

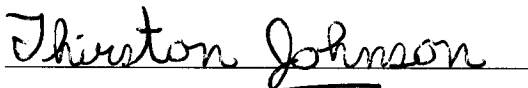
**Evaluating Commercially Available Buffers for the Decolorization of Anthocyanins  
with Chlorine Dioxide**

Project SEED  
Summer 2006

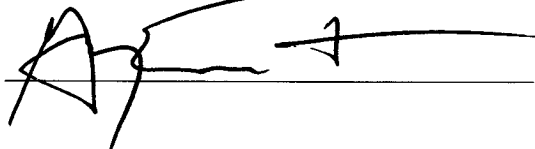
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A handwritten signature in black ink that reads "Thirston Johnson". The signature is written in a cursive style and is positioned above a horizontal line.

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## I. INTRODUCTION

The most common form of water disinfection in the United States is chlorination. Chlorination produces chlorine ( $\text{Cl}_2$ ), hypochlorous acid ( $\text{HOCl}$ ) and hypochlorite ion ( $\text{OCl}^-$ ) which are termed free available chlorine species (FACs). Due to chlorination, disinfection byproducts like trihalomethanes (THMs) and haloacetic acids (HAAs) are produced, which are carcinogens. As a result, another possible water disinfection was needed, chlorine dioxide ( $\text{ClO}_2$ ). In the past, concern over the use of  $\text{ClO}_2$  by-products such as chlorite ion ( $\text{ClO}_2^-$ ) and chlorate ion ( $\text{ClO}_3^-$ ) were an issue. However, recent studies have shown that these by-products may not be a health concern [1]. Previous research has shown that  $\text{ClO}_2$  will decolor organic dyes such as amaranth [2] and Congo red [3]. These dyes are expensive; therefore, we are proposing to use a naturally occurring dye, such as cabbage extract, as a promising reagent for the determination of  $\text{ClO}_2$  and in drinking water.

The purpose of my research was to find a buffer that can be made from a commercially available product, and to find an uncomplicated and inexpensive way to measure  $\text{ClO}_2$  concentrations in drinking water.  $\text{ClO}_2$  will react to decolorize the red cabbage dye in aqueous solutions. Studies showed that after exposing  $\text{ClO}_2$  to cabbage dye that the mixture resulted in a decolorization. Various pH's were studied with different consumer grade buffers and MDL, accuracy, and precision studies were performed at two different pH's.

## II. EXPERIMENTAL

Most of my research over the summer dealt with the batch method with cabbage dye using the disinfectant  $\text{ClO}_2$  and making buffer out of a product that is commercially available. First, I had to extract the dye from the red cabbage, which is simple to do. To extract the dye, the red cabbage is chopped into fine chunks. Second, I placed the chopped red cabbage into a 4000mL beaker (depending on how much cabbage I used) and I packed the red cabbage down slightly, which made my volume of cabbage decrease to 2000mL. Third, I added enough water to submerge the red cabbage. Fourth, I took the beaker and sat it on a hotplate, and boiled it at a temperature of  $100^\circ\text{C}$ . Fifth, after the

cabbage came to a boil and the cabbage turned light purple in color, I took the beaker containing the cabbage off the hot plate. Sixth, I filtered the cabbage dye by taking a funnel and lined the inside of it with filter paper. The dye extraction took about two hours to complete.

Next, I had to find commercially available item that I could make a buffer out of. So, my lab partner bought three inexpensive items from the grocery store (vinegar (Acetic Acid), baking soda (sodium bicarbonate), and MSG (Monosodium Glutamate)) and wanted me to first, look up the items' molecular weights and second, calculate how many grams or mLs of each item it would take to make 500mL of buffer. After careful calculation, it takes 60.096mL of vinegar to make 500mL of 0.1M vinegar buffer, 4.2g of baking soda to make 500mL of 0.1M baking soda buffer, and 8.45g of MSG to make 500mL of 0.1M MSG buffer (depends on how much you want).

Even though they're different products, the procedure is basically the same when making each buffer. First, measure out the certain amount of product you need to make the buffer. Second, place the product in a 600mL Erlenmeyer beaker and dilute to 400mL. Third, use hydrochloric acid or sodium hydroxide to change the pH of each buffer in the presence of a pH meter. Fourth, pour the solution in a 500mL volumetric flask and fill to volume.

Last but not least, I had to make some  $\text{ClO}_2$  since it deals with half of my research. First, I took 16.0g of sodium chlorite and mixed it in 100mL of reagent water. Second, I took 8.0g of potassium persulfate and mixed it in 100mL of reagent water. Third, I took both solutions and mixed them together for twenty minutes in a gas washing bottle until the solution turns dark brown. Fourth, I bubbled nitrogen through the solution at a very slow pace; the gaseous  $\text{ClO}_2$  was collected in 500mL of reagent water in the dark; the bottle of reagent water was wrapped in foil and was placed in an ice bath.

### **III. RESULTS AND DISCUSSION**

The purpose of this experiment was to run a UV-Vis on solutions that were made by mixing 20mL of red cabbage dye with 20mL of the different commercial buffers that were set at different pH's. Since I wanted my buffers to be at a pH where they'll stay constant, I chose pH's that were close to the commercial products' pKa. For example,

vinegar has a pKa at 4.756, the pH's I chose for vinegar buffer(s) were 4.8 and 4.2. The MSG's pKa(s) were 2.16, 4.30, and 9.96 so I chose pH 2.3, pH 3.2, and pH 4.2. For baking soda, I chose pH 5.3 and pH 6.3 since its pKa was 6.351. After testing each and every buffer, results showed that out of all the buffers, the MSG buffer at pH 2.3 was the best one to use (as shown in Figures 1 thru. 5).

Figure 1. Spectra of Baking Soda Buffer at pH 5.2

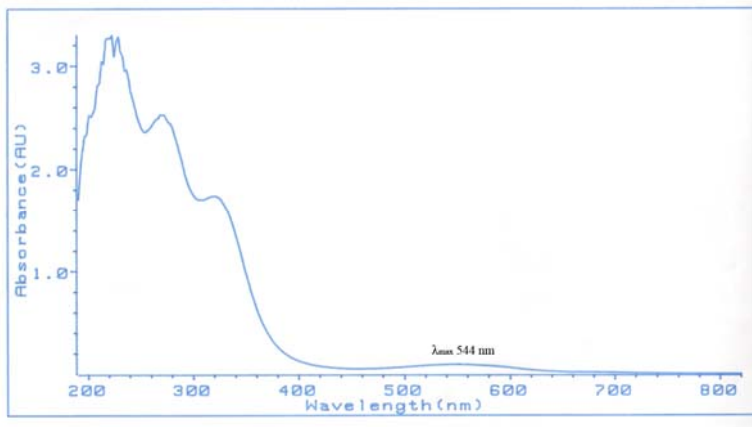


Figure 2. Spectra of Baking Soda Buffer at pH 6.3

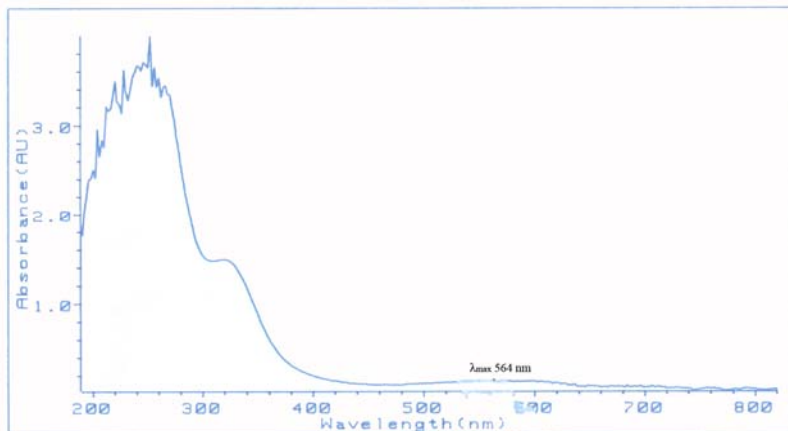


Figure 3. Spectra of MSG Buffer at pH 2.3

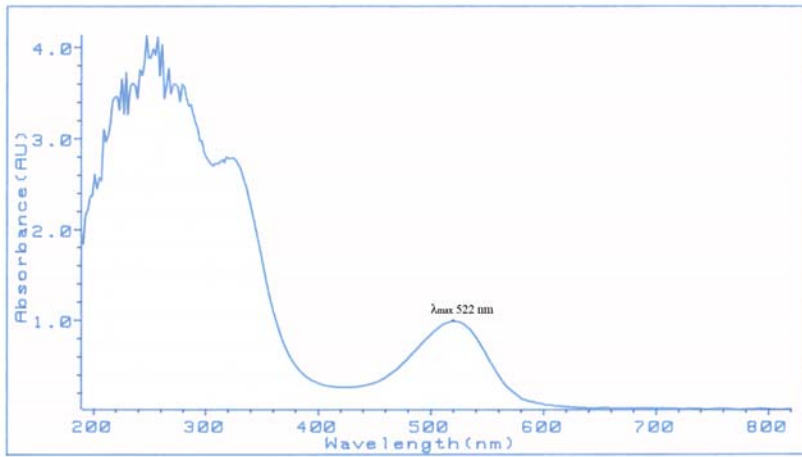


Figure 4. Spectra of MSG Buffer at pH 3.2

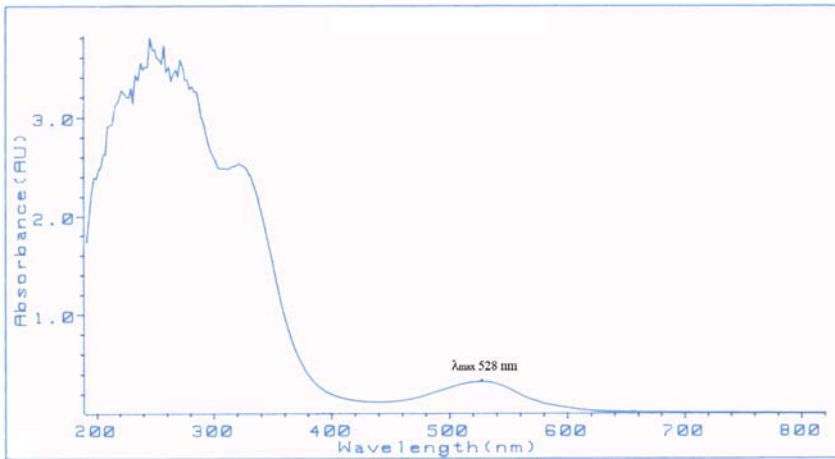
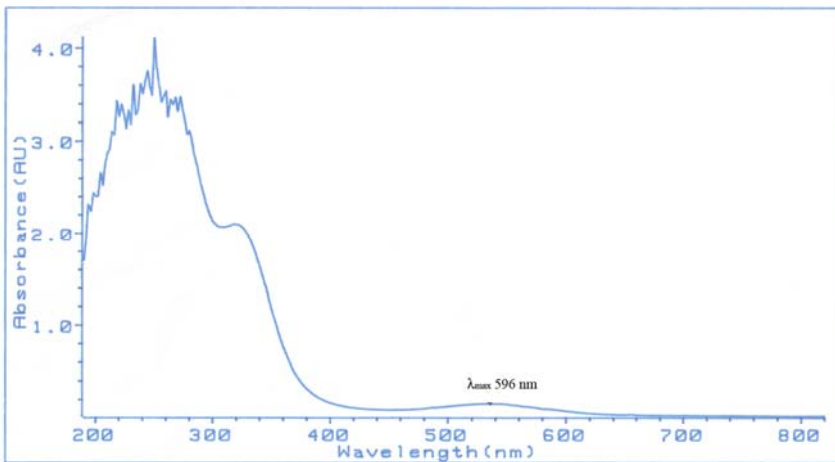


Figure 5. Spectra of MSG Buffer at pH 4.2



As you can see, the MSG buffer at 2.3 an absorbance of 1.02 at 522nm which is in the visible region (between 400nm and 800nm); this is exactly what I wanted to see. This buffer will truly allow me to see how much has the ClO<sub>2</sub> decolorize of the red cabbage dye in my batch method experiment.

Now that I have found the best buffer that has been made from a commercially available product, I can start my batch method experiment. This experiment deals with the Beer-Lambert Absorbance Law (Beer's Law). Beer's Law is represented by  $A = \epsilon bc$  (A stands for absorbance (no units),  $\epsilon$  stands for molar absorptivity (L / (mol) (cm)), b stands for path length (cm), and c stands for molar concentration (mol / L)). The reason why A doesn't have any units is because that since  $A = \epsilon bc$ , when you take  $\epsilon$ 's, b's, and c's units and multiply them together they cancel each other out. In this experiment, 20mL of red cabbage dye and 20ml of MSG buffer at pH 2.3 was evenly distributed to seven 100mL Erlenmeyer flasks. Each Erlenmeyer flasks had their own concentration of ClO<sub>2</sub> and were wrapped in aluminum foil because ClO<sub>2</sub> decomposes if it's exposed to sunlight. However, I first have to find out the seven concentrations of ClO<sub>2</sub>. To do this, I first inject 0.07mL of ClO<sub>2</sub> in a 5cm cylindrical quartz cuvette that has a stirbar that is 7mm in length and 2mm in width. Second, I wrap the cuvette in foil and let it stir on a stir plate for three minutes. Third, I removed the foil and took three consecutive UV-Vis Spectra's. Finally, I plugged in my results into a Microsoft Excel spreadsheet, which uses Beer's Law to calculate the seven concentrations I need to perform my experiment.

After standardizing my ClO<sub>2</sub>, I started making up my seven solutions for testing. Even though the MSG buffer at pH 2.3 was the best buffer, I also used the pH 3.2 MSG buffer in my batch method just to see how my calibration curve would look.

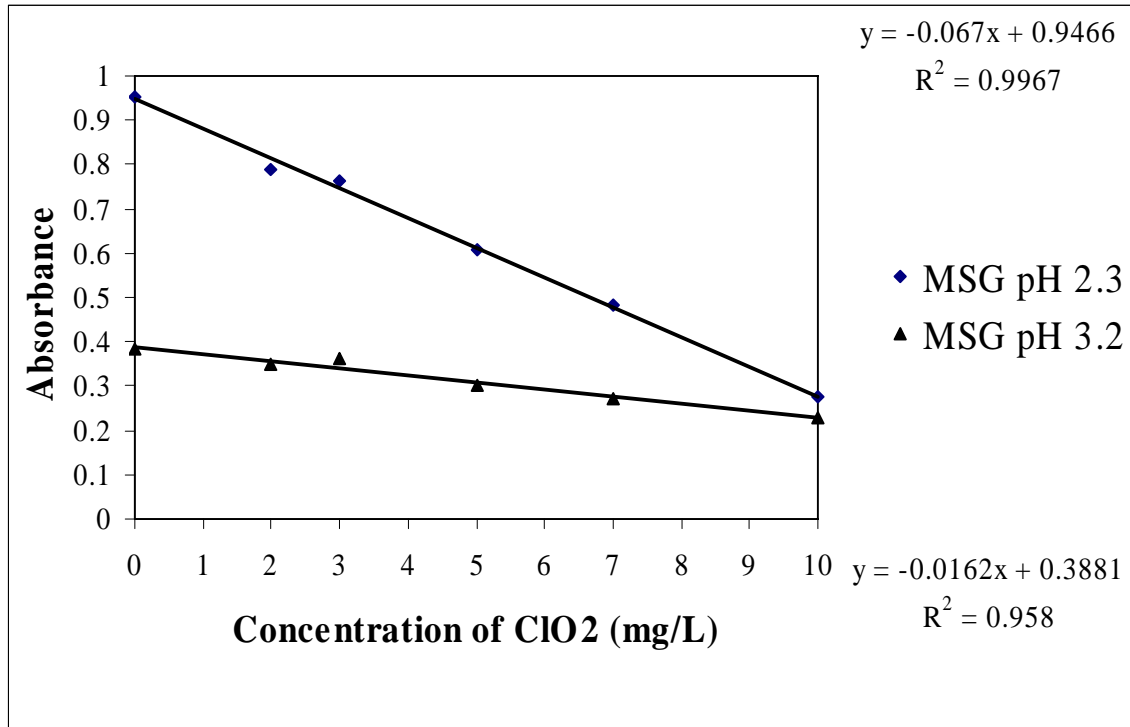


Figure 6. Calibration Curves Using MSG Buffers at pH 2.3 and pH 3.2.

Table 1. Absorbance Values and Calculated Concentrations for Check Standard Data

Check Standard #	MSG Buffer at pH 2.3		MSG Buffer at pH 3.2	
	Absorbance	Concentration (mg/L)	Absorbance	Concentration (mg/L)
1	0.77704	2.53	0.3436	9.01
2	0.78873	2.35	0.33344	9.16
3	0.78722	2.38	0.3391	9.07
4	0.78181	2.46	0.3474	8.95
5	0.77524	2.56	0.3456	8.98
6	0.77808	2.51	0.34038	9.06
7	0.78001	2.48	0.33528	9.13
<b>Average</b>		2.47		9.05
<b>Std. deviation</b>		±0.08		±0.08

As you can see, the batch method when I was using the pH 2.3 MSG buffer came out to be really good. The slope was really steep, which was exactly what I was looking for. The batch method when I used the pH 3.2 MSG buffer came out good too but its slope wasn't steep enough.

Method detection limit (MDL), mean percent recovery, and percent relative standard deviation (% RSD) of the two calibration curves in Figure 8 are located in Table 1. The MDL is the lowest concentration distinguishable from noise. It's good for the MDL to be as low as possible because the lower it is, the better the method is. The mean percent recover or accuracy is how close my measurements were. To the true value the % RSD or precision is how well I reproduced a measurement. Each sample has an individual absorbance, concentration, and % recovery. To calculate the percent recovery, divide each calculated concentration by the check standard, which is 2.5 mg/L, and multiple by one hundred. This is a calculation to detect how accurate we are and ideally, mean % recovery should be  $100 \pm 5\%$ . The mean % recovery was 98.5 for pH 2.3 and 362 for pH 3.2. To calculate MDL, take the standard deviation of the samples and multiply by the student's T-value at 98% confidence level, which is 3.143. The MDL for pH 2.3 is 0.24 mg/L and pH 3.2 is 0.24 mg/L. To calculate % RSD, take the standard deviation and divide by the average concentration of the samples and then multiple by one hundred and %RSD should be  $\pm 10\%$ . The %RSD is 3.1% for pH 2.3 and pH 3.2 is 0.86%.

Table 2. Results from MDL, Accuracy, and Precision Studies

	<b>MSG Buffer at pH 2.3</b>	<b>MSG Buffer at pH 3.2</b>
<b>MDL (mg/L)</b>	0.24	0.24
<b>Mean % Recovery (Accuracy)</b>	98.7	362
<b>% RSD (Precision)</b>	3.1	0.9
<b>R<sup>2</sup></b>	0.9967	0.958

## VI. CONCLUSIONS

I have learned that buffers can be made from commercially available products and since the red cabbage dye was a natural product, the red cabbage dye is a good reagent for the determination of ClO<sub>2</sub>. At pH 2.3, the ClO<sub>2</sub> can be detected as low as 0.24 mg/L with good accuracy and precision. However, at pH 3.2, the accuracy is very high because the sensitivity is low. This is great because it shows that there is an inexpensive way to test and disinfect drinking water.

## VII. REFERENCES

- [1] Chemical Manufacturer's Association, 1997, Final Report, Sodium Chlorite Drinking Water Rat Two-Generation Reproductive Toxicity Study, Study CMA/17/R, Arlington VA.
- [2] Emmert, G.L., Coutant, D. E., Sweetin, D. L., Gordon , G., Bubnis, B., "Studies of Selectivity in the Amaranth Method for Chlorine Dioxide", *Talanta*, 51, 879-888, 2000.
- [3] Emmert, G.L., Puckett, S.D., Zhang, H., "A Survey of Alternative Colorimetric Reagents for Measuring Chlorine Dioxide Concentrations in Drinking Water", A invited review article appearing in *Recent Research Developments in Pure and Applied Analytical Chemistry*, Vol 4, 2002, 77-87.