

Beer's Law & Swimming Pool Chemistry

As you are well aware (or should be) the Sonoran Desert that envelopes Yuma and La Paz Counties receives copious amounts of year-round solar radiation. In the summer the intensity (amount of solar radiation, measured in $\text{J}\cdot\text{s}^{-1}$, impinging upon an area per unit time) is greater than in the winter on account of the position of the Earth's rotational axis relative to the sun. Also, observations reveal that the Yuma area has a significant number of swimming pools. Next time you fly out of Yuma look down below and notice the myriad number of blue dots located behind resident's homes.

If you own a swimming pool, then you are aware of the continual upkeep necessary to keep the pool's waters clean and sanitary for swimming. Continual maintenance typically means routinely adjusting the 1) pool's pH, 2) water hardness (Ca^{+2} and Mg^{+2} concentrations....for which the analytical procedure was done in lab during the first semester), 3) alkalinity (concentration of carbonate and bicarbonate anions), and 4) "chlorine" concentration (from addition of sodium or calcium hypochlorite).

In today's lab we'll begin discussion of swimming pool chemistry with respect to chlorination, that is the presence of the active disinfectant in swimming pool water at a pH typical for pools- hypochlorite anion and hypochlorous acid.

What is the molecular structure for hypochlorite anion and hypochlorous acid?

anion = _____ acid = _____

So how is the sum total concentration of hypochlorite anion and hypochlorous acid in pool water measured or quantify? Rather simply by taking advantage of the fact that both hypochlorite anion and hypochlorous acid react selectively via an oxidation-reduction process with a chemical called DPD (N,N-diethyl-p-phenylenediamine). The resulting product formed is a magenta (red-pink) color. The amount of visible radiation at some wavelength that the red-pink product absorbs (A) is directly proportional to the total concentration (c) of hypochlorite anion-hypochlorous acid initially present. Which mathematical expression below illustrates this relationship?

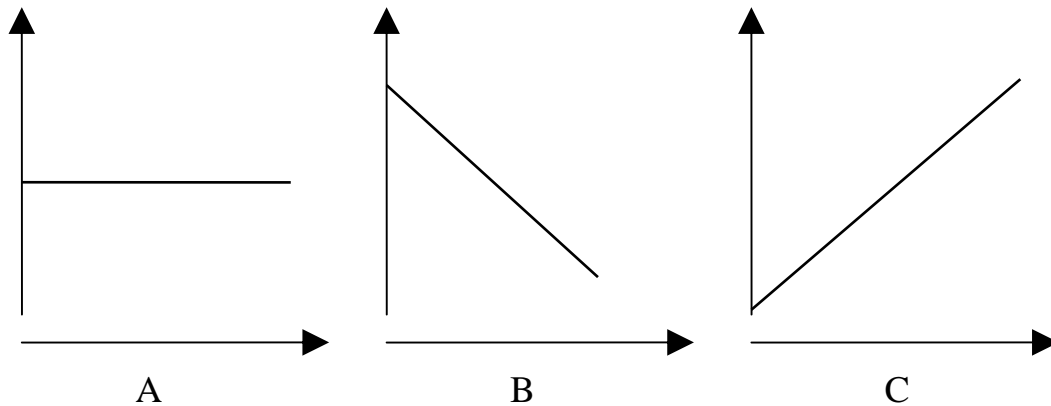
$$A \propto c \qquad A \propto c^{-1}$$

In today's experiment you'll use a colorimeter to set up a standard hypochlorite-hypochlorous acid concentration curve (absorbance of colored

product vs. total hypochlorite anion-hypochlorous acid concentration). From the standard curve you will then be able to determine the total concentration of hypochlorite-hypochlorous acid in your swimming pool or hot tub and also the total concentration of hypochlorite anion-hypochlorous acid in a swimming pool under various environmental conditions such as pH and exposure to varying wavelengths of ultraviolet (UV) radiation.

As stated previously the magnitude of absorbance (A) of the colored product of some wavelength is directly proportional to the total concentration (c) of hypochlorite anion-hypochlorous acid initially present. If this relationship is linear over a range of concentrations under consideration, then the standard curve is said to follow a Beer's Law relationship. Which graph below then best illustrates a Beer's Law relationship?

x-axis: concentration *y-axis*: absorbance



Answer: _____

The magnitude of absorption by the red-pink colored product formed from the reaction between hypochlorite anion-hypochlorous acid and DPD is measured using a colorimeter, a "color measuring" instrument. Let's review how a colorimeter is designed and how it works (you did an experiment with a colorimeter previously).

The colored sample is held in a small rectangular container called a cuvette. The cuvette has a specific width or path length through which the selected wavelength of visible radiation passes. As the selected wavelength of visible radiation passes through the colored solution sample (see handout schematic), some of the radiation is absorbed by the radiation-absorbing species (chemical) in the solution. The rest passes through unabsorbed. The amount absorbed is directly proportional to how much (concentration) radiation-absorbing species is in solution.

Notice carefully how I wrote just above- “As the selected wavelength of visible radiation...”. The colorimeter has three wavelength settings (knobs)- 470nm, 565nm, and 635nm. Which setting is the best for determining the magnitude of absorption by the colored species? How is the wavelength to be determined?

First, determine in which region (red, orange, yellow, green, blue, indigo, violet) of the visible electromagnetic spectrum is each wavelength setting is found.

470nm = _____ 565nm = _____

635nm = _____

The color of a **solution** is really the combination of wavelengths that are not absorbed by the radiation-absorbing species in the solution. Study the artist’s color wheel in your textbook. The color absorbed (wavelengths absorbed) can be determined from the color observed. The color observed and absorbed generally (but not always) have a complementary relationship as indicated on the color wheel in your text by being on opposite sides of the color wheel.

So based on the color wheel as applied to a colored solution and knowing that the colored product in today’s experiment is red-pink (magenta), which of the three wavelength settings on the colorimeter should be used for analysis for the total chlorine concentration in pool water?

wavelength setting = _____

With this background you’re now ready to set up a standard curve that follows Beer’s Law.

Procedure:

Before setting up the standard curve via experimentation you first need to do some simple calculations in order to make some standard solutions (20.00mL in volume, no more or no less), that is solutions that have a known concentration of hypochlorite-hypochlorous acid.

Label six clean, dry 50mL (or 100mL) beakers 1 through 6. Beaker 6 is to be used for a 20.00mL sample from the AWC swimming pool. A DPD tablet will then be added to each standard solution and the absorbance of the standard solution measured.

First, make the 20.00mL standard solutions ($1.0\text{mg}\cdot\text{L}^{-1}$, $2.0\text{mg}\cdot\text{L}^{-1}$, $3.0\text{mg}\cdot\text{L}^{-1}$, $4.0\text{mg}\cdot\text{L}^{-1}$, and $5.0\text{mg}\cdot\text{L}^{-1}$ hypochlorite anion) from a standard solution of hypochlorite anion with a concentration = $50.0\text{mg}\cdot\text{L}^{-1}$. To accomplish this you need to make some dilution calculations that will allow you to make 20.00mL standard solutions at the five concentrations listed above all from a standard $50.0\text{mg}\cdot\text{L}^{-1}$ solution.

To illustrate let's start off with a simple dilution. How would you make 20.00mL of $25.0\text{mg}\cdot\text{L}^{-1}$ hypochlorite solution from the standard $50.0\text{mg}\cdot\text{L}^{-1}$ solution? The logic applied to solve this dilution problem is no different than the logic needed to solve the other dilution calculations at lower concentrations than $25.0\text{mg}\cdot\text{L}^{-1}$.

You'd transfer 10.00mL of the standard $50.0\text{mg}\cdot\text{L}^{-1}$ solution from a buret to a beaker and then add 10.00mL distilled water to the beaker as well. Abracadabra! A $25.0\text{mg}\cdot\text{L}^{-1}$ hypochlorite anion standard solution.

In the space on the next page do the necessary calculations for the 5 standard solutions. Show the calculations to the instructor before moving onward. Fill in the chart below.

beaker #	$50.0\text{mg}\cdot\text{L}^{-1}$ (mL)	distilled water (mL)	hypochlorite concentration ($\text{mg}\cdot\text{L}^{-1}$)
1			
2			
3			
4			
5			
6			

Calculations:

Setting up the Calculator-CBL Data Logger-Calorimeter

Assemble the colorimeter, CBL unit, and graphing calculator. Start the CHEMBIO program (press PRGM) on the calculator and go to the MAIN MENU by pressing ENTER when necessary. Follow the steps below.

- Select SET UP PROBES from the MAIN MENU
- Enter “1” for the # of probes
- Select COLORIMETER from the SELECT PROBE menu
- Enter “1” for the channel #

Now, you need to calibrate (standardize) the colorimeter. First prepare a blank by filling a cuvette 75% full with distilled water. **Handle the cuvettes**

only by the top edge of the RIBBED sides! Position the cuvette with the reference mark facing toward the white reference mark at the right of the cuvette slot on the colorimeter.

- Place the blank cuvette in the cuvette slot and close the lid. Turn the wavelength knob to the 0% T position. When the voltage reading displayed on the CBL screen stabilizes, press TRIGGER on the CBL and enter “0” in the calculator.
- Now turn the wavelength knob to the green LED (565nm) position. In this position the colorimeter is calibrated to show that 100% of the green light is transmitted through the blank solution. When the voltage display has stabilized on the CBL, press TRIGGER and enter “100” in the calculator.
- Press ENTER to return to the MAIN MENU.

After calibrating at the correct wavelength follow the directions below to set up a Beer’s Law standard curve.

- Select COLLECT DATA from the MAIN MENU
- Select TRIGGER/PROMPT from the DATA COLLECTION menu

Once the standard solution calculations are checked by me, the standard solutions made, and the chart filled-in, cut off the end of a DPD plastic pillow and then pour the white DPD powder into the beaker containing the standard $1.0\text{mg}\cdot\text{L}^{-1}$ solution. Swirl the contents thoroughly making certain that as much of the powder dissolves. Some powder may not dissolve which is OK.

Repeat the procedure in the above paragraph for each 20.00mL standard solution. One DPD powder pillow per standard solution !!!!!

Wipe the outside of the cuvette with a tissue (NOT A PAPER TOWEL), and fill the cuvette ~75% full with the colored analyte solution obtained from the $1.0\text{mg}\cdot\text{L}^{-1}$ standard. Place the cuvette in the colorimeter chamber and close the lid. ***Start with the least concentrated solution and proceed to the greatest concentrated standard solution.**

- After the %transmittance value on the CBL screen has stabilized, press TRIGGER and enter the concentration value in the calculator. The transmittance value will then be automatically converted mathematically

to the corresponding absorbance value and this value stored in the calculator data list, L2. Concentration values will also have been saved for the first solution. Discard the colored solution in the beaker located in the fume hood.

- Select MORE DATA. Rinse the cuvette with distilled water and repeat as before for each of the remaining solutions

Now let's look at the Beer's Law relationship.

- Select STOP AND GRAPH from the DATA COLLECTION menu. Record the experimental absorbance (y-axis) value for each standard concentration (x-axis) value on the table found on the last page. For your records print a copy of the graph from the PC located in the lecture hall.

Is the data relationship as visually expressed in the graph consistent with Beer's Law? By visual inspection one could say either YES or NO but this doesn't really mean anything. This question has to be answered using statistical tools, namely linear regression.

In linear regression analysis the experimental data is taken and fit to the theoretical best fit linear curve ($y = ax + b$). If the experimental data are consistent with Beer's Law, the theoretical regression line should 1) closely fit the five experimental data points **and** 2) should pass through (or very near) the origin of the graph.

How is "...closely fit..." measured or determined to be acceptable? By use of a statistical parameter called a correlation coefficient, r . The correlation coefficient measures how closely data points match up (fit) to the theoretical regression line, that is how "tight" are the data to the regression line. Correlation coefficients are measured from either +/- 0.0 - 1.0 with 1.0 indicating an exact fit of the data points to the regression line. A negative correlation coefficient means that the x-variable is negatively (inversely) related to the y-variable.

Follow the directions below to determine if the experimental data are consistent with Beer's Law.

- Press ENTER and select NO to return to the MAIN MENU
- Select FIT CURVE from the MAIN MENU.

IMPORTANT: Do not select SET UP PROBES on the MAIN MENU-
doing so will clear all your data!

- Select LINEAR L1, L2. The linear regression curve statistics for these two data lists are displayed for the equation in the form:

$$y = ax + b$$

What variable does y represent? _____

What variable does x represent? _____

What is the value of the slope in the linear regression curve? _____

Does the y-intercept for the linear regression curve pass directly through the origin?

If NO, is it very near the origin? _____

What is the value of the correlation coefficient? _____

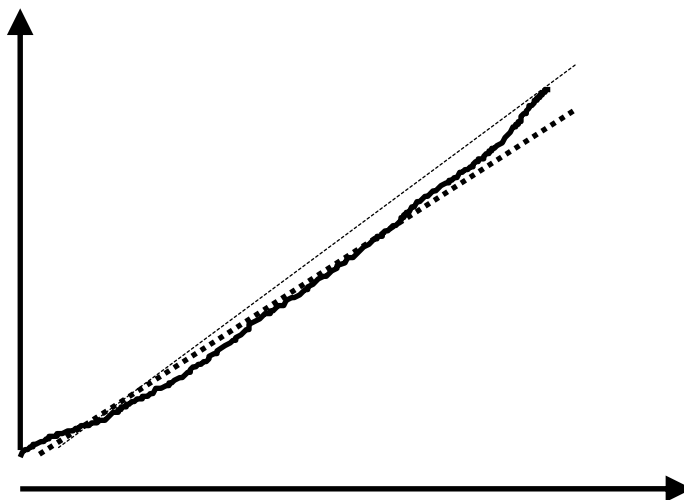
- To display the linear regression curve on the graph of A vs. concentration press ENTER, then select SCALE FROM 0 from the SCALE DATA menu. Print a copy of the graph from the PC located in the lecture hall.

From the best fit curve graph on the calculator screen record the absorbance (y-axis) value for each standard concentration (x-axis) value on the table found on the last page.

OK, what did you just do in the last bullet above? You told the calculator to find the best fit curve (line) that fits the EXPERIMENTAL DATA as closely as possible! In doing so the best fit linear curve (theoretical) is transposed over the experimental curve to give a visual (humans are visual creatures) perspective. Let's illustrate this below.

Suppose your experimental curve looks like the curve represented by the solid black line on the graph on the next page. Notice that upon visual inspection the "line", which comes from the experimental data, is slightly curved. A linear regression analysis will fit the best linear curve to the data below. The dotted line represents, for sake of argument, the best fit linear curve for the experimental data whereas the other dotted line with larger

dashes would not be the best fit linear curve to the experimental data. Why? On average the larger dashed line is farther away on both axes from the experimental data compared to the other smaller dashed best fit linear curve. In statistical terms the larger dashed line has a greater variance than the smaller dashed curve from the real experimental data. Remember, there is typically only one best fit curve.



**Graph by hand the best fit curve data as recorded in the table on the last page. Use no less than 90% of the area of the graph paper, title the graph, and label the axes correctly.

Now from the AWC swimming pool completely fill a small plastic bottle with pool water. In the lab deliver from a buret 20.00mL pool water to a beaker and add a DPD pillow. Set up the colorimeter for analysis as before but instead of using the TRIGGER/PROMPT command from the DATA COLLECTION menu select the MONITOR INPUT command. Place the colored solution in the cuvette holder and read the absorbance value from the calculator screen.

What is the total concentration of chlorine (Σ hypochlorite anion, hypochlorous acid) in the AWC swimming pool?

Answer: _____

*Place the result from the swimming pool on the blackboard.

DATA TABLE

Beaker	A (experiment)	A (best fit line)	Concentration, ppm
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1.0 mg•L⁻¹

2.0 mg•L⁻¹

3.0 mg•L⁻¹

4.0 mg•L⁻¹

5.0 mg•L⁻¹