# Determination of Chlorine in Campus Drinking Water

**Purpose**: We will determine the concentration of chlorine in campus drinking water and the effectiveness of activated carbon water filters for removal of $Cl_2$.

Added $Cl_2$ to potable water discourages the growth of harmful bacteria. The chlorination of drinking water supplies in the U.S beginning in 1908 was a significant advancement in public health. The first chlorination was designed to prevent the spread of cholera and typhoid fever. A typical target $Cl_2$ concentration range at the tap is 0.2-1.0 mg/L.

Colby has recently installed several water bottle filling stations in association with drinking fountains. The purpose of the filling stations is to decrease the use of plastic beverage bottles. Some of the filling stations have multi-layer filters that remove sediment. These filters also contain activated carbon, which removes naturally occurring colored organic matter that give a brown color and bad taste to the water. Similar filters are found on refrigerator ice machines and tap water filters, such as Brita filters. The faculty lounge in Lovejoy also has a filtered water system that is produced by a company owned by a Colby alum.[1] The activated carbon also removes $Cl_2$ from the drinking water. The removal of $Cl_2$ from drinking water supplies without replacement by another disinfectant would be irresponsible, if the water has the possibility of sitting for any period of time after dispensing. The bottle filling stations incorporate plastic components or resin coatings that contain zeolite materials that are loaded with $Ag^+$ ion. The $Ag^+$ ion leaches into the dispensed water at very low concentration to act as a disinfectant. Each pair will analyze two unfiltered tap water samples that are collected during the lab period. The data for the class will be pooled to determine the concentration of $Cl_2$ in our tap water and the effectiveness of the $Cl_2$ removal on campus.

Drinking water supplies are often chlorinated by the addition of sodium hypochlorite. The hypochlorite ion is in equilibrium with dissolved $Cl_2$:

$$ClO^- (aq) + Cl^- (aq) + H_2O \rightleftarrows Cl_2 (aq) + 2\ OH^- (aq)$$

Monochloroamine, $NH_2Cl$, may form upon the reaction of $Cl_2$ with dissolved organic matter. The $Cl_2$ analysis will be accomplished by a standard colorimetric method that is sensitive to $Cl_2$, $ClO^-$, and monochloroamine.[2] This experiment compliments the lecture material by providing a first experience with spectrophotometric determinations, which depend on the quantum interaction of light with matter. The experiment also integrates the important material from past laboratory exercises on limiting reagents, redox reactions, and volumetric analysis.

## Sampling Protocol

Consistent and careful sampling protocols are necessary for effective drinking water determinations. The concentration of $Cl_2$ from a faucet varies significantly as a function of the time of sample collection, beginning with small chlorine concentration immediately after the tap is turned on and increasing after the "old water" has been flushed from the pipes. For tap water determination, the tap should be turned on for a predetermined time before sampling and the sample bottle should be rinsed three times with the running water before filling. The sample bottle should be filled completely, allowing no air space, and be tightly capped. Dissolved $Cl_2$ readily escapes from solution as a gas. For the bottle filling stations, sample the water as you

would fill a water bottle with the few extra rinses (once again--tightly capped with no air space). The samples should be analyzed as quickly as possible after collection.

## Spectrophometric Determination Using DPD

The spectrophotometric determination of $Cl_2$ is rapid, sensitive, and reliable.[2] The $Cl_2$ in the sample reacts with the organic dye DPD, N, N-diethyl-p-phenylenediamine. The oxidized form of DPD produces an intensely colored solution, Figure 1.[3]

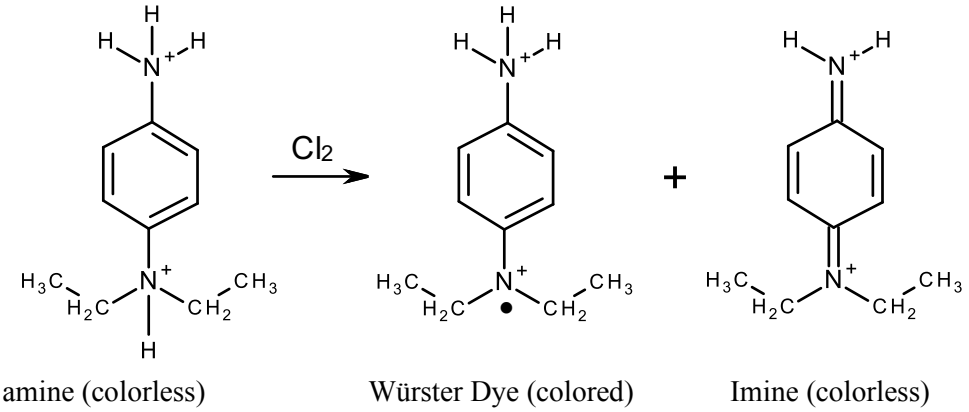


Figure 1: DPD (N, N-diethyl-p-phenylenediamine) is oxidized to a colored product by $Cl_2$.

The concentration of the dye is determined by visible light absorption. A beam of white light is passed through the solution, Figure 2. After interaction with the sample, the light is dispersed into its component colors using a diffraction grating. The resulting spectrum is detected and converted to a digital signal using a photodiode array, PDA. The spectrum is displayed by computer. A photodiode array spectrophotometer allows the simultaneous detection of multiple wavelengths. The multiple wavelengths allow the determination of the spectrum baseline and the absorbance at the wavelength of maximum absorption, simultaneously.

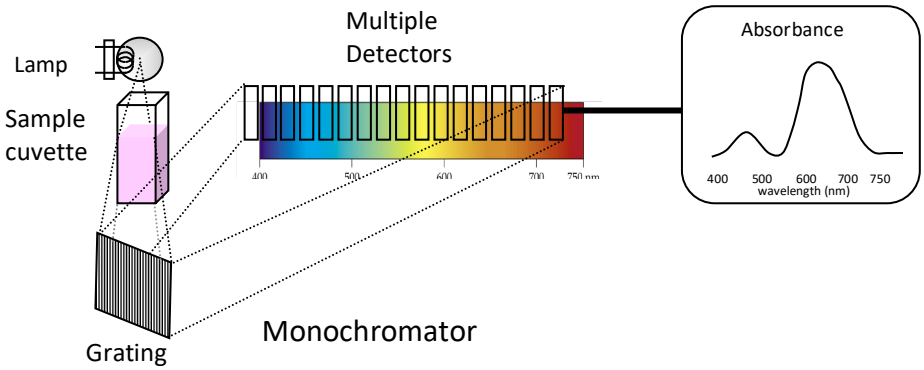


Figure 2: A spectrophotometer based on a multi-wavelength detector (PDA).

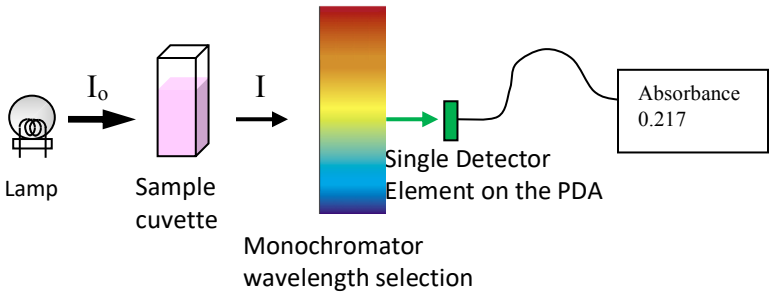


Figure 3: The intensity falling on the sample is $I_o$ and the intensity after absorption by the sample is I. The intensities are measured separately at each wavelength.

At each successive wavelength, the intensity of the light falling on the sample is $I_o(\lambda)$. Some of the light is absorbed, depending on the wavelength. The intensity of the light after interaction with the sample is $I(\lambda)$. The absorbance at wavelength $\lambda$ is defined as $A_\lambda = \log[I_o(\lambda)/I(\lambda)]$. The absorbance is read-out directly from the instrument. The absorbance is related to the concentration of the sample by the **Beer-Lambert Law**:

$$A_\lambda = \varepsilon_\lambda \, \ell \, c \qquad (1)$$

where $\varepsilon_\lambda$ is the absorption coefficient, which is different for each wavelength, $\ell$ is the light path length in the cuvette, and c is the concentration of the absorbing substance. The more a molecule absorbs light the bigger absorption coefficient. The absorption coefficient is big if photons have the correct energy to cause electronic transitions from ground state to electronic state molecular orbitals. The absorption coefficient is determined experimentally by measuring the absorbance of solutions with known concentrations. The path length of the cuvette is 1.00 cm. The units of the concentration are flexible. If the units of concentration are mol/L then the units of $\varepsilon_\lambda$ are $mol^{-1}$ L $cm^{-1}$. If the units of concentration are mg/L then the units of $\varepsilon_\lambda$ are $mg^{-1}$ L $cm^{-1}$. Concentrations in mg/L are conventional for drinking water analysis.

The baseline of the absorbance spectrum corresponds to no light absorption, which should be at 0.000 absorbance. 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. The absorbance of DPD is determined by subtracting the baseline absorbance at 700 nm from the maximum absorbance, $A_{533} - A_{700}$. Baseline subtraction is necessary for concentrations at the low end of the calibration range. For calibration, the absorbance of solutions of known concentration is plotted versus the concentration. The absorption coefficient is given by the slope of the calibration curve, Figure 4.

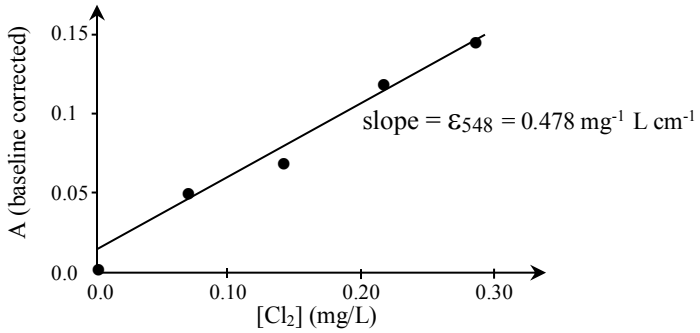

Figure 4: The calibration curve for DPD with concentrations expressed as mg/L $Cl_2$.

For a typical water sample with 1 mg/L of $Cl_2$, the calibration curve would predict an absorbance of 0.48.

## Calibration Solutions for DPD $Cl_2$ Determination

Standard solutions of $Cl_2$ are difficult to prepare and are unstable. Rather, the standard method uses $KMnO_4$ solutions to prepare standards with an "equivalent" concentration of $Cl_2$. In other words, the DPD dye doesn't care if it is oxidized by $Cl_2$ or $KMnO_4$, the result is the same. The balanced half-reactions for $MnO_4^-$ (as you determined in Exp. 4) and $Cl_2$ acting as oxidizing agents are:

$$MnO_4^- (aq) + 8\ H^+ (aq) + 5\ e^- \rightarrow Mn^{2+} (aq) + 4\ H_2O\ (l)$$

$$Cl_2 (aq) + 2\ e^- \rightarrow 2\ Cl^- (aq)$$

The molar ratios are then 1 mol $MnO_4^-$ = 5 mol $e^-$ while 1 mol $Cl_2$ = 2 mol $e^-$. The conversion from the concentration of $KMnO_4$ in mol/L to the equivalent concentration of $Cl_2$ in mg/L is:

$$[Cl_2] = [MnO_4^-]\left(\frac{5\ \text{mol}\ e^-}{1\ \text{mol}\ MnO_4^-}\right)\left(\frac{1\ \text{mol}\ Cl_2}{2\ \text{mol}\ e^-}\right)\left(\frac{70.9054\ \text{g}\ Cl_2}{1\ \text{mol}\ Cl_2}\right)\left(\frac{1000\ \text{mg}}{1\text{g}}\right) \quad (2a)$$

$$[Cl_2]\ \text{in mg/L} = ([MnO_4^-]\ \text{mol/L}) * 1.77 \times 10^5 \quad (2b)$$

## Procedure

### Equipment and Reagents

1 x 25 mL volumetric flask
4 x 100 mL volumetric flasks
plastic dropper
1000 μL micro-pipettor
100 μL micro-pipettor
1 x glass water sampling bottle, screw cap or stopper (pre-soak in dilute bleach)

7 x plastic cuvettes (or rinse wet cuvettes with the next sample)
plastic film or Parafilm strip to seal the top of the cuvette while shaking

PPD-2 Powder Pop Dispenser, HF Scientific (powdered DPD dye and buffer salts)
0.0100 M $KMnO_4$
Spectrometer (https://youtu.be/VoaJkNQlQc0)

The 0.01000 M stock solution of $KMnO_4$ is too concentrated to conveniently prepare the low concentration standard solutions needed for this experiment. An intermediate working standard solution is prepared and used to make the final standard solutions. The scheme for preparing the standard solutions is shown in Figure 5 and described in the following instructions.

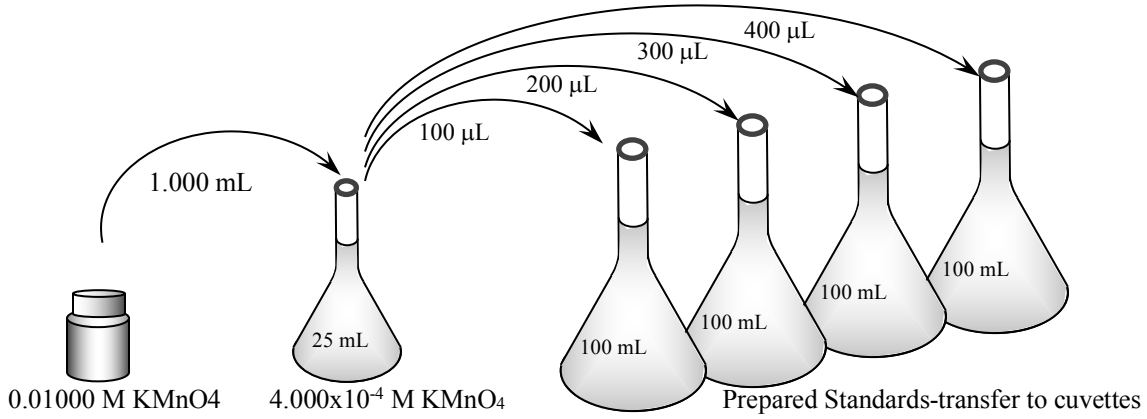


Figure 5: Successive dilutions scheme for the preparation of 0.709-0.284 mg/L equivalent $Cl_2$ standards from 0.01000 M $KMnO_4$.

1. Prepare a $4.00x10^{-4}$ M working standard solution by transferring 1.000 mL of 0.0100 M $KMnO_4$ solution to a 25-mL volumetric flask using a 1000 µL micro-pipettor. Dilute to the mark with deionized water using a plastic dropper (to avoid overshooting the mark). Shake well.

2. Using a 100 µL micro-pipettor, transfer 100 µL, 200 µL, 300 µL, and 400 µL of the $4.00x10^{-4}$ M working standard solution into separate 100-mL volumetric flasks. Dilute each to the mark with deionized water using a plastic dropper. Shake well.

3. Using your sample bottle, find a unique water source on campus and collect a sample. Record the location and time of the sample. You are now on the clock as your sample is changing with time. Return to lab without delay. Each partner should collect their own sample.

4. Rinse a 1000 µL micro-pipettor tip twice with the most concentrated sample. Transfer 3 mL of the most concentrated standard into a cuvette. The volume of the sample does not need to be exact; a micro-pipettor is used only for convenience and to minimize the use of laboratory consumables. Use the Powder Pop Dispenser to add a dose of DPD reagent into the cuvette. Cover the cuvette with plastic film or Parafilm and shake for 12 sec. Repeat this procedure for all of your standards and samples.

5. The instructions for using the spectrometer are posted on the lab page as a video. Calibrate the spectrophotometer using a cuvette filled with deionized water.

6. Confirm that the dye solution is well mixed in all samples. Tap the cuvette holding the most concentrated sample gently on the bench top to dislodge bubbles trapped on the cuvette sides. Determine the absorbance spectrum. Find the wavelength of the dip between the two absorbance peaks (about 533 nm). Record the wavelength and use this same wavelength for all subsequent samples. Record the absorbance at 700 nm to determine the baseline for the spectrum. Subtract the baseline absorbance from the absorbance at the wavelength of maximum absorption; call this absorbance the "corrected" absorbance.

7. Repeat the corrected absorbance determination in the previous step for each standard and sample, at the same wavelength.

## Calculations

Convert the volume of $KMnO_4$ working standard to the equivalent $Cl_2$ concentration in mg/L for each calibration standard, using Eq. 2b. Prepare a calibration curve and determine the DPD absorption coefficient from the slope of the calibration curve. Calculate the $Cl_2$ concentrations for your two water samples, using Eq. 1. Enter your tap water sample locations, collection time, corrected absorbances and corresponding $Cl_2$ concentrations in the class Google Doc.

## What Should Be in Your Notebook?

- The exact concentrations of the 0.010 M $KMnO_4$ stock solution and the $4.0 \times 10^{-4}$ M working stock solution, to three significant figures.
- The volume of $KMnO_4$, the resulting equivalent $Cl_2$ concentration, the absorbance at the wavelength of maximum absorption, and the absorbance at the baseline at 700 nm of each standard solution.
- The absorbance at the wavelength of maximum absorption, the absorbance at the baseline at 700 nm, and the resulting concentration of each sample.
- The date, time, and location of sampling of the tap water.
- The calibration curve should be taped into your lab notebook upon return after grading.

## What Should Be In Your Report?

You will write this lab report on your own, following the guidelines established in the earlier lab reports this semester. There is no report form. Your report should be no more than two pages, with an additional page for the attached calibration curve. Use complete sentences.

*Introduction*: Provide a brief (2-sentence maximum) introduction to the experiment. Don't include results or conclusions in this introduction.

*Procedure*: Reference this laboratory write-up. Include any procedural details that deviated from experimental procedure given in this laboratory write-up. Did something spill? Did you over-shoot the

calibration mark on a volumetric flask? Etc. You do not need to re-write the experimental procedure given in this write-up.

*Data/Results*: Tabulate and report your data for the stock solution, working stock solution, and standard solution concentrations. Report the corrected absorbance and concentration of each standard and your two samples. All tables and graphs must be labeled by a caption. Reference each table and your calibration curve graph explicitly in a sentence in the Results section. Report the concentration of your water samples. Be sure to use proper significant figures.

*Discussion/Conclusions:*
(a). Provide a subject sentence for the paragraph by restating the purpose of the experiment as completed goal. Report the concentration of your tap water samples.
(b). Discuss the important sources of random and systematic error. Which measurement or measurements determined the number of significant figures (the precision) in the final results? Give an important source of systematic error. Give a concise explanation of how this systematic error may have directly changed the final results (did the error make the results too high, too low, etc., explain exactly how that worked).
(c). Why isn't the exact volume of water sample delivered to the cuvette a source of error? The Powder Pop Dispenser does not deliver exactly the same amount of DPD reagent each time. Why isn't the reagent amount a significant source of error?
(d). Briefly answer the following questions about Colby's water:

1. Is the concentration of $Cl_2$ in tap water consistent over time and space?
2. Does activated carbon remove a significant amount of $Cl_2$ (or it's equivalents) from tap water?
3. Where are you going to fill your water bottle in the future?

Attach a copy of your calibration curve.

## Literature Cited:


1. Blue Reserve, LLC, Stoneham MA, http://www.bluereserve.com/ (last accessed 10/14/2013).
2. Standard Methods for the Examination of Water and Wastewater; 22nd Ed., Method 4500-Cl G., p. 4-69.
3. http://www.hach.com/cms-portals/hach_com/cms/documents/pdf/LIT/L7019-ChlorineAnalysis.pdf (last accessed 11/14/2018)