Must be Something in the Water: Chlorine Concentration in Water Samples

Pre-lab Assignment:

Reading:
1. Chapter sections 20.1 and 20.2 in your course text.
2. This lab handout.

Questions: Balance the following half reactions:

\[
\begin{align*}
\text{Half-Reaction 1} & & \quad \text{MnO}_5(aq) + \text{H}^+(aq) + 5 e^- \rightarrow \text{Mn}^{2+}(aq) + \text{H}_2\text{O}(l) \\
\text{Half-Reaction 2} & & \quad \text{Cl}_2(aq) + 2 e^- \rightarrow \text{Cl}^-(aq)
\end{align*}
\]

Introduction:

This week you will collect water samples from around campus and determine their chlorine (Cl\(_2\)) content. You will be introduced to UV-vis spectroscopy, standard curves, and analysis of combined data sets.

In this experiment, you will quickly and completely react chlorine, Cl\(_2\) with an organic dye, N,N-Diethyl-p-phenylenediamine (DPD). As shown in Scheme 1, DPD reacts with a strong oxidizing agent such as Cl\(_2\) to produce an intensely colored product called Würster dye.

![Scheme 1](image)

Scheme 1. The reaction of DPD with an oxidizer forms a colorful dye. This reaction is also used in chlorine test kits for swimming pools.

You can relate the concentration of Cl\(_2\) (or any oxidizer!) to the amount of Würster dye formed. The amount of Würster dye formed can be determined by using Beer’s Law, which relates the absorbance of light by the dye to its concentration.

\[
A = \varepsilon \cdot \lambda \cdot [C]
\]

We won’t worry too much about the details of this expression beyond defining \(A\) as the absorbance of light measured at a wavelength \(\lambda\), \([C]\) as the concentration of our substance, and the
product $\varepsilon \ell$ linearly relates concentration to absorbance. The absorption coefficient $\varepsilon$ is defined at the same wavelength as the measured absorbance and is determined by how the absorbance of the substance increases with concentration. The path length $\ell$ is the distance the light travels through the solution, which is 1 cm in this experiment.

Two points to bear in mind:
1. Absorbance is a unitless measure, so the product $\varepsilon \ell$ has units of inverse concentration.
2. The wavelength of maximum absorbance of Würster dye will be used in this study.

In this experiment, you will measure the absorbance of light by Würster dye that was produced via the reaction shown in Scheme 1. Using the stoichiometry of that reaction, you will generate a standard curve similar to Figure 1 to determine the concentration of Cl$_2$ in water samples.

![Calibration Curve for Cl$_2$ Analysis](image)

**Figure 1.** A calibration plot for analysis of chlorine concentration with the linear trend predicted by the stoichiometry of the reaction in Scheme 1 and Beer’s Law. The baseline correction in the ordinate and the Cl$_2$-equivalent abscissa are described in *Data Analysis* below. Here, the slope is $0.48 \pm 0.03$ L/mg, and the y-intercept is $-0.001 \pm 0.005$ – consistent with zero as predicted by Beer’s law.

**Procedure:** (please work with your assigned partners)

Spectroscopic data collection will require the Vernier data interface and the Logger Pro data collection software. These steps refer to the Logger Pro Instructions, which will be available at your lab station.

1. Following the Logger Pro Instructions, start the software to warm up the SpectroVis Plus spectrophotometer.
2. Collect water samples from around campus, one per group member. The sample bottle needs to be filled completely and capped to prevent \( \text{Cl}_2 \) from escaping as gas, and the sample should be analyzed as soon as possible.

3. Each group member should prepare a standard solution using the provided 1000 \( \mu \text{L} \) micro-pipettor to transfer either 250, 350, 450, or 550 \( \mu \text{L} \) of the 4.000\( \times 10^{-4} \) M \( \text{KMnO}_4 \) stock solution provided into separate 100 mL volumetric flasks. DI (deionized) water should be used to dilute to the mark. The flask should be stoppered and mixed.

4. Set up a cuvette rack and prepare the following cuvettes by filling each up to the line (3 mL) with the following: 1 cuvette with DI water (this is your blank), 1 cuvette for each of your standard solutions, and 1 cuvette for each of your water samples.

5. Use the Powder Pop Dispenser to add a dose of the DPD reagent into each of the nine cuvettes. Cover the cuvettes with Parafilm and shake for 12 seconds. Tap the cuvettes gently to dislodge bubbles.

6. Following the Logger Pro Instructions, collect the absorbance spectrum for your most concentrated standard solution. Find \( \lambda_{\text{max}} \), the wavelength of maximum absorbance. Record this wavelength, and use it for all subsequent samples. Make sure to save this spectrum and print it for your lab notebook.

7. For each cuvette (blank, standards and sample), record the absorbance at the previously determined wavelength of maximum absorption and the absorbance at 700 nm. We’ll use this second absorbance to correct the baseline.

**Data Analysis:**

*Conversion from \([\text{KMnO}_4]\) to \([\text{Cl}_2]_{\text{equiv}}\)*

Standard solutions of \( \text{Cl}_2 \) are difficult to prepare and are unstable. But we can oxidize DPD as in Scheme 1 with any strong oxidizer. In this experiment, you will use \( \text{KMnO}_4 \). You just need to correct for the difference in the number of electrons given up by \( \text{KMnO}_4 \) compared to \( \text{Cl}_2 \). The two half-reactions you balanced in your pre-lab exercise tell us how many electrons are transferred per equivalent oxidizer.

The molar equivalents of \( \text{KMnO}_4 \) to \( \text{Cl}_2 \) is 5 to 2. Using this result and dimensional analysis to convert from molarity \( \text{KMnO}_4 \) to mg/L \( \text{Cl}_2 \), the molar equivalent concentration of \( \text{Cl}_2 \) is:

\[
[\text{Cl}_2]_{\text{equiv}} = [\text{KMnO}_4] \left( \frac{5 \text{ mol e}^-}{1 \text{ mol KMnO}_4} \right) \left( \frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-} \right) \left( \frac{70.90 \text{ g Cl}_2}{\text{mol Cl}_2} \right) \left( \frac{1000 \text{ mg}}{\text{g}} \right)
\]

For example, a standard solution prepared by diluting 200.0 \( \mu \text{L} \) of the 4.000\( \times 10^{-4} \) M \( \text{KMnO}_4 \) stock solution to 100.0 mL gives:

\[
[\text{KMnO}_4] = 4.000 \times 10^{-4} \text{ M} \left( \frac{200.0 \times 10^{-6} \text{ L}}{0.1000 \text{ L}} \right) = 8.000 \times 10^{-7} \text{ M}
\]

\[
[\text{Cl}_2]_{\text{equiv}} = 8.000 \times 10^{-7} \text{ mol KMnO}_4 \text{ L}^{-1} \left( \frac{5 \text{ mol e}^-}{1 \text{ mol KMnO}_4} \right) \left( \frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-} \right) \left( \frac{70.90 \text{ g Cl}_2}{\text{mol Cl}_2} \right) \left( \frac{1000 \text{ mg}}{\text{g}} \right) = 0.1418 \text{ mg L}^{-1}
\]
Baseline-Corrected Absorbance
At zero concentration of dye, our solution shouldn’t absorb light. However, repositioning of the cuvette, differences between cuvettes, and variable amounts of suspended particulates or dissolved colored matter cause a shift in the baseline from sample to sample. We’ll correct for this by using baseline-corrected absorbances: \( A_{BC} = A_{\lambda_{\text{max}}} - A_{700\text{nm}} \). For each sample, we simply calculate the difference in absorbance we recorded at the wavelength of maximum absorbance minus the absorbance we recorded at 700 nm.

Determining [Cl\(_2\)] in the Samples
1. Make a standard curve as in Figure 1 using the baseline corrected absorbances and [Cl\(_2\)]\(_{\text{equiv}}\) for the blank and standard solutions. Use Linest to get errors on the slope and intercept to determine the significant figures.
2. Use the standard curve to determine the concentration of chlorine in each water sample.

What should be in your laboratory notebook?
1. Title for the experiment, names of all partners, and date.
2. All observations, including wavelength and absorbances for all samples.
3. One sample calculation for conversion from [KMnO\(_4\)] to [Cl\(_2\)]\(_{\text{equiv}}\).
4. One sample calculation for Cl\(_2\) content in your sample of water.
5. As always, cite your literature source used to complete your work.
6. A copy of the spectra for the 550 µL solution (from which \( \lambda_{\text{max}} \) was determined).

What should be in your laboratory report? Please submit an individual lab report of one page.

- A title for the experiment, names of all authors, lab section, and date.
- An abstract not to exceed 150 words that summarizes the objective of your experiment, the methods employed, results, and at least one suggestion for a future experiment based on your findings. [This abstract should be written separately by each individual and should not be shared with other members of the group].
- A figure of your calibration graph with an appropriate title, properly labeled axes, and equations for the trend lines with \( R^2 \) values included. The figure should contain a caption, not to exceed 3 lines. [This figure and caption may be shared by all members of the group].