

Electrochemical Study and Determination of Electroactive Species with Screen-Printed Electrodes

Daniel Martín-Yerga,* Estefanía Costa Rama, and Agustín Costa García

Nanobioanalysis Group, Department of Physical and Analytical Chemistry, University of Oviedo, 8 Julián Clavería, 33006 Oviedo, Spain

S Supporting Information

ABSTRACT: A lab appropriate to introduce voltammetric techniques and basic electrochemical parameters is described in this work. It is suitable to study theoretical concepts of electrochemistry in an applied way for analytical undergraduate courses. Two electroactive species, hexaammineruthenium and dopamine, are used as simple redox systems. Screen-printed electrodes are used in order to allow the students to focus on the electrochemistry and avoid tedious instrumentation preparation. The analytical determination of the species studied with sensitive techniques such as differential-pulse or square-wave voltammetry is also performed.



KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Electrochemistry, Instrumental Methods

INTRODUCTION

Electrochemistry is an important part of the general chemistry curricula, but its principles are not easy to teach. On the one hand, lectures are typically based on teaching theoretical concepts, techniques, and electrodes without an applied approach. On the other hand, electrochemistry lab experiments are usually focused in the use of techniques with an analytical aim for the determination of analytes. The gap between the theoretical lectures and the lab experiments could be the main reason why electrochemistry is one of the least followed/liked subjects by undergraduate students. Closing this gap could improve the feeling of students on electrochemistry and highlight the importance of the theoretical lectures in experimental applications.

Several lab experiments using electrochemical techniques have been previously published. However, these experiments are relatively basic and are directed to the study of one or few important (thermodynamic or kinetic) parameters of the electrochemical reactions involved.^{1–5} In the lab described herein, several electrochemical parameters are studied in an applied way using two model species. The use of screen-printed electrodes (SPEs) instead of conventional electrodes, such as carbon paste or glassy carbon electrodes, contributes to show some trends in analytical chemistry such as miniaturization.⁶ The lab experiments previously published, where SPEs are used, are focused in the analytical determination of an analyte,^{7,8} but these kind of low-cost disposable electrodes are perfectly useful for the characterization of electrochemical reactions, as shown by this lab. Furthermore, all the electrochemical studies in this lab are performed using two different species in order to compare their behavior, since the literature suggests that comparison activities can lead to better learning than traditional instruction.⁹

The main objectives of this lab experiment are the study of electrochemical reactions using cyclic voltammetry, the estimation of several electrochemical parameters, and highlight the analytical utility of voltammetric techniques. Several electrochemical and analytical concepts, summarized in Scheme 1, are studied. For instance, electrochemical parameters such as the reversibility of the redox processes and the formal potential are estimated. Kinetic characteristics of the reactions such as the rate-limiting step or the heterogeneous electron transfer rate are also evaluated. The electroactive area and the double-layer capacitance of the electrode are calculated. Important analytical concepts such as calibration plots, limit of detection, reproducibility, or the standard additions method are also examined.

This lab experiment fits in the curricula between two important areas such as electrochemistry and analytical chemistry. Connecting the experimental determination and the theoretical study of electrochemical reactions could help to improve the understanding of the concepts explained in lectures where these techniques are described in detail. In our experience, the teaching of electrochemical parameters with an

Received: October 12, 2015 Revised: March 26, 2016





Scheme 1. Schematic Representation of the Different Concepts Studied in This Lab Experiment

applied philosophy is the way forward in order to have a better response by the students to the electrochemistry concepts. Due to the limited time proposed to carry out this experiment, it is not possible to explain in detail all the concepts examined, and this lab should be complementary to lectures where the theoretical bases of the electrochemical techniques are studied. It could be interesting, although not mandatory, that, previously, the students had an introduction to voltammetric techniques. This lab could replace the typical labs where the electrochemical techniques are used for the analytical determination of analytes. A good complement would be a lab studying other basic electrochemical techniques (i.e., potentiometry, ion selective electrodes, or chronoamperometry). In more advanced and specialized courses, it might be interesting the application of these techniques in processes of industrial/commercial importance such as the development of electrochemical sensors, corrosion studies, or batteries/fuel cells.

THEORY

The theoretical foundations used to estimate the electrochemical parameters studied in this laboratory practice are briefly described in the Student Handout (see Supporting Information). More information can be found in several publications¹⁻³ and textbooks.^{10–12}

EXPERIMENTAL SECTION

Reagents and Instrumentation

Hexaammineruthenium(III) chloride, dopamine hydrochloride, and potassium chloride were purchased from Sigma-Aldrich. Ultrapure water obtained with a Millipore Direct Q5 purification system from Merck-Millipore was used throughout this work. Electrochemical measurements were carried out with an Autolab PGSTAT12 (Metrohm) potentiostat/galvanostat interfaced to a computer system and controlled by Autolab GPES 4.9. Commercial screen-printed carbon electrodes (SPCEs) were purchased from DropSens (ref DRP-110). Lab-made or commercial SPCEs from other companies such as Pine Instrument, BVT Technologies, BST Bio Sensor Technology, or Gwent could also be employed. All indicated potentials are related to the silver pseudoreference screen-printed electrode. More information on these electrodes can be found in the Supporting Information. The SPCEs were connected to the potentiostat through a specific connector (DropSens, ref DSC). All measurements were performed at room temperature by adding 40 μ L of the specific solution to the electrochemical cell. Working solutions of [Ru(NH₃)₆]³⁺ and dopamine were prepared in 0.1 M KCl solution.

Voltammetric Measurements

For $[Ru(NH_3)_6]^{3+}$, cyclic voltammetry was performed from +0.1 to -0.5 V with a potential step of 4 mV and square wave voltammetry (SWV) was performed from 0.0 to -0.4 V with 6 mV step potential, 25 mV amplitude, and 30 Hz frequency. For dopamine, cyclic voltammetry was performed from -0.2 to +0.9 V and differential pulse voltammetry (DPV) was performed from 0.0 to 0.7 V with a step potential of 6 mV, a modulation amplitude of 25 mV, a pulse width of 0.01 s, and a pulse period of 0.5 s.

Sample Treatment and Standard Addition Method

A 0.5 mM dopamine solution in tap water was used as sample. Tap water was employed due to its easy sampling in a lab environment, and furthermore, it exhibits matrix effects if the dopamine is directly analyzed. To determine the dopamine concentration by the standard addition method, 4 solutions were prepared as follows: 500 μ L of sample are added for each solution; then, 0, 100, 200, or 300 μ L of 1 mM dopamine solution in 0.2 M KCl is added, respectively; last, the necessary volume of 0.2 M KCl solution is added in order to prepare 1 mL of final solution.

Lab Duration

Working in pairs or in groups of three students, a 4 h period is enough to complete all the experimental work. Solutions can be prepared in 30–40 min; all of them should be prepared in 1 mL micro test tubes because a volume of 1 mL is enough for carrying out all the necessary measurements. Cyclic voltammetry experiments take about 30 min. The voltammetric curves (SWV, DPV) for the electroanalytical studies take about 60 min. To save time, the measurement of the parameters should be carried out just after obtaining the voltammetric curves. Analysis of the parameters from the voltammograms could take about 40 min. Students should use the remaining time (about 60–70 min) to solve their doubts and to begin the necessary calculations.

HAZARDS

Hexaammineruthenium(III) chloride causes skin and eye irritation and may cause respiratory irritation. Avoid breathing dust and handle with gloves and safety glasses. Dopamine hydrochloride is harmful if swallowed and very toxic to aquatic life. Avoid release the solid and solutions to the environment. Dispose to a specific waste container.

RESULTS

First, students have to prepare all the solutions indicated in the Student's Handout (see Supporting Information). They should consider and discuss the safety aspects of the reagents employed in order to work safely and handle the waste. The results presented below were obtained by a group of three students of a fourth-year undergraduate course. Teachers should encourage discussion between the students of the same group and between different groups of students throughout the lab experiment.

Cyclic Voltammetry for the Evaluation and Characterization of Electrochemical Systems

Cyclic voltammograms at several scan rates for the two model species, $[Ru(NH_3)_6]^{3+}$ and dopamine, using a concentration of 500 μ M, were recorded. The purpose of the experiment should be described and it should be explained that the different scan rates can change the properties of the electrochemical systems allowing to evaluate these properties.

For $[Ru(NH_3)_6]^{3+}$, the potential was swept from +0.1 to -0.5 V to carry out the reduction to $[Ru(NH_3)_6]^{2+}$. For dopamine, the potential was swept from -0.2 to +0.9 V to generate the oxidized species. Students should be clear as to why the different potential sweeps are applied (initial and final potential, direction). A previous discussion can be useful to understand the studied processes. CV was performed at different scan rates such as 10, 25, 50, 75, 100, 250, and 500 mV/s (see Figure 1). The experiment was conducted using the same electrode for all the scan rates, and it was performed by triplicate. The SPCE was rinsed with water and dried with a paper towel between each CV scan, and a new drop was added to the electrode in order to do a new measurement. Peak currents and potentials for the anodic and cathodic peaks were registered. It should be explained to students that with only one experiment different theoretical principles can be evaluated or get different (kinetic or thermodynamic) parameters of electrochemical reactions.

The characterization of the electrochemical processes in terms of the rate-limiting step (diffusion or adsorption) was carried out. According to the theory, a diffusion controlled



Figure 1. Cyclic voltammograms for (A) $[Ru(NH_3)_6]^{3+}$ and (B) dopamine in 0.1 M KCl at different scan rates: 10, 25, 50, 75, 100, 250, and 500 mV/s.

process shows a peak current linearly dependent with the square rate of the scan rate, so it is possible for students to test easily theoretical principles with experimental data. Peak currents (cathodic and anodic) were plotted against the scan rate and the square root of the scan rate for the two evaluated systems. A clear linearity was found between the peak currents and the square root of the scan rate for both redox species (Figure 2). The students should conclude that these results mean that the electrochemical processes follow the Randles-Sevcik equation for a reaction controlled by the diffusion of the species to the electrode surface, and the experimentation confirms the theory for these species and conditions. Students often show interest in experiments that follow theoretical concepts.

The reversibility of the electrochemical processes was also evaluated. It should be emphasized that the electrochemical reversibility provides kinetic information on the reaction rate. As indicated in the theoretical foundations of this work (see Supporting Information), the potential difference between the anodic and cathodic peaks (Δ Ep) for reversible processes should be, ideally, equal to 59/*n* mV and be constant with the scan rate. For less reversible processes, an increment of the Δ Ep with the scan rate is usually observed. Figure 3 shows the variation of the Δ Ep for [Ru(NH₃)₆]³⁺ (A) and dopamine (B) versus the scan rate.

An increment of the Δ Ep with the scan rate was obtained for dopamine, while for $[Ru(NH_3)_6]^{3+}$, the Δ Ep was practically constant until high scan rates (>250 mV/s) where a small increment was obtained. These results indicated that the dopamine system presents a lower reversibility than $[Ru-(NH_3)_6]^{3+}$, where the values obtained (74 mV) are closer to the theoretical value of 59/*n* mV. It is important to explain that this theoretical value is complicated to obtain experimentally due to different effects that can influence it, such as the uncompen-



Figure 2. Relationship between (A) the cathodic peak current for $[Ru(NH_3)_6]^{3+}$ and the scan rate, (B) the cathodic peak current for $[Ru(NH_3)_6]^{3+}$ and the square root of the scan rate, (C) the anodic peak current for dopamine and the scan rate, and (D) the anodic peak current for dopamine and square root of the scan rate.

sated cell resistance, increasing the experimental value of the Δ Ep. Therefore, a process may behave, practically, as a reversible system although the experimental Δ Ep value were greater than 59/*n* mV. Different groups of students could compare their results and discuss if they find some variation.

An alternative approach used to evaluate the reversibility of an electrochemical process is the ratio between the anodic and cathodic peak currents. As explained in the Supporting Information, this ratio would be near 1 if the system is fully reversible, whereas this value will move away from 1 when the system shows a less reversible behavior. This parameter was calculated for every scan rate: values from -0.82 to -0.96 were found for $[Ru(NH_3)_6]^{3+}$ and values from -1.32 to -1.63 were found for dopamine (Table 1). A higher reversibility is also obtained for $[Ru(NH_3)_6]^{3+}$ because the values are closer to 1 than for the dopamine processes. As both the Δ Ep and peak currents ratio provide information about the reversibility of the electrochemical reaction, it is interesting to let students compare and discuss both parameters jointly.

With the results obtained by measuring the cyclic voltammograms at different scan rates, other parameters can be estimated. For instance, the formal potential of the redox couple could be calculated for $[Ru(NH_3)_6]^{3+/2+}$ and dopamine processes at SPCE in 0.1 M KCl (25 °C) with the following equation:

 $E^{\circ'}(\text{Ep} + \text{Ep})/2$

where Ep_a and Ep_c represents the peak potentials for the anodic and cathodic processes, respectively. For $[Ru(NH_3)_6]^{3+/2+}$, the $E^{\circ\prime}$ did not change with the scan

For $[Ru(NH_3)_6]^{3+/2+}$, the $E^{\circ'}$ did not change with the scan rate, obtaining a value of -238 ± 1 mV, while that for dopamine, the calculated $E^{\circ'}$ was increasing slightly with the scan rate. Therefore, to calculate the $E^{\circ'}$ for dopamine, the $E^{\circ'}$ results were extrapolated to zero scan rate to obtain a value of +291.4 \pm 0.6 mV.

On the other hand, the rate constant of electron transfer can be estimated following the Nicholson method.¹³ The dimensionless function (ψ) calculated by the Swaddle method¹⁴ obtained at each scan rate is plotted against the reciprocal of the square root of the scan rate (see Figure 4A for dopamine), and the standard heterogeneous rate constant (k^0) value is calculated using the following equations:

$$\ln \psi = 3.69 - 1.16 \ln(\Delta Ep - 59)$$

$$\psi = k^0 (RT)^{1/2} (\pi n FD \nu)^{-1/2}$$

where ΔEp is the potential difference between the anodic and cathodic peaks, D is the quotient between $D_{\rm O}$ and $D_{\rm R}$ that can be approximated to unity (where D_{0} and D_{R} are the diffusion coefficient for the redox couple species) (cm^2/s) , R is the universal gas constant (J/mol K), T is the absolute temperature (K), n is the number of electrons transferred, F is the Faraday constant (C/mol), and v is the scan rate (V/s). Rate constants of 1.6×10^{-3} and 1.15×10^{-4} cm/s for $[Ru(NH_3)_6]^{3+/2+}$ and dopamine processes were obtained, respectively. These results are consistent with the results obtained for the reversibility of the electrochemical reactions, because a more reversible process, usually, has a faster electron transfer. Students should reach this conclusion, and understand how the different parameters are in agreement and provide important information about kinetics. The rate constant is a parameter that can be used to compare electrochemical processes, as in this work, or to compare different electrode surfaces using the same electrochemical process. After the cyclic voltammetry experiment and the evaluation of these parameters, students should



Figure 3. Relationship between the peak potential separation (Δ Ep) and the scan rate of the cyclic voltammetry for (A) dopamine and (B) [Ru(NH₃)₆]³⁺.

have a better knowledge of electrochemical reactions or be able to compare the kinetics between two model species.

The electroactive area of the electrode can be estimated using the Randles-Sevcik equation:

ip =
$$(2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$

where ip is the peak current intensity (A), *n* is the number of electrons transferred in the electrochemical reaction, *A* is the electrode area (cm²), *C* is the bulk concentration of the analyte (mol/cm³), *D* is the diffusion coefficient of the analyte, and *v* is the scan rate (V/s). Representing the peak current versus the root of the scan rate, a straight line is obtained for a diffusion-controlled process, as previously described. The slope of the plot can be used to estimate the electroactive area knowing the rest of the parameters (diffusion coefficient, number of electrons, concentration, ...). The data from the [Ru-(NH₃)₆]^{3+/2+} species were employed since it is a reversible system with better electroactive area was 0.08 ± 0.01 cm². This value is lower than the geometric area of the electrode (0.125 cm²) as it is likely that part of the carbon

surface is passivated or not available for the electroactive species and does not participate in the electron transfer. It would be interesting to describe to the students the fabrication material of SPCEs (carbon powder, nonelectroactive polymers) and the surface structure (rough, nanoparticulate-like), and they should discuss different possibilities that match the electroactive area experimentally obtained (in comparison to the geometric area).

Another interesting parameter to evaluate is the double layer capacitance. As described in the Supporting Information, the electroactive species do not produce an effect on this parameter, but it is mainly due to the electrolyte and electrode used. However, the applied potential has a strong influence on the Cdl, and this potential depends on the electroactive species being studied. For that reason, the Cdl was evaluated in the same electrolytic medium (0.1 M KCl) but at potentials near the formal potential of the studied systems. Cyclic voltammograms for 0.1 M KCl applying the same potential sweep as for the electroactive species at several scan rates were recorded. The capacitive currents measured at +0.29 and -0.24 V for dopamine and $[Ru(NH_3)_6]^{3+}$, respectively, were represented against the scan rate (see Figure 4B). The value of the double layer capacitance was obtained employing the slope of each plot and solving the following equation:

ic = ACdlv

where ic (μ A) is the capacitive current, A (cm²) is the electrode area, Cdl (μ F/cm²) is the double layer capacitance, and ν (V/s) is the scan rate of the cyclic voltammetry. Cdl values of 5.3 and 14.7 μ F/cm² were obtained for potentials at +0.29 and -0.24 V, respectively. These results confirm that the applied potential influences the Cdl and, therefore, the capacitive current.

As a general summary, a list of the different electrochemical parameters estimated in this lab experiment for the two redox species and values found in the literature is shown in Table 2. For dopamine, the literature values were obtained in a 0.1 M H₂SO₄ solution,¹⁵ while that for RuHex were also obtained in 0.1 M KCl and found in two different references.^{16,17} Students could add this summary to the report, encouraging the discussion and comparison with their own results.

Analytical Evaluation of the Electroactive Species

To show the analytical application of the electrochemical techniques, students carried out a calibration plot for $[Ru(NH_3)_6]^{3+}$ and for dopamine using different voltammetry techniques. Moreover, dopamine concentration was determined in a real sample by the standard addition method. If students have a good background in analytical chemistry, they should perform this experiment on their own as much as possible. They should solve the problems arising, encouraging the discussion between the different groups and helping when necessary. Students should discuss why DPV and SWV are used for the two analytes, according to the results obtained with cyclic voltammetry (reversibility) and the excitation waveform of these techniques.

First, a calibration plot for $[Ru(NH_3)_6]^{3+}$ was carried out using SWV technique. SWV was employed due to the higher reversible character of this electrochemical process. For

Table 1. Values for the Ratio	o <i>in /in</i> vorsus the Sc	an Rate for [Ru(NH)] $^{3+/2+}$	and Donamine Processes
Table 1. values for the Ratio	p_a/p_c versus the SC	an Kate for $[Ku(INH_3)_6]$	and Dopannie Processes

ip _a /ip _c	10 mV/s	25 mV/s	50 mV/s	75 mV/s	100 mV/s	250 mV/s	500 mV/s
$[Ru(NH_3)_6]^{3+/2+}$	-0.82	-0.85	-0.88	-0.89	-0.90	-0.96	-0.96
Dopamine	-1.45	-1.63	-1.54	-1.54	-1.45	-1.40	-1.32



Figure 4. (A) Relationship between the dimensionless function and the reciprocal of the square root of the scan rate for dopamine. (B) CVs at different scan rates for 0.1 M KCl at the formal potential of $[Ru(NH_3)_6]^{3+/2+}$ and relationship between the capacitive currents and the scan rate.

 Table 2. Values for the Different Parameters Estimated in

 This Lab Experiment and in Some Literature References

Parameters	Redox Species	This Work	References ^a		
$\begin{array}{c} \Delta Ep \ (50 \ mV/s) \\ (mV) \end{array}$	$[Ru(NH_3)_6]^{3+/2+}$	74	59		
	Dopamine	360	295		
$E^{\circ\prime}$ (mV)	$[Ru(NH_3)_6]^{3+/2+}$	-238	-252		
	Dopamine	+291.4	+183		
$k^0 (\mathrm{cm/s})$	$[Ru(NH_3)_6]^{3+/2+}$	1.6×10^{-3}	1.1×10^{-3}		
	Dopamine	1.15×10^{-4}	3.6×10^{-4}		
$A (cm^2)$	$[Ru(NH_3)_6]^{3+/2+}$	0.08 ± 0.01	0.114		
	Dopamine	-	0.074 ± 0.005		
Cdl (μ F/cm ²)	$[Ru(NH_3)_6]^{3+/2+}$	14.7	-		
	Dopamine	5.3	26		
^{<i>a</i>} The reference values were found in refs $15-17$ for dopamine in 0.1 M					

 H_2SO_4 and for $[Ru(NH_3)_6]^{3+/2+}$ in 0.1 M KCl.

different concentrations of $[Ru(NH_3)_6]^{3+}$ in 0.1 M KCl solutions, square wave voltammograms were performed (cleaning the SPCE between each measurement; each concentration was measured by triplicate using three different SPCE). With the use of the cathodic peak current as analytical signal, the equation of the calibration plot obtained for $[Ru(NH_3)_6]^{3+}$ was *i* (μ A) = 82.8 [$[Ru(NH_3)_6]^{3+}$] (mM) + 0.2; $R^2 = 0.9998$ (Figure 5A), and the linear range was 0.005–0.500 mM. It is important from an analytical point of view that the students calculate the limit of detection (LOD), the limit of quantification (LOQ), the repeatability, and the reproducibility. LOD and LOQ were calculated according to the following equations: LOD = $3s_b/m$ and LOQ = $10s_b/m$, where *m* is the

slope of the linear range of the corresponding calibration plot, and s_b was estimated as the standard deviation of the intercept. The values obtained for this analyte using SWV were, respectively, 4.8 and 16.1 μ M. To calculate the repeatability, 6 square wave voltammograms of a 0.1 mM $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in 0.1 M KCl solution were performed using the same electrode (cleaning the SPCE between each measurement). The reproducibility was calculated performing SWV of a 0.1 mM $[\text{Ru}(\text{NH}_3)_6]^{3+}$ solution, using 6 different electrodes. The values for repeatability and reproducibility achieved were 1.8% and 2.1%, respectively.

In the case of dopamine, a calibration plot was carried out by DPV technique. Differential pulse voltammograms were recorded for different concentrations of dopamine in a 0.1 M KCl solution (each concentration was measured by triplicate). In this case, the anodic peak current was chosen as the analytical signal. The equation of the calibration plot obtained was $i (\mu A) = 7.58$ [Dopamine] (mM) - 0.03; $R^2 = 0.9990$ (Figure 5B), and the linear range was 0.01-1.00 mM. The LOD and LOQ calculated were 0.03 and 0.09 mM, respectively. The values obtained for the repeatability and reproducibility were 1.6% and 3.1%, respectively.

For the determination of dopamine by the standard addition method, 12 solutions were prepared with dopamine additions as the Experimental Section indicates, and measured by DPV. With the use of the anodic peak as analytical signal, a calibration plot with the following equation is achieved: $i (\mu A) = 3.8$ [dopamine] (mM) + 1.0; $R^2 = 0.997$ (Figure 5C). With this equation and considering how the solutions with analyte



Figure 5. Calibration plot for $[Ru(NH_3)_6]^{3+}$ in 0.1 M KCl by SWV (A) and for dopamine in 0.1 M KCl by DPV (B). Calibration plot for dopamine determination by standard addition method (C).

additions were made, the dopamine concentration calculated in the sample was 0.53 \pm 0.03 mM.

LAB DISCUSSION

This practice is adequate for four-year undergraduate or master students. To evaluate the students, they should prepare a lab report explaining the calculations made and the experimental results obtained in a critical way. Students may have errors in the solution preparation and calculations, and therefore, the final results may not be the expected ones. Special care must be taken in these steps. The information explained in the Student Handout may be enough to help students to prepare the lab report, but other bibliographic information should be provided. In general, students feel that the experimentation is simple (plug-and-play instrumentation), and that the lab helps to study some electrochemical concepts in an easier way than only with lectures, and in a short period of time. Students learned to use cyclic voltammetry to calculate kinetic and thermodynamic parameters of an electrochemical reaction (which usually is only performed in specialized courses). Concepts like the reversibility of an electrochemical reaction and its difference with the reversibility of a chemical reaction can be easier to explain in an applied way and comparing two different species like in this lab experiment. Students also learned to use the standard addition method when the measuring solution is static. They liked the easy handling of screen-printed electrodes, and how they could perform many measurements in a short time.

CONCLUSIONS

In this lab experiment, using simple and fast cyclic voltammetry measurements, students can relate, apply and understand the equations studied in lectures in order to test theoretical principles with real experimental data. Students also work with other voltammetric techniques (DPV and SWV) and use them for analytical purposes. The determination of an analyte in a real sample using the standard addition method makes the practice more relevant and attractive to the students than if it was only about electrochemistry fundaments, and allows them to be more confident to face future real-world analytical problems. Employing SPEs allows students to focus on electrochemical concepts without wasting time in situations like preparation, cleaning and maintenance of electrodes. In this lab experiment, students can also develop transversal disciplines like group work, correlate theoretical basis with experiments, conduct practical work in an electrochemistry lab, solve problems through experimentation and write a scientific report. As stated in the article, students should be encouraged to discuss and compare the data obtained as much as possible in order to improve the understanding of the electrochemistry concepts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00755.

Notes for instructors and a complete student handout with theoretical introduction (PDF, DOCX)

AUTHOR INFORMATION

Corresponding Author

*E-mail: martindaniel@uniovi.es.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the FC-15-GRUPIN-021 project from the Asturias Regional Government. Daniel Martín-Yerga thanks the Spanish Ministry of Economy and Competitiveness for the award of a FPI Grant (BES-2012-054408).

REFERENCES

(1) Kissinger, P. T.; Heineman, W. R. Cyclic voltammetry. J. Chem. Educ. 1983, 60 (9), 702–706.

(2) Van Benschoten, J. J.; Lewis, J. Y.; Heineman, W. R.; Roston, D. A.; Kissinger, P. T. Cyclic voltammetry experiment. *J. Chem. Educ.* **1983**, *60* (9), 772–776.

(3) Anderson, L. B.; Reilley, C. N. Teaching Electroanalytical Chemistry: Diffusion-controlled processes. J. Chem. Educ. 1967, 44 (1), 9–16.

(4) Tanimoto, S.; Ichimura, A. Discrimination of inner and outersphere electrode reactions by cyclic voltammetry experiments. *J. Chem. Educ.* **2013**, *90* (6), 778–781.

(5) Doña Rodríguez, J. M.; Herrera Melián, J. A.; Pérez Peña, J. Determination of the real surface area of Pt electrodes by hydrogen adsorption using cyclic voltammetry. *J. Chem. Educ.* **2000**, 77 (9), 1195–1197.

(6) Mermet, J.-M.; Otto, M.; Valcárcel Cases, M. Analytical Chemistry: A Modern Approach to Analytical Science, 2nd ed.; Wiley & Sons, 2004.

(7) Amend, J. R.; Stewart, G.; Kuntzleman, T. S.; Collins, M. J. Affordable cyclic voltammetry. *J. Chem. Educ.* **2009**, *86* (9), 1080–1081.

(8) Alberich, A.; Serrano, N.; Díaz-Cruz, J. M.; Ariño, C.; Esteban, M. Substitution of mercury electrodes by bismuth-coated screen-printed electrodes in the determination of quinine in tonic water. *J. Chem. Educ.* **2013**, *90*, 1681–1684.

(9) Alfieri, L.; Nokes-Malach, T. J.; Schunn, C. D. Learning through case comparisons: A meta-analytic review. *Educational Psychologist* **2013**, 48 (2), 87–113.

(10) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2001.

(11) Girault, H. H. Analytical and Physical Electrochemistry, 1st ed.; EPFL Press: Switzerland, 2004.

(12) Compton, R. G.; Banks, C. E. Understanding Voltammetry, 2nd ed.; Imperial College Press: London, U.K., 2010.

(13) Nicholson, R. S. Theory and Application of Cyclic Voltammetry for Measurement of Electrode Reaction Kinetics. *Anal. Chem.* **1965**, 37, 1351–1355.

(14) Swaddle, T. W. Homogeneous versus heterogeneous selfexchange electron transfer reactions of metal complexes: insights from pressure effects. *Chem. Rev.* **2005**, *105*, 2573–608.

(15) Randviir, E. P.; Brownson, D. C.; Metters, J. P.; Kadara, R. O.; Banks, C. E. The fabrication, characterisation and electrochemical investigation of screen-printed graphene electrodes. *Phys. Chem. Chem. Phys.* **2014**, *16* (10), 4598–4611.

(16) Fanjul-Bolado, P.; Hernández-Santos, D.; Lamas-Ardisana, P. J.; Martín-Pernía, A.; Costa-García, A. Electrochemical characterization of screen-printed and conventional carbon paste electrodes. *Electrochim. Acta* **2008**, 53 (10), 3635–3642.

(17) Grimaldi, A.; Heijo, G.; Méndez, E. A Multiple Evaluation Approach of Commercially Available Screen-Printed Nanostructured Carbon Electrodes. *Electroanalysis* **2014**, *26* (8), 1684–1693.