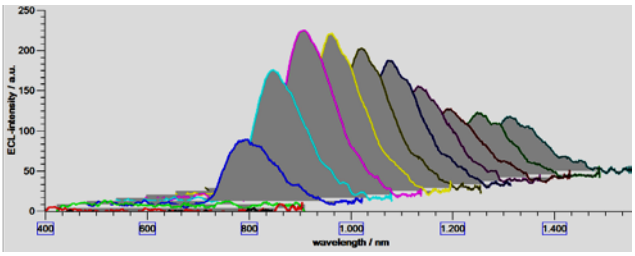


Figure 19. ECL spectra of $[Ru(bpy)_3]^{2+}$ at different potentials from 0 V to 1.3 V and reverse. Top: Measured with fiber spectrometer, bottom: measured with microspectrometer

3. Summary and Outlook

The aim of this paper was to show that useful measurements for spectroelectrochemical investigations can be obtained with low-cost equipment.

This paper is aimed at university lecturers who wish to introduce students to the principles of spectroelectrochemistry, in this case electrogenerated chemical luminescence, with low-cost equipment.

ECL electrochemistry can be extended to absorption voltammetry by using transparent ITO electrodes or bifurcated light guides with separate excitation and emission processes. However, this requires a continuous light source, such as a deuterium-halogen lamp. The same applies to fluorovoltammetric measurements, which require an external LED light source.

ACKNOWLEDGEMENT

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Supporting information: Python program for stepping motor

```
# Ingmar Stapel modified by Achim Habekost

from time import sleep
import RPi.GPIO as GPIO
import os
#from random import randint
import random
GPIO.setmode(GPIO.BCM)

# coupling Pins des ULN2003A with Pins Rapberry Pi
durchgang=1
IN1=6 # IN1
IN2=13 # IN2
IN3=19 # IN3
IN4=26 # IN4
IN5=5 # IN5
# Waiting time regulates the speed at which the motor rotates.
time = 0.001
# Define Pins as output and Pin 5 as input
GPIO.setup(IN1,GPIO.OUT)
GPIO.setup(IN2,GPIO.OUT)
GPIO.setup(IN3,GPIO.OUT)
GPIO.setup(IN4,GPIO.OUT)
#GPIO.setup(IN5,GPIO.IN)
GPIO.setup(IN5,GPIO.IN, pull_up_down=GPIO.PUD_UP)

# First, all pins set to False.

GPIO.output(IN1, False)
GPIO.output(IN2, False)
GPIO.output(IN3, False)
GPIO.output(IN4, False)

# The 28BYJ-48 stepper motor is designed so that the motor inside requires
# 8 steps for one revolution. Due to the operations,however, it requires 512 x 8 steps for the axis to
# rotate once around itself, i.e. 360 rev..
# Definition of steps 1 - 8 via pins IN1 to IN4
# There is a short wait between each movement of the motor so that the motor armature reaches its # position.

def Step1():
GPIO.output(IN4, True)
```

```
sleep (time)
GPIO.output(IN4, False)
def Step2():
GPIO.output(IN4, True)
GPIO.output(IN3, True)
sleep (time)
GPIO.output(IN4, False)
GPIO.output(IN3, False)
def Step3():
GPIO.output(IN3, True)
sleep (time)
GPIO.output(IN3, False)
def Step4():
GPIO.output(IN2, True)
GPIO.output(IN3, True)
sleep (time)
GPIO.output(IN2, False)
GPIO.output(IN3, False)
def Step5():
GPIO.output(IN2, True)
sleep (time)
GPIO.output(IN2, False)
def Step6():
GPIO.output(IN1, True)
GPIO.output(IN2, True)
sleep (time)
GPIO.output(IN1, False)
GPIO.output(IN2, False)
def Step7():
GPIO.output(IN1, True)
sleep (time)
GPIO.output(IN1, False)
def Step8():
GPIO.output(IN4, True)
GPIO.output(IN1, True)
sleep (time)
GPIO.output(IN4, False)
GPIO.output(IN1, False)
GPIO.setup(IN5, GPIO.IN)

while durchgang<1000:

GPIO.wait_for_edge(5,GPIO.FALLING)
sleep(5.0)
print ('run',durchgang)
durchgang = durchgang+1
if GPIO.input(5):
print('low')
else:
print('high')

#wait for trigger edge: high -> low

# Turn left

def left(step):


for i in range (step):

# slows down the movement of the motor too much.

Step1()
```

```
Step2()
Step3()
Step4()
Step5()
Step6()
Step7()
Step8()
print ("Steps left: ",i)
# Turn right

# This determines how far the motor turns.
# left(random.randint(10000, 10000))
#else:

GPIO.cleanup()
```