

NAME \_\_\_\_\_

OREGON STATE UNIVERSITY

DEPARTMENT OF CHEMISTRY

## Experiment 5

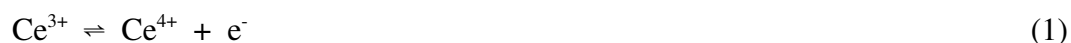
Integrated Laboratory Experiment - CH 461 &amp; CH 461H

**COULOMETRIC TITRATION AND SPECTROMETRIC ENDPOINT DETECTION**

I. Introduction	2
II. Overview of Experiment	3
III. Instrumentation	4
Fig 1 - UV Visible Molecular Absorption Spectrometer Setup	4
Fig 2 - Timer Counter & Electronics Setup	5
IV. Experimental	7
A. Solutions	7
B. Preparation of Instrumentation	7
1. control circuit and constant current source;	7
2. sensor circuit with the PMT;	9
3. coulometry cell with the rest of the circuit	11
C. Determination of Unknown $As_2O_3$	12
Waste Disposal	13
V. Lab Report	14

## I. INTRODUCTION

A coulometric titration is based on Faraday's law which states that 96,486 coulombs of electricity oxidizes or reduces one gram equivalent of an electroactive substance. Thus, for example, ferrous ion can be determined by adding excess cerous ion to the sample solution. The cerous ion is then electrolytically oxidized at an anode



while hydrogen ion is reduced at a shielded cathode



The electrolytically generated ceric ion reacts with the ferrous ion



in a manner analogous to a conventional redox titration.

The advantages of coulometric addition of titrant include:

1. Standard solutions are generated electrolytically rather than by adding them from a buret. Actually, electrical current is a most versatile reagent, and a constant-current supply can be used to generate acids, bases, oxidizing agents, reducing agents, precipitating agents, and complexing agents in almost any strength desired. In other words, the coulomb becomes a primary standard replacing a host of chemical standards.

2. Because reagents may be generated and used on the spot, unstable reagents which are not useful for volumetric work may actually be employed because time for them to decompose or evaporate is considerably decreased. An excellent example of this is the use of chlorine (generated very simply from a saline solution).

3. Ease of micro-addition of reagent. The magnitude of the current (analogous to the concentration of a volumetric reagent) can be set accurately to almost any level, and extremely small quantities can easily be added near the equivalence point. The electric switch takes the place of the stopcock of the buret.

4. Addition of electrons as a reagent causes no dilution which is important in certain cases. Because of the electrical mode of generation, coulometric procedures are ideal for remote operation and for automatic procedures.

## II. OVERVIEW OF EXPERIMENT

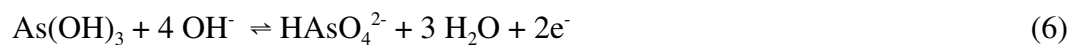
In this experiment, the molarity of an arsenic trioxide ( $\text{As}_2\text{O}_3$ ) solution will be determined by titration with electrochemically generated  $\text{I}_2$ . The reaction is carried out in a buffer with a pH value of about 8.3. When  $\text{As}_2\text{O}_3$  is dissolved, aqueous arsenious acid,  $\text{As}(\text{OH})_3$  is formed according to equation 4.



If an iodide solution is placed in an electrochemical cell and a sufficient potential is applied between the cathode and anode, iodine is generated at the anode by the half-reaction



If some of the arsenite solution is added to this cell, the electrochemically generated  $\text{I}_2$  will oxidize the arsenite to arsenate ( $\text{HAsO}_4^{2-}$ ) through the half-reaction



When all the  $\text{As}(\text{OH})_3$  has reacted, an excess of  $\text{I}_2$  appears. If starch is present in the cell, the excess  $\text{I}_2$  and the starch indicator will form a purple complex. These reactions take place in a buffer with a pH value of approximately 8.3, at which the  $\text{As}(\text{OH})_3$  and  $\text{HAsO}_4^{2-}$  are the primary forms of As(III) and As(V) in solution.

In this experiment, the current passing through the cell is kept constant with a constant current generator and the time for the titration (the time to reach the starch endpoint) is measured. From the known current ( $I$  in amperes) and time ( $t$  in seconds), the charge ( $q$  in coulombs) can be calculated,  $q = I t$ . The number of moles of electrons can be calculated from the charge with Faradays law,  $N_e = q / F$ , where  $F$  is the Faraday constant,  $96485 \text{ C / mol}$ . The moles of reactants and products can then be calculated from the reaction stoichiometry. From the value of  $N_e$  and equations 4 and 6, the number of moles of  $\text{As}_2\text{O}_3$  added to the cell can be calculated.

The starch endpoint can be detected visually to determine at what time to turn off the current generator and the timer. In this experiment, the end point will be detected spectrophotometrically and the signal will be used to turn off the current generator and timer automatically.

### III. INSTRUMENTATION

The purpose of this section is to describe how the instrumentation works. The actual setup procedure is described in the next section.

Diagrams of the optical and electrical instrumentation are shown in Figures 1 and 2, respectively. Spectrophotometric endpoint detection is provided by a UV-visible molecular absorption spectrophotometer (Figure 1). The reaction cell (a 180-mL beaker) will be placed into the sample module so the light beam passes through the cell. Because the sample module lid is not used, the monochromator is placed after the sample module to reject most of the room light.

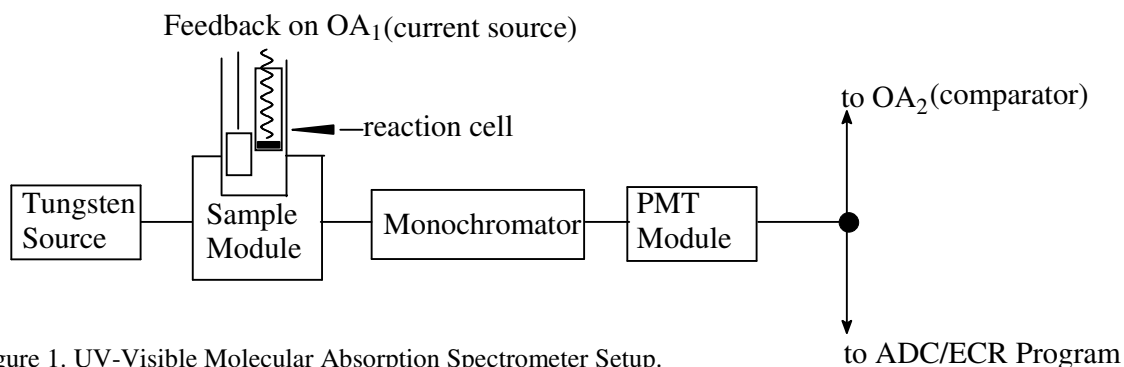


Figure 1. UV-Visible Molecular Absorption Spectrometer Setup.

Figure 2 on the next page illustrates the timer/counter electronic schematic. OA-1 is used to provide a constant current through the reaction cell and OA-2 is used as a comparator. The Timer-Counter module provides a timer with 1/60 of a second resolution and an electrical relay to control the passage of current to the reaction cell.

*Constant-current circuit.* First, consider the circuit involving OA-1 that provides a constant current to the cell. When the switch on the Timer-Counter module is in the TIME (ON) position and the RELAY is in the normally closed (NC) position, the +5 V is transferred from the power supply to the 1000  $\Omega$  input resistor of OA-1 (Point A). Then a current of 5 mA flows through the 1000- $\Omega$  into the summing point of OA-1. An equal current of 5 mA flows through the feedback loop and a current of 5 mA is maintained through the reaction cell (independent of the cell resistance). The exact current, which you will measure, depends on the actual voltage of the supply and the resistance.

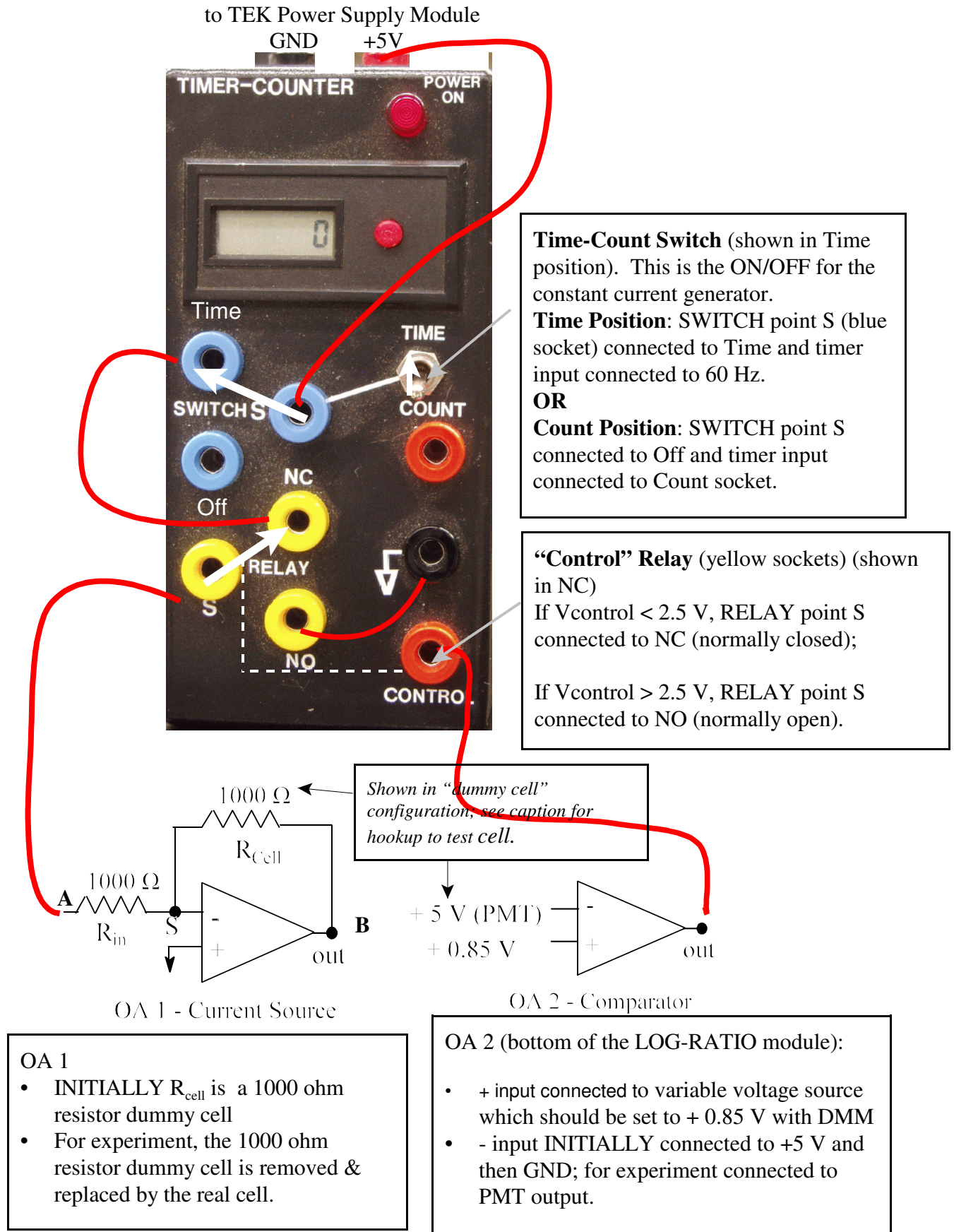


Figure 2. Timer Counter & Electronics setup.

*Comparator circuit.* The voltage output signal of the PMT module is compared to the pre-set voltage from the voltage source. The output of OA-2 is connected to the CONTROL plug of the timer-counter. The photoanodic current is determined by the absorbance of the solution in the reaction cell. At the endpoint of the titration, the formation of the iodine-starch complex causes the absorbance to increase or the transmittance and photodetector signal to decrease. Before the titration begins, the voltage from the PMT module is adjusted so that its output is 0 V for 0% T (shutter closed) and about 1.0 V for 100% T (do not adjust at this time). The voltage source is pre-set to +0.85 V or equivalently 85% T.

Before the endpoint, the transmittance is at its highest and the voltage at the inverting input (-) of OA-2 is near 1.0 V and more positive than the 0.85 V at the non-inverting input (+). Because there is no feedback element, the output is driven to its maximum negative value (-12 to -15 V) before the endpoint.

As the endpoint is approached, the voltage from the PMT module at the inverting input drops below 1.0 V due to the absorption by the blue iodine-starch complex. When it becomes less than 0.85 V, the OA-2 output swings from -15 V to its maximum positive potential (+12 to +15 V). A voltage more positive than about 2.5 V at the CONTROL of the Relay on the timer-counter activates the relay so Relay point S is now connected to the normally open (NO) terminal and hence ground potential. This action stops the current and turns the timer off.

Note that the overall result is that the timer and current flow to the reaction cell are only activated if **the timer-counter switch is in the TIME position and the transmittance is greater than 85%**. A titration is initiated by placing the timer-counter switch in the TIME position and it is automatically terminated by the spectrophotometric detection system when the endpoint is reached. From the time indicated on the counter display (the time in seconds is the number of counts divided by 60) and the current, the number of coulombs delivered to the cell and the equivalents of iodide oxidized can be calculated. **The Time-Count switch is the ON-OFF switch for the constant current generator.**

## IV. EXPERIMENTAL

### A. Solutions

The following will be provided: an unknown aqueous solution of  $\text{As}_2\text{O}_3$ , a 0.05 M KI in 0.12 M  $\text{NaHCO}_3$  solution, and a filtered 2% (w/v) starch solution. The 100-mL graduated cylinder, 50-mL beaker, 1-mL graduated pipet, and 2-mL volumetric pipet are provided for you in the laboratory. Wear gloves and goggles. No food or drink in the lab.

Waste Disposal. The As solutions are toxic. Deposit all As-containing solutions in the As waste container in the hood in Gbad 313 when you are done and rinse glassware into this waste jar.

### B. Preparation of Instrumentation

The spectrometer is normally set up for you as indicated in Fig. 1. The **600- $\mu\text{m}$**  monochromator slits should be used. The coulometric cell is the 180-mL beaker with the stopper, 2 electrodes, and a large magnetic stirring bar. Secure the coulometric cell in the special holder in the sample module on top of the water-driven magnetic stirrer. Carefully push the cell down tightly so it is at the bottom of the cell holder.

**The electronics will be set up and tested in three stages:**

- 1. control circuit and constant current source;**
- 2. sensor circuit with the PMT;**
- 3. and the coulometry cell with the rest of the circuit.**

**1. Control circuit and constant current source.** In this step you will check the constant current source and the control circuit without actually hooking up the coulometric cell.

**A. Electronics Setup.** Before you start checking the wiring, set the following switches, grounds and voltage sources:

#### ***OA-1, constant current source***

- the lowest yellow dummy input of OA-1 is **not** grounded (the switch should be to the right)
- the feedback loop of OA-1 is open (switch to left)
- the non-inverting input of OA-1 is grounded (the bottom grounding switch to the right).

***OA-2, comparator (on the bottom of the LOG-RATIO module)***

- the + input of OA-2 is **not** grounded (switch to left)

***Grounds***

- a ground from both OA modules is connected to ground of both voltage sources and to the ground of the timer counter box

***Voltage source***

- Turn the TEK power supply on, set the variable voltage source to  $+ 0.85 \pm 0.01$  V as measured with the DMM, and then turn the TEK power supply off; connect the + 0.85 V to the non-inverting input of OA-2.
- the timer counter box is connected to the + 5V power supply with a double banana cable

**B. Setup up a “dummy cell” and a “dummy PMT” to test out the experiment before using any chemicals:**

- “dummy cell” is the 1 k $\Omega$  resistor in the feedback loop of OA-1; this dummy cell will allow you to test the constant current source before you make any connections to the real cell.
- “dummy PMT” is made by connecting the inverting input of the comparator OA-2 to +5 V; normally this input will be connected to the PMT output, but for now you can use the voltage source to simulate the PMT output (+5 V is 100% T and 0 V is 0%T).

**C. Now complete the wiring as indicated in Fig. 2.****D. Simulate the “titrate” and “hold” modes of the circuit and verify that they work as designed.**

- Turn the Time / Count switch to the Count position (OFF) and turn the TEK module power on.
- **Simulate “titrate”** by moving the Time / Count switch to the Time (ON) position (with the inverting input of OA-2 connected to + 5 V to simulate 100% T from PMT).
- Use the DMM to verify that:
  - Point A (Fig. 2) is +5 V (to drive constant current source);
  - Point B (Fig. 2) is -5V (to sink current);
  - Control point is at -12 to -15 V (leaving the relay switch in the NC (up) position);
  - Verify that the counter is counting.



- **Next use the DMM to measure accurately and record in your lab notebook the current through the dummy cell resistor** when the circuit is in the titrate mode. Recall that the DMM must be inserted in series to measure current. You will use this value of current to calculate the charge passed in your coulometric analysis. Verify that the current is close to the value expected from Ohms law and the nominal values of voltage and resistance before you proceed. When finished, remove the DMM from the circuit and move the Time / Count switch to count (OFF).
  
- **Now simulate “hold”** by moving the Time / Count switch to the Time position (ON) to start the titrate mode and then move the “dummy PMT” lead from the inverting input of OA-2 to ground to simulate 0 %T and “hold”.
  
- Use the DMM to verify that:  
Points A and B are at 0 V (no current flows through dummy cell);  
Control point is at +12 to +15 V;  
and the counter is not counting.
  
- Move the Time / Count switch back to count (OFF). Check with an instructor if any test fails.

**2. Sensor circuit.** In this step you will fill the cell with solution and then hook up and adjust the PMT and open the ECR recorder program. Then you will use the shutter to block the light and simulate the endpoint of the titration, and verify the operation of the control circuit.

**A. Setup coulometric cell:**

- Obtain about 60 mL of the potassium iodide solution in a graduated cylinder and add to the coulometric reaction cell (the beaker).
- Add 6 drops of the filtered starch solution (in a dropper bottle) to the reaction cell.
- Securely place the stopper containing the electrodes into the top of the reaction cell. The platinum-foil electrode is delicate so be careful not to hit it against anything. Make sure that the electrodes do not touch the bottom of the beaker or the stirring bar. **Do not connect the electrodes at this point.**

- Fill the counter electrode compartment (**the fritted tube** with wire) with a little of the KI solution and make sure that the frit end stays immersed in the solution in the coulometric reaction cell and that the tube doesn't run dry.
  - Make sure the electrodes don't block the light path by rotating the stopper as necessary and then gently turn on the water to the water driven stirrer so that the stirbar is spinning smoothly.
- B. Hook up and adjust the PMT.** The connection of the PMT module to OA-2 is critical.
- Remove the wire in the inverting input of OA-2 that was serving *as the dummy PMT* and attach a BNC-to-double-banana-plug adapter to the PMT cable. Plug this adapter into the yellow and green sockets on OA-2. **The ground side of the double-banana-plug goes to the yellow socket, which must also be connected to the OA-2 module ground with a wire.**
  - Use a cable to connect the PMT output to the ADC channel 0. Set the ADC to +/-1-V full scale in the ECR program.
  - Set the monochromator wavelength to 575 nm by manually turning the stepper motor shaft.
  - Turn the lamp on.
  - Be sure the PMT power supply is connected to the wall socket and turn the PMT on.
  - Set 0% T for the PMT: Close the light source shutter (0% T) and use the DMM to measure the PMT output. If necessary adjust the **PMT zero control** so the output is 0 V.
  - Use the DMM to check that the output of the comparator OA-2 is +12 to +15 V. If not, check with an instructor.
  - Set 100% T on the PMT. Open the shutter (100%T) and adjust the **PMT bias voltage or PMT module gain** so the PMT output voltage is about 1.0 V.
  - Start the ECR chart recorder program. You will see some noise in this signal, which sometimes can be reduced by adjusting the speed of the stirrer. If the cell is not pushed down enough there can be excess noise due to light reflecting off the rotating stirring bar.

- Check that the output of OA-2 with the DMM reads -12 to -15 V. Check with an instructor if you have excessive noise or the OA-2 output is **not negative**.

**C. Test the circuit.** You will use the shutter to simulate the endpoint of the titration.

- Turn the Time / Count switch to Time (ON).
- Open the shutter so the PMT output is 1 V (100% T). Check that Point A is about +5 V and that the counter is counting.
- Gradually close the shutter until the PMT output falls to +0.85 V as indicated by the ECR program. Point A should drop to 0 V and the counter should stop counting. Verify this behavior of the circuit before you proceed.

**3. Coulometry cell circuit.** In these steps you'll check the operation of the cell.

- Be sure the Time / Count switch is set to Count (OFF).
- Remove the dummy cell (1 k $\Omega$  resistor) from the feedback loop of OA-1 and replace it by attaching the **cell anode (large Pt sheet electrode)** to the **summing point of OA-1** and the **cell cathode (wire counter electrode in fritted tube)** to the **output of OA-1**.

**A. Check that there is generation of I<sub>2</sub> at the large Pt electrode.**

1. Verify that the stirrer is rotating smoothly and the PMT output is about 1 V.
2. Flip the Time / Count switch to Time (ON). When you do this you should see a blue-gray stream indicating generation of I<sub>2</sub> (w/starch) at the large Pt electrode. At the counter electrode you may be able to see bubbles of H<sub>2</sub> (sometimes hard to detect). **As soon as you see the blue-gray stream, flip the switch back to Count (OFF).**
3. If you did not see the I<sub>2</sub>, something is wrong with the wiring of the part of the circuit involving OA-1. Check with a TA. Otherwise, \*Congratulations\* - your automatic titration system is ready to go!

**B. Trial run of entire system.**

1. Obtain about 20 mL of the unknown arsenite solution (As(III)) in a 50-mL beaker. Now add about 2.0 mL of the arsenite solution to the reaction cell beaker for a trial run. The solution in the cell should now be colorless (not light blue or gray). If the solution is still colored, too much  $I_2$  was generated in the previous step so add a little more arsenite solution until the color disappears. The ECR program should indicate about 100% T.
2. Reset the timer (small black button next to display) and flip the Time / Count switch to Time (ON). You should see the timer counting and, slowly over a minute or two, the ECR recorder will indicate a slow decrease in % T. At about 0.85 V on the ECR program, the endpoint for the titration is reached and the timer and the current to the reaction cell will automatically shut off. The solution color should be light blue/gray due to a small excess of  $I_2$  reacting with the starch. Wait about 30 s to ensure that the endpoint has really been reached.
3. **Now flip the Time/Count switch to the COUNT position and read the number of counts displayed and record in your notebook.** Divide the number of counts by 60 to obtain the number of seconds that the current flowed through the system.

**C. Determination of the concentration for the unknown solution of  $As_2O_3$  - Analytical Work!**

1. Using a 2.00 mL volumetric pipet ( $\pm 0.006$  mL), add exactly 2.00 mL of the unknown arsenite solution to the reaction cell beaker through **the hole in the stopper** (do not add this to the counter electrode tube). **This step is absolutely critical** and the most common cause for having to make extra runs. You must use your best volumetric technique to deliver exactly 2.00 mL. Be sure the bottom of the meniscus is exactly at the mark before inserting the pipet in the hole in the cell stopper. You should visually check that the pipet tip is all the way through the stopper hole so no solution is caught on the stopper and that it is not touching the solution before delivery. Release and let the pipet drain for 20 s. You may need to carefully tap the pipet to dislodge the last hanging drop but don't blow out the pipet. **Be careful** not to move the reaction cell or the electrodes.
2. Close the shutter and adjust the 0%T signal with the PMT zero control. Open the shutter and adjust the 100%T signal with the PMT module gain or HV bias voltage so that the signal is within 0.01 V of the same position on the ECR scale as in part B.

3. **Reset the timer counts to zero.**
  4. To initiate the titration, turn the Time/Count switch to Time (ON).
  5. After the timer first stops, wait 30 s to ensure that the endpoint has been reached and then turn the Time/Count switch to Count. Record the time (130-150 s). Divide the counts observed by 60 to convert to seconds.
  6. **Reset the timer for the next run.**
  7. Next run: Add another 2.00 mL aliquot of the arsenite solution with the pipet and repeat the above procedure. Check that the timer still reads 0 and reset if necessary. Be careful not to move or jar the beaker.
- \*\*\* It is very important that the 0 and 100% T are adjusted to within 0.01 V on the same ECR scale for each run.\*\*\***
8. **Also make certain to turn the** Time/Count switch to **off** between runs or the timer and cell current will be activated when you add new arsenite solution.
  9. Repeat the above procedure until you obtain 4 consecutive runs with a range (maximum - minimum) of titration times that is 10 s or less.

**Note:** If the cell becomes too full of solution (i.e., up to the stopper), empty the cell in the As waste container in the hood. Start the solution setup over: put 60 mL of iodide solution, 6 drops of starch solution, and 2.0 mL of arsenite into the cell, readjust the 0 and 100% T, titrate to the endpoint, and proceed with the Analytical part IVC on page 12.

**Waste Disposal:** Dispose of the contents of the cell and any extra arsenite in the waste jug marked for this purpose and stored in the hood.

## V. LAB REPORT

Include in the lab report an abstract, a copy of your lab notebook pages for this experiment, ECR recorder charts plotted in Excel, and a response to the following items:

- A. Report the exact current you measured through the dummy cell. Also show how you calculated the expected value of current from the nominal values of the voltage and the resistance using Ohms law.
- B. Report the raw data for the number of counts for each run. Calculate the average time (seconds) equivalent to the counts, standard deviation (seconds), and the relative standard deviation (RSD) of your last four runs with times that produced a range of less than 10 s.
- C. Write the three balanced equations that describe the chemistry (i.e, dissolution of  $\text{As}_2\text{O}_3$ , and both redox half reactions). Give the overall balanced chemical reaction for the complete oxidation of  $\text{As}_2\text{O}_3$  by  $\text{I}_2$  in aqueous solution buffered to pH 8.3 to form the final products  $\text{HAsO}_4^{2-}$  and  $\text{I}^-$  (including  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{H}_2\text{O}$  as necessary to balance the reaction). Make sure that  $\text{As}_2\text{O}_3$  and  $\text{I}_2$  appear as reactants,  $\text{HAsO}_4^{2-}$  and  $\text{I}^-$  appear as products,  $e^-$  does not appear in the final overall balanced reaction, and that the reaction is completely balanced.
- D. Calculate the following quantities showing the formulas and reasoning you used:
- Average charge ( $q$ ) used in the titration. Find this from the number of coulombs of electrons passed based on the current you measured for the dummy cell.
- Number of mole of :**
- electrons used
  - $\text{As}(\text{OH})_3$  oxidized
  - $\text{As}_2\text{O}_3$  oxidized.
- Number of mole per liter of:**
- $\text{As}_2\text{O}_3$  in the solution in the reagent bottle marked “unknown”.
- E. Give two or three main sources of error for the calculated molarity of the unknown solution in the reagent bottle. (Note: don't claim “human error” unless you have good reason to.)