EXPERIMENT 6
COULOMETRIC AND AMPEROMETRIC TITRATION OF ARSENIC
(2008)

Coulometric analysis is the technique of determining the quantity of a substance by measuring the quantity of electricity required to effect its complete reaction in an electrolysis cell. In one form of coulometry, the analyte is selectively oxidized or reduced at constant potential and the total charge passed when all of the analyte has been consumed is recorded. However, in a coulometric titration, charge is usually added at a constant rate (constant current) and some external means is used to determine the end point of the reaction. The analyte is oxidized or reduced directly by an electrode in a primary coulometric titration. In a secondary coulometric titration, which is the most commonly used type, the analyte reacts with another substance generated by an electrode. The present experiment involves a secondary coulometric titration.

In this experiment, a solution of As$_2$O$_3$ will be titrated with electrochemically generated I$_2$. The quantity of I$_2$ used can be calculated very precisely from the charge passed during the titration, using Faraday’s law. The equivalence point for the I$_2$ titration will be determined using starch as an indicator in Part II, and by an amperometric method employing two Pt polarizable electrodes in Parts I and III. Generally in coulometric titrations, any of the methods used to determine the equivalence points in conventional titrations (indicators, spectrophotometry, potentiometry, etc.) can be used. The amperometric method can also be applied to conventional titrations, as demonstrated in Part I of this lab.

Part I. Amperometric Titration of As$_2$O$_3$ with I$_2$ [2.5 marks].

1. Prepare 100 mL of a standard I$_2$ solution using 0.07 g of accurately weighed KIO$_3$ (primary standard) dissolved in water (ca. 20 mL), 50 mL of 0.1 M KI and 20 mL of 0.5 M H$_2$SO$_4$.

2. Put 50 mL of 0.25 M Na$_2$HPO$_4$ solution into a 150 mL beaker.

3. Put the beaker on a magnetic stirrer and arrange the Indicating electrodes so that they do not impede the stirrer bar. You will be shown how to connect the electrodes and set-up the Cypress System to record the data. Two small Pt electrodes (the Indicating electrodes) with a constant potential difference (200 mV) between them will be used to follow the course of the titration. The current flowing between the indicating electrodes will be recorded as a function of the volume of titrant. The current will rise sharply immediately after the equivalence point.

4. Use the mouse to obtain the main menu and select chronoamperometry.
   Set Parameters at:
   
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial E(mV)</td>
<td>-200</td>
</tr>
<tr>
<td>forward step E</td>
<td>-200</td>
</tr>
<tr>
<td>Reverse step E</td>
<td>-200</td>
</tr>
<tr>
<td>Step width (ms)</td>
<td>300,000</td>
</tr>
</tbody>
</table>
Current range 100 : A
Noise filter (us) 55,000

5. Add 5.000 mL of the \( \text{As}_2\text{O}_3 \) solution using a pipet, turn on the stirrer and cell, and titrate. Add the \( \text{I}_2 \) solution in aliquots of ca. 1 mL and record the current (shown at the bottom left of the screen) in your notebook after each addition. Switch to ca. 0.1 mL additions as you pass through the equivalence point (estimated from a rough titration) and record at least 5 points beyond the eq. pt. Turn the cell off and empty and wash the cell. Determine the equivalence point from a plot of the current vs the volume of \( \text{I}_2 \) solution.

6. Repeat to obtain 3 good results.

7. Calculate the average concentration of the \( \text{As}_2\text{O}_3 \) based on the 3 best titrations. Report the standard deviation, relative standard deviation, and the 95% confidence limits.

**Part II. Coulometric Titration of \( \text{As}_2\text{O}_3 \) with Electrochemically Generated \( \text{I}_2 \) [2.5 marks].**

1. Put 75 ml of 0.1 M \( \text{KI} \) solution, 75 ml of 0.25 M \( \text{Na}_2\text{HPO}_4 \) solution and 10 drops of starch indicator into a 250 ml beaker.

2. Put the beaker on a magnetic stirrer and arrange the Generating and Counter electrodes so that they do not impede the stirrer bar. Two large area Pt electrodes (the generating electrodes) will be used to generate \( \text{I}_2 \) at a constant rate. At the enclosed counter-electrode hydrogen, \( \text{H}_2 \), will be generated and allowed to escape from the apparatus.

3. Add 1.000 ml of the \( \text{As}_2\text{O}_3 \) solution using a pipet, reset the timer on the coulometer and titrate (i.e. press the black button to start the current). The solution should be stirred rapidly throughout the titration. Watch the cathode within the fritted tube - current flow is indicated by vigorous gassing there.

4. Turn off the coulometer as soon as the whole solution becomes blue. Record the time on the clock. (If you over shot the equivalence point, carefully add \( \text{As}_2\text{O}_3 \) to just remove the blue colouration before the next titration)

5. Repeat steps 3 and 4 to obtain three more results (or two more if you are short of time and the first agrees with the second and third).

6. Calculate the average concentration of the \( \text{As}_2\text{O}_3 \) based on the last 3 titrations (the first may be inaccurate because of impurities in the \( \text{KI}/\text{H}_2\text{SO}_4 \) solution). Report the standard deviation, relative standard deviation, and the 95% confidence limits.

**Part III. Coulometric Titration of \( \text{As}_2\text{O}_3 \) with \( \text{I}_2 \) (Amperometric Equivalence Point Detection) [2.5 marks].**

1. Put 75 ml of 0.1 M \( \text{KI} \) solution and 75 ml of 0.25 M \( \text{Na}_2\text{HPO}_4 \) solution into a 250 ml beaker.
2. Put the beaker on a magnetic stirrer and arrange the electrodes so that they do not impede the stirrer bar.

3. You will be shown how to connect the electrodes and set-up the Cypress System to record the data. Two large area Pt electrodes (the generating electrodes) will be used to generate I$_2$ at a constant rate. At the enclosed counter-electrode hydrogen, H$_2$, will be generated and allowed to escape from the apparatus. Two small Pt electrodes with a constant potential difference between them (the indicating electrodes) will be used to follow the course of the titration. The current flowing between the indicating electrodes will be recorded as a function of time (proportional to charge or moles of I$_2$).

4. Use the mouse to obtain the main menu and select chronoamperometry.

Set Parameters at: Initial E(mV) 0
forward step E -200
Reverse step E -200
Step width (ms) 300,000
Current range 5: A
Noise filter (us) 55,000

* Change path to your directory

5. Add 1.000 ml of the As$_2$O$_3$ solution using a pipet.

6. To collect data, use the function keys to turn the cell on and then run. When a constant current is established, reset the clock to zero and press the black button to start the titration. When the end point has been passed (i.e. continuously rising current), stop the titration (press button).

*Note the time on the clock.

7. Add 1 mL of As$_2$O$_3$ solution to the beaker for the next titration and wait for the screen display to finish. Save and plot your data by selecting the options in the utilities menu. Do a total of four titrations (or three if you are short of time and the first agrees with the second and third) using the same KI solution, all with a coulometric current of 10 mA. Use 3mA if the time is too short or 20 mA if too long.

8. Calculate the average concentration of the As$_2$O$_3$ based on the last 3 titrations (the first may be inaccurate because of impurities in the KI/Na$_2$HPO$_4$ solution). Report the standard deviation, relative standard deviation, and the 95% confidence limits.

Note that after each titration the solution contains some excess I$_2$. This can be accounted for by subtracting the titration time of the previous titration, as recorded by the Cypress System, from the total time that current was passed, as recorded by the coulometer.
Questions

1. Write equations for all reactions that occur in all of the titrations (including the formation of the I₂ titrant in Part I) [1 mark].

2. Compare the results from each part of the lab, and discuss the advantages and disadvantages of each method [1.5 marks].