Determination of an Unknown: Measuring Acetaminophen using Cyclic Voltammetry

This experiment is designed as an approachable introductory experiment for students to learn the linear relationship between current and concentration in cyclic voltammetry experiments.

Estimated Time

We estimate that this experiment can be completed in one three-hour class period.

Tips

1. In the Electronic Resources you will find PDF and word-processing files of the student experiment. You can print the PDF, distribute it to students electronically, or post the file to a password-protected class web page or learning management system. Edit the word-processing file if you would like to tailor the experiment to suit your equipment and students. Sign in to your account at **www.vernier.com/account** to access the Electronic Resources.

2. Due to the pH-dependent electrochemical behavior of acetaminophen, it is important to consider the buffer provided to the students. For best results, use a slightly alkaline buffer solution because acetaminophen maintains its electrochemical reversibility at higher pH. Additionally, use a buffer that is free of significant redox peaks in the potential region where acetaminophen undergoes redox reactions (from –0.5 V to +1.0 V). Borate buffers meet this criteria well and are recommended for this experiment.
   a. Contact lens rinsing and storage solution serves as an consumer product for borate buffer solutions. This ready-to-use borate buffer is available in most drug stores. Look for brands that contain the ingredients: boric acid, sodium borate, and sodium or potassium chloride. A small amount of preservative such as edetate disodium (also known as EDTA) has negligible effects, but other additives, such as polymers containing ethylene diamine, tend to give interfering oxidation peaks located in the same potential region as that for acetaminophen (e.g., Equate Lens Cleaner: Multi-Purpose Solution, purchased from Wal-Mart).
   b. Alternatively, you can prepare a borate buffer with sodium tetraborate decahydrate (borax, $Na_2B_4O_7 \cdot 10H_2O$, MW 381.37 g/mol). Dissolving sodium tetraborate in water produces a buffer of pH ~9.24 (first pKa of boric acid, H_3BO_3).

3. To prepare the sample with an unknown concentration of children's acetaminophen medication suspension:
    a. Due to the viscosity of the sample, it is recommended that you weigh the medication sample during the preparation of the stock solution and calculate the sample volume using its density. The density of the children's Tylenol® is typically 1.31 g/mL. The acetaminophen concentration in the suspension is about 32 g/L.
    b. To prepare 100 mL of a 10 mM children's medication stock solution, weigh out 6.2 g of the children's medication suspension into a 100 mL volumetric flask and dilute to the mark with buffer. Make sure you record the exact mass, you will want to give the value to students so they can compare their experimentally determined value with the known value.
    c. This stock solution is too high for optimal measurements using cyclic voltammetry. You will need to prepare a 1:10 dilution of this stock solution and give it to students. Each student needs about 30 mL of the diluted sample. To prepare 500 mL of this sample, dilute 50 mL of the stock solution to 500 mL with buffer solution in a volumetric flask.

4. If students get a signal greater than 2 mA for their 0.0 mM buffer solution, replace the SPE with a new one.

5. It is prudent to try this experiment with the solutions you have prepared ahead of giving the solution to your students to ensure proper concentrations and experimental parameter setting. Modify the student procedure if necessary.

6. Here are some generic troubleshooting tips if the voltammogram has additional peaks or if signal saturation occurs:
    a. While testing your solution before giving it to the students, make sure the recommended parameters in the Student instructions are still appropriate. You may want to modify the Switching Potentials.
    b. Particularly when using acetaminophen suspension samples, it is common for the electrode to get fouled due to additives like colors, flavors, and suspension stabilizers. A fouled electrode cannot accurately quantify the acetaminophen concentration because the effective electrode area decreases. If you or your students start to see irregular peaks, it is best to replace the SPE with a new, unused SPE.
    c. Students have a tendency to wipe the SPE surface too hard. This can also lead to issues with the voltammogram. If students are measuring solutions from least concentrated to most concentrated, they can omit this step.
    d. If the voltammogram stops plotting in the middle of a run, it is likely that your sample is too concentrated, dilute your sample and rerun.
    e. If your voltammogram is too noisy, consider changing the current setting in the parameters.

Hazard Alerts

The chemical safety signal words used in this experiment (DANGER and WARNING) are part of the Globally Harmonized System of Classification and labeling of Chemicals (GHS). Refer to the Safety Data Sheet (SDS) that came with the chemical for proper handling, storage, and disposal information. SDS can also be found online from the manufacturer.

Acetaminophen, solid, $CH_3CONHC_6H_4OH$: **WARNING**: Acute toxicity, oral. Harmful if swallowed. Do not eat, drink or smoke when using this product. Skin and serious eye damage, corrosion or irritation. Causes skin and serious eye irritation. May cause respiratory irritation. Product should be treated as a chemical and is not for consumption as it has been stored with other non food grade chemicals. Store in a locked poison cabinet.

Answer to Pre-Lab Activity

Use $M_1V_1 = M_2V_2$ to answer this activity in serial dilution calculations.

M_1 (mM)	V_1 (mL)	M_2 (mM)	V_2 (mL)
1.0	8.0	0.8	10.0
0.8	7.5	0.6	10.0
0.6	6.7	0.4	10.0
0.4	5.0	0.2	10.0

1. To prepare 10 mL of a 0.8 mM solution from the 1.0 mM acetaminophen stock solution, pipet 8.0 mL of 1.0 mM stock solution into a small beaker or vial. Then pipet 2.0 mL of additional buffer into the same small beaker or vial and mix.

2. To prepare 10 mL of a 0.6 mM solution from the 0.8 mM acetaminophen solution, pipet 7.5 mL of 0.8 mM solution into a small beaker or vial. Then pipet 2.5 mL of additional buffer into the same small beaker or vial and mix.

3. To prepare 10 mL of a 0.4 mM solution from the 0.6 mM acetaminophen solution, pipet 6.7 mL of 0.6 mM solution into a small beaker or vial. Then pipet 3.3 mL of additional buffer into the same small beaker or vial and mix.

4. To prepare 10 mL of a 0.2 mM solution from the 0.6 mM acetaminophen solution, pipet 5.0 mL of 0.6 mM solution into a small beaker or vial. Then pipet 5.0 mL of additional buffer into the same small beaker or vial and mix.

Data Table

Acetaminophen concentration in solution (mM)	Peak current (µA)
0.00	1.7
0.20	14.6
0.40	27.7
0.60	40.3
0.80	52.7
1.00	64.5
unknown	24.9

Sample Voltammograms
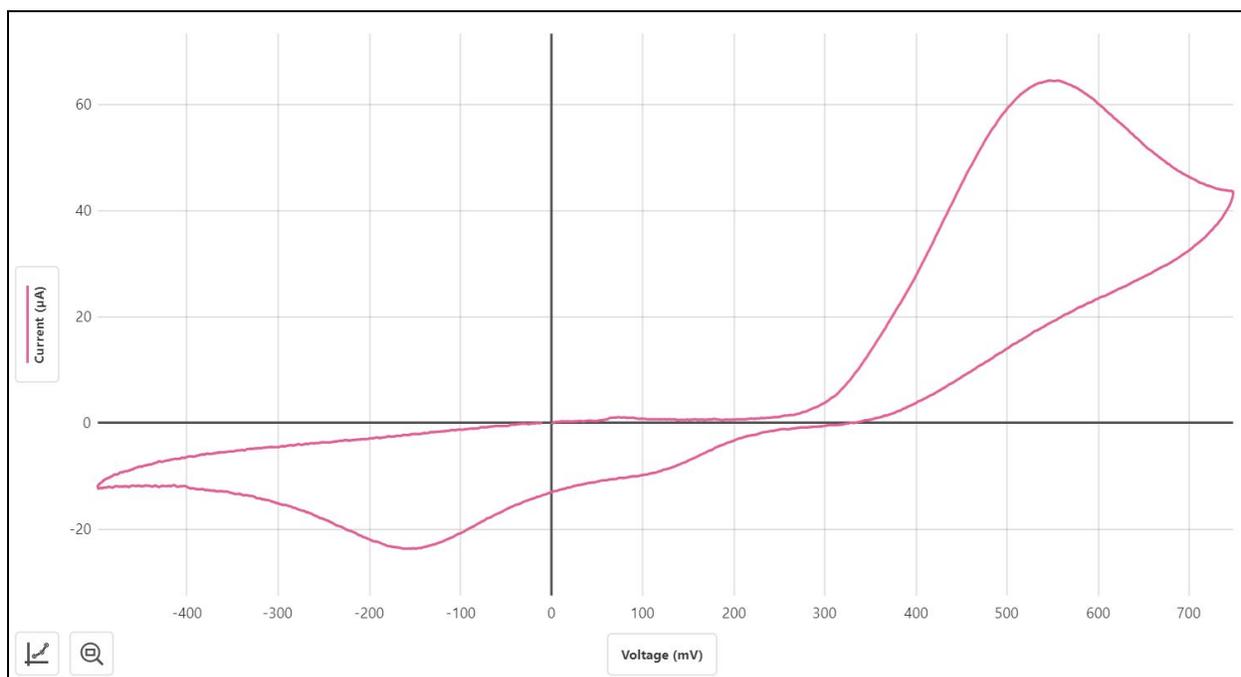
Figure 1 CV of 1.0 mM acetaminophen solution
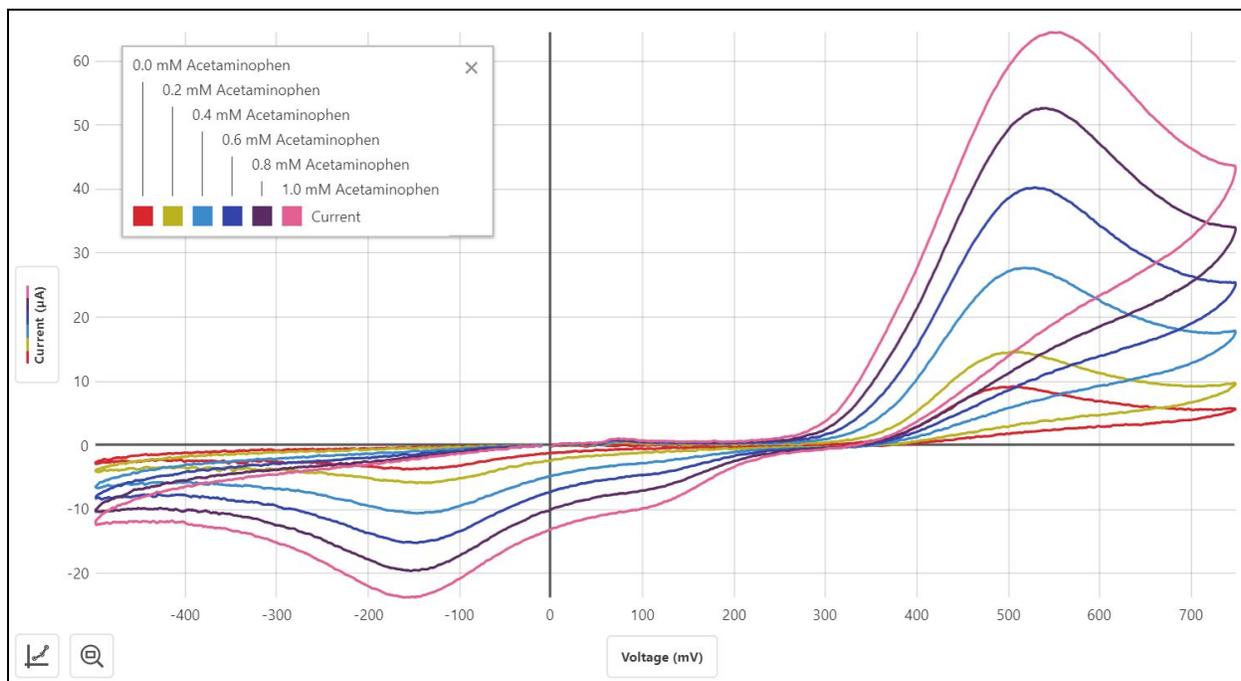
*Figure 2 CV of all acetaminophen standard solutions*
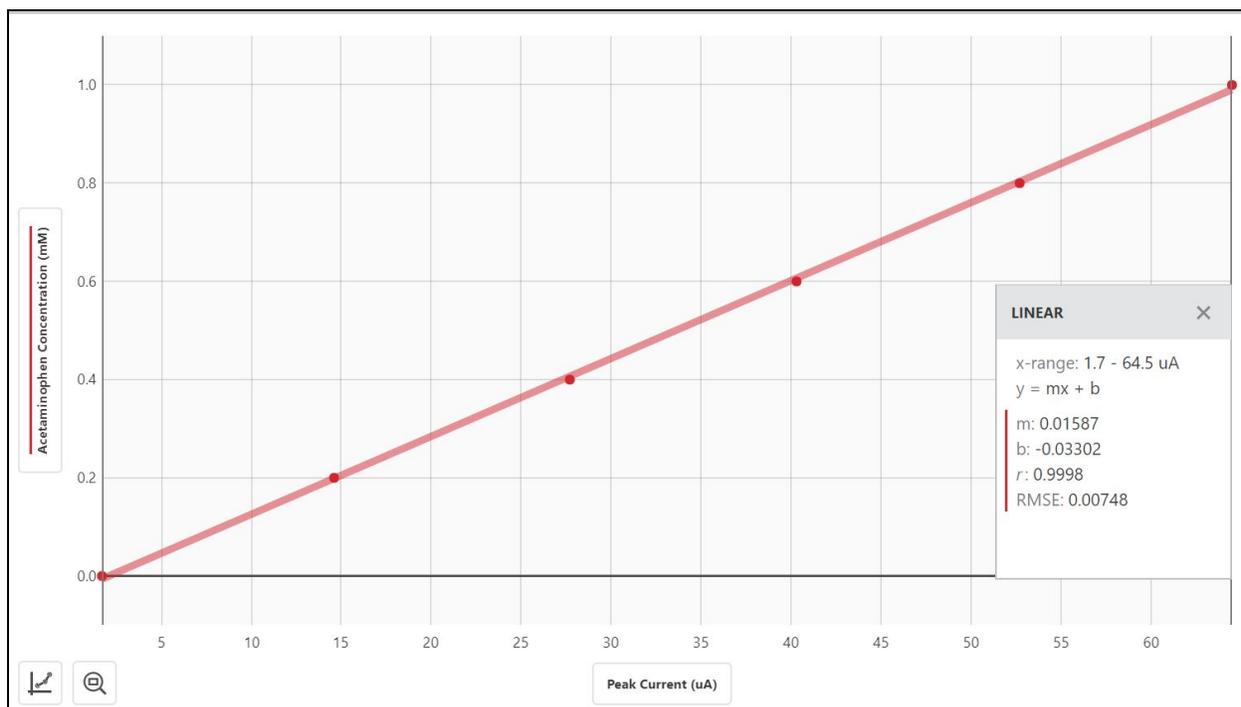
*Figure 3 Calibration curve of acetaminophen standards*
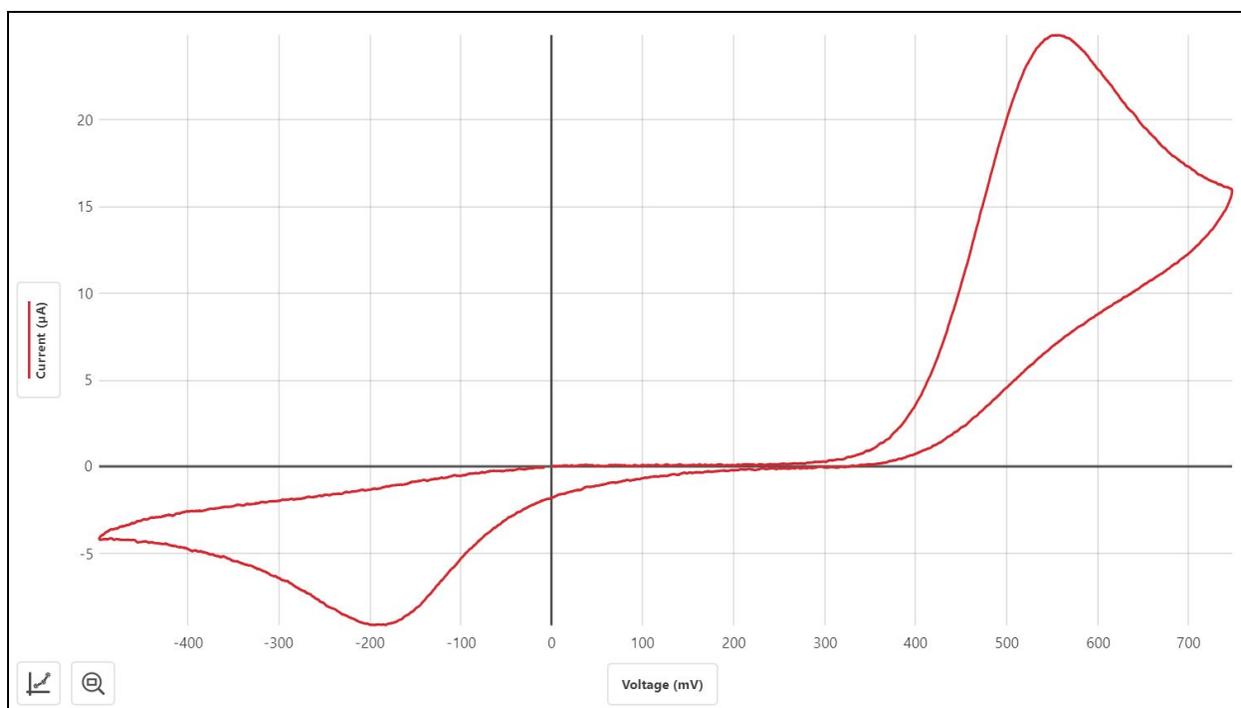
Figure 4 CV of unknown children's Tylenol sample

Answers to Analysis Questions

1. See Figure 3.

2. From Figure 3, the calibration curve is y = 0.01587 x + (–0.033)

   The observed peak current of the children's Tylenol sample is 24.88 µA. Using this value for x, the concentration of the unknown sample is calculated to be 0.36 mM. To take into account the dilution of this sample by an overall factor of 400,
   3.6×10^{-4} M × 400 = 0.144 M

3. The observed peak current is 64.5 µA. By definition, 1 ampere = 1 coulomb/second. Thus, the observed peak current can equivocally be written as 64.5 µC/sec. With Faraday's constant, 96485 C/mol, Avogadro's number, 6.022×10^{23} electrons/mol, and careful attention to units, the current flow is calculated to be 4.03×10^{14} electrons/s.

   This is chemically equivalent to oxidizing 2.02×10^{14} molecules of acetaminophen per second (since two electrons are removed per acetaminophen molecule).

   64.5×10^{-6} C/s × $1/(96485$ C·mol$^{-1})$ × 6.022×10^{23} electrons/mol = 4.03×10^{14} electrons/s

4. Answers will vary based upon experimental data and concentration of acetaminophen in the commercial medication solution. The first step is to convert the manufacturer label to units of molarity. Our sample data was collected with 110 mg acetaminophen per 5 mL.

0.110 g × (1 mol / 151.163 g) × (1 / 0.005 L) = 0.145 mol/L

From question 2 above, we determined 0.144 M as the experimental concentration of acetaminophen. Therefore, we can calculate the percent error:

((0.144 M – 0.145 M) / 0.145 M) × 100% = 1% error

Depending on the number of trials collected in this laboratory, this is an excellent opportunity to introduce some statistical analyses, such as confidence intervals.

Extension
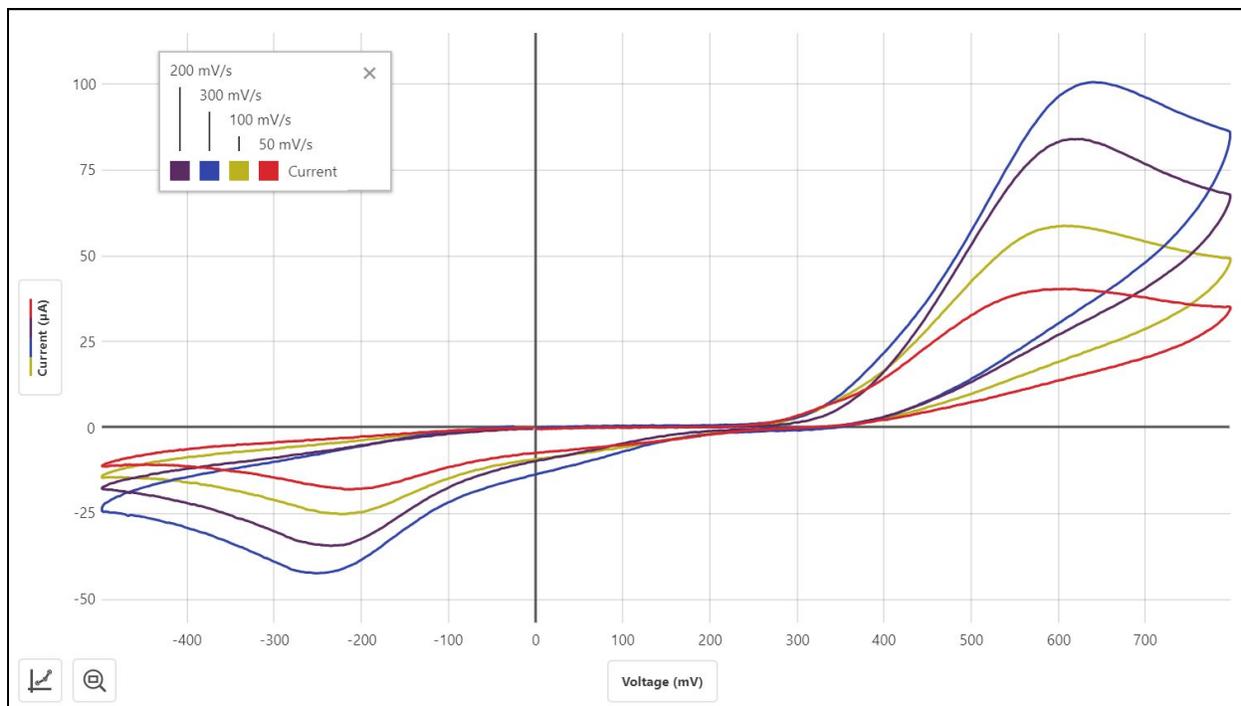
Figure 5 CV with varied scan rates of 1.0 mM acetaminophen standard

Sweep rate (mV/s)	Peak current (µA)
0	0.5
50	40.38
100	58.79
200	84.00
300	100.58

The relationship between sweep rate and peak current is described via the Randles-Sevcik equation:

$$i_{pc} = 2.69 \times 10^8 \; n^{3/2} \; A \; D^{1/2} \; \nu^{1/2} \; C$$

where, i_{pc} = peak current in A; n = number of electrons involved; A = electrode area in m^2; D = diffusion coefficient in m^2/s; C = concentration in mol/L; and ν = scan rate in V/s

Students can graph the sweep rate *vs.* peak current and fit a power equation to the data to discover the square root relationship as shown in Figure 6.
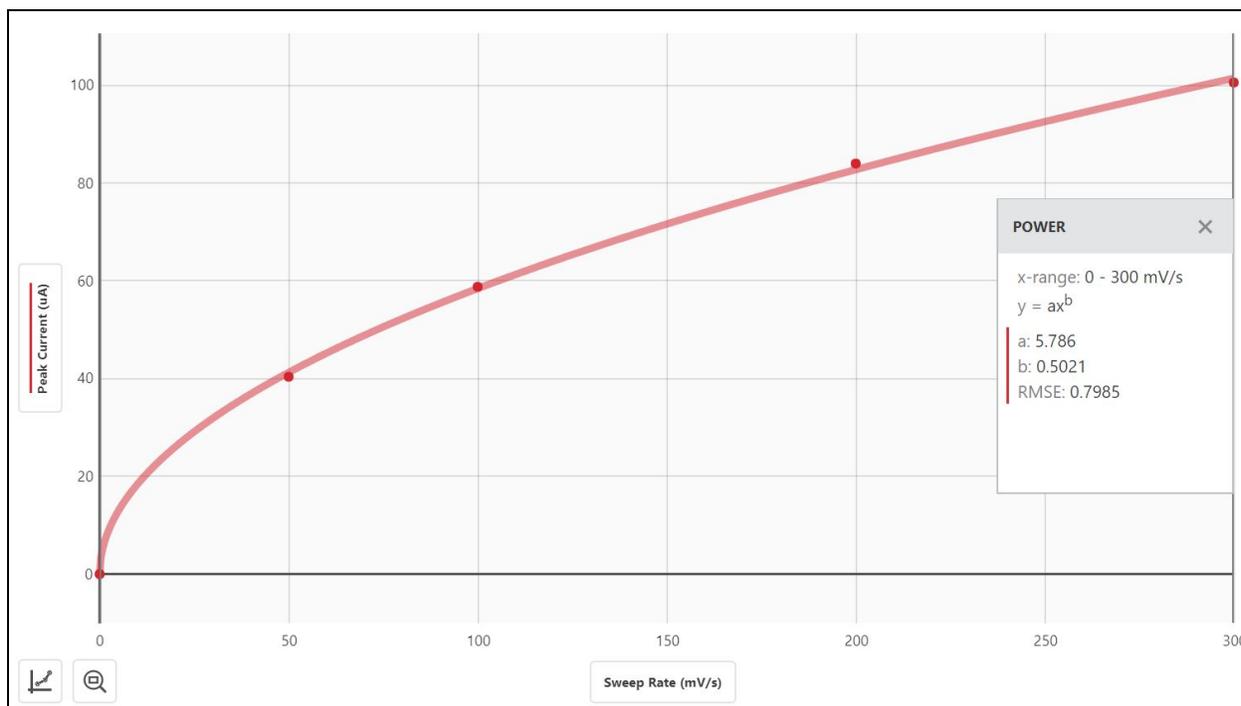

Figure 6 Sweep rate vs. peak current with power equation fit of acetaminophen