Use of Excel to Obtain Voltammetric Information on Microelectrodes

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Analysis with Microelectrodes Using Microsoft Excel Solver

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Abstract

The use of curve fitting for the analysis and interpretation of voltammetric data obtained while working with microelectrodes is discussed as a useful exercise for introducing students to the principle of problem solving using least-squares curve-fitting techniques. The advantages associated with this approach to data processing over the approach where the limiting current (i_L) alone is used are discussed and its limitations are highlighted.

This technique was applied to the determination of unknown concentrations of ferrocyanide and the most satisfactory recovery of concentrations was found when both the values of the formal potential (E\text{\text{\textsuperscript{\text{\textcircled{f}}} \text{\textcircled{f}}}}) and concentration (C) were varied to match the experimental results with an equation characterizing the current potential curve for a reversible couple. In this case recoveries of 100% ± 5% were obtained for the concentration range 5 \times 10^{-4} to 1 \times 10^{-2} M. It was also found that Solver was unable to fit the equation when the sum of squared residuals was <2 \times 10^{-9}. This technique can be generalized for use with a number of other electrochemical experiments such as polarography, rotating disk electrochemistry, and normal pulse polarography.

Keywords
Analytical Chemistry; Computer Assisted Instruction; Electrochemistry
Considerable interest has been shown in the use of fitting experimental data to nonlinear functions as a means of introducing undergraduate students to the principle of problem solving using least-squares curve-fitting techniques (1–5). The purpose of this article is to demonstrate the use of a least-squares curve-fitting technique for voltammetric analysis. The problem of determining the concentrations of analyte in a solution using linear-sweep voltammetry at a microelectrode is chosen because the degree of experimental difficulty is less than, for example, in polarography, rotating disk electrochemistry, or normal pulse polarography. Furthermore, the limiting current magnitude in each of these techniques has typically been used for chemical analysis. This paper outlines a method which employs the full voltammetric curve to yield analytical information.

The current response obtained by the application of a linear ramp waveform to a microelectrode in a solution of ferrocyanide at a sweep rate of 10 mV/s is shown in Figure 1(•). The height of the plateau corresponds to the limiting current ($i_L$), which is proportional to the concentration of the analyte in solution. However, a problem arises in the determination of $i_L$ because only rarely is the limiting current plateau parallel to the baseline. Extrapolating the tails of the trace and measuring the perpendicular distance between them is another option, but again, a problem arises if the tails are not parallel. These conditions introduce an element of subjectiveness into the determination of $i_L$. This problem also arises in other voltammetric methods, for example, polarography, rotating disk electrochemistry, and normal pulse polarography (6–8).

Microelectrodes were employed in this work as a model for other voltammetric techniques because they are safer to use with microelectrodes using Microsoft Excel Solver

The figures in cells A1 to E1 and A2 to B2 are experimental parameters and constants, which must be entered by the student, and row 3 consists of a series of labels. A typical set of experimental parameters and constants corresponding to the conditions detailed in the experimental section are included in the figure legend. Columns A and C are filled by importing experimental data for potential and current, respectively. The model values (column B) are generated by entering the following equation in cell B4:

$$F = \frac{4nF_D C}{1 + \exp\left(nF_E - E^0\right)}$$

The Edt-­+Fill-­Down command is then used to create the column of data. Column D contains a list of the square of the residuals between each pair of model and experimental current data points and the number in cell E4 is the sum of squared residuals (SSR). This is the value which Solver will attempt to minimize during the curve-fitting process. Either a single variable, $C$, or two variables, $C$ and $E^0$, can be optimized during this operation. At this stage the simulation is a straightforward procedure and could be included in the practical as an introductory exercise in program writing for the student. Once these columns of data have been generated, Solver is activated (1, 11).

With microelectrodes the currents involved tend to be quite small, typically nanoamps. Original attempts to fit the experimental and theoretical data sets for these experiments gave unsatisfactory results, Solver failing to fit the data sets perhaps because it was unable to process the small numbers involved. To overcome this problem both the theoretical and experimental data sets were multiplied by a factor of 10⁶. This enhanced the performance of the curve fitting to an acceptable level. On further investigation it was found that Solver was unable to function when the value of the SSR fell below 2.10⁻⁹.

Figure 1(a) shows the current profiles corresponding to the experimental data in Figure 2, Figure 1(b) is the current profile produced by the model before fitting with an initial guess by eye of the value of $C$ of 4 x 10⁻⁶ moles cm⁻³, and Figure 1(c) is the current profile returned by the model on completion of the fitting process. For the reason outlined above, both the theoretical and experimental data sets were multiplied by a factor of 10⁶ before activation of Solver. In
this example both $C$ and $E^\circ$ are variable parameters. From the
answer report it was seen that the SSR was reduced from
425.18 to 3.37 and that a value for $C$ of 4.94 x 10^4 M was
returned. This is a recovery of 98.8% on a standard concen­
tration of 5.00 x 10^3 M [Fe(CN)_6]^{4-}. The constraints that
were applied to the operation of the fitting process were
chosen to prevent Solver from returning a negative value for
concentration or formal potential.

To test the validity of this technique, a series of solutions
of known concentration was prepared and analyzed using this
method. Table 1 contains the nominal concentrations of the
standard solutions ($C$) and the concentrations returned by
Solver ($C'\prime$). The percentage recovery is also quoted and serves
as a measure of the correlation between the data sets.

It can be seen that the concentration values returned by
Solver correlate well with the nominal concentrations over
the range 1 x 10^-2 M to 5 x 10^-4 M. However, at lower concen­
trations the correlation becomes less satisfactory. Noise,
although present in all the traces, becomes a problem at lower
currents because it alters the overall shape of the trace, as can
be seen in Figure 3. Below concentrations of 5 x 10^-4 M the
experimental trace deviates from the sigmoidal shape and
the model is unable to compensate for this. Obviously this
greatly affects the ability of Solver to fit the experimental and
theoretical data sets and therefore affects the accuracy of the
results. The presence of this noise is a limitation of the
model and not the ability of the potential to be fitted. In this
work and there appears to be no reason why lower concentra­
tions could not be analyzed with the aid of a more noise-free
system.

It was also found that fitting the experimental and
theoretical data sets by allowing Solver to simultaneously vary
the values of $C$ and $E^\circ$ (the formal potential) resulted in
concentration values closer to the nominal values than those
obtained by varying only $C$, as can be seen in Table 1.
In this way the information contained in the full sigmoidal
shape is employed to yield an answer, rather than just the
limiting current. The value of fitting the model with two vari­
ables can be clearly seen. Students should be encouraged to
fit the curve with $C$ and then with $C$ and $E^\circ$.

It is possible therefore to use curve-fitting techniques as
a means of determining unknown concentrations for a
reversible system to a high degree of accuracy, the limits of
quantitation being governed by the presence of noise in the
system. Any one or a combination of the other variables in
the model can be determined in a similar fashion. This
application of curve-fitting techniques using Microsoft Excel
Solver provides a useful method of introducing students to
this concept through practical experience. This method can
also be adapted for use as an analytical tool with other
voltammetric techniques such as polarography, rotating disk
electrochemistry, and normal pulse polarography, substitution
of the appropriate expression for the limiting current being
the only modification required.

Experimental Details

Solutions of $K_4[Fe(CN)_6]$ were prepared in 0.1 M KCl. All
solutions were degassed before collecting data, and a positive
nitrogen pressure was maintained over the cell during voltam­
metric analysis. A three-electrode one-compartment cell with
SCE as reference and a carbon rod auxiliary was employed
and an EG&G M394 system was used to acquire data. The

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    tals and Applications; Wiley: New York, 1980; p 159.
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Figure 1. Current profiles corresponding to (a) experimental data, where microelectrode radius = 2.53 x 10^-3 cm, sweep rate = 10 mV s^-1, concentration of [Fe(CN)₆]⁴⁻ = 5 mM in 0.1 M KCl; (c) theoretical data set from Fig. 2 after the fitting process has been completed; and (d) theoretical data set from Fig. 2 before activating Solver. Prior to fitting, a value of 4 x 10^-3 M was used in the model for the concentration of [Fe(CN)₆]⁴⁻.

Figure 2. Typical layout of the Excel spreadsheet before activating Solver. Typical values for experimental parameters and constants are n = 1, F = 96.487 C mol⁻¹, r = 2.53 x 10^-3 cm, D = 6.5 x 10^-6 cm² s⁻¹, C = unknown, E° = 0.15 V, nF/RT = 39.608. Columns B and C are multiplied by a factor of 10⁹ to improve the quality of the fitting process.

Table 1. Comparison of Standard Concentration Values with Values Returned by Solver

<table>
<thead>
<tr>
<th></th>
<th>Only C Varied</th>
<th>Bath C and E° Varied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. / mol dm⁻³</td>
<td>Conc. / mol dm⁻³</td>
<td>Recovery (%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>9.86 x 10⁻³</td>
<td>98.6</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>4.86 x 10⁻³</td>
<td>97.2</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>1.06 x 10⁻³</td>
<td>100</td>
</tr>
<tr>
<td>5 x 10⁻³</td>
<td>5.12 x 10⁻³</td>
<td>102.4</td>
</tr>
<tr>
<td>1 x 10⁻²</td>
<td>2.22 x 10⁻⁴</td>
<td>45.0</td>
</tr>
</tbody>
</table>

*Calculated as (value returned by Solver/standard concn) x 100. This is a measure of the correlation between the calculated and real concentrations.