Development and Analysis of a Double Displacement Method to Detect Nitrates, Sulfates, and Phosphates

### Tony Zheng\*\*

Water is vital for life; thus, monitoring the health of water is essential. Nutrients are considered a major threat to the health of water bodies worldwide. There are numerous methods to detect for nutrients; however, many of them are extremely costly per test, qualitative, take a 2 hour period or longer, and/or are difficult to fund for long periods of time. This study includes the development and analysis of a novel method to detect nutrients. To assess the novel method,  $SO_4^{-2}$ ,  $NO_3^{-}$ , and  $PO_4^{-3}$  ions were tested and compared. Forty-six water samples were gathered from the Metedeconk River, NJ and a Brick MUA, NJ tap water source. Samples were tested using the novel method against a LaMotte® SMART 2 Colorimeter. Results were then compared to the Brick MUA's state lab test methods. Results suggest that the novel method was 10 times faster, 23.48% more accurate, and 970 times cheaper compared to the colorimeter. Compared to the Brick MUA Lab, the novel method is 180 times faster, with 3.83% error, 12,500 times cheaper.

Keywords: nutrient runoff, water contamination, Hurricane Sandy, double displacement, colorimeter, novel method

\*\*Contact: tzheng12@gmail.com

### Introduction

Throughout history, clean water has proven to be an essential part of life. The human body is comprised of 70% water. Water provides a substrate for red blood cells and hemoglobin to travel [9]. Without hemoglobin to provide the human body with the necessary oxygen, the muscle and nerve systems would not function. This is why people feel light-headed and nausea following dehydration. Cells require water to transport nutrients, waste, and to reproduce [9]. Without water life would not exist. However, most of the water on Earth is contaminated with either chemicals or bacterial. Statistics from The Pacific Institute show that over 2 million tons of sewage, agricultural, industrial, and human waste is discharged the world's water [13]. Worldwide, 2.5 billion live without improved sanitation [5]. Water contamination is a prevalent issue and must be dealt with.

Nutrient runoff in the form of nitrates, sulfates, and phosphates is a huge contributor to water contamination; hence, it is a global environmental crisis. Nationally, fertilizer runoff is

the cause of a 6,000 square mile death zone west of the Mississippi River and off the coast of Louisiana [6]. Nutrients enter a water body and provide phytoplankton and macroalgae with excessive nutrients. Phytoplankton and macroalgae respond to this sudden outbreak of nutrients by increasing reproduction. The water system becomes overflown with algae and other primary producers competing for the same resources like sunlight. Eventually, the primary producers, particularly algae, will grow to cover the water body surface and block sunlight for the organisms below. This will cease oxygen production as many primary producers will not obtain the required amount of sunlight. A lack of oxygen will eliminate heterotrophs, and the area becomes a dead zone [15]. Constant nutrient monitoring is essential to ensure the health of water bodies across the globe.

The most widely used and accepted method to date to detect for nitrates, sulfates, and phosphates is a colorimeter [19]. Beer-Lambert's law states that the amount of light absorbed by a solution is directly proportional to the concentration

of the solutions [16]. Colorimeters apply this law to detect for contaminants. To do this, a reagent is mixed into the sample. Upon contact with the desired contaminant, the reagent will produce a characteristic color (nitrate: pink, phosphate: blue, sulfate: white). The colorimeter emits ultraviolet light through the sample and determines the amount of solute present based on color absorbance [19]. This method is effective; however, color development takes 10-15 minutes, the machine and reagents are expensive, the reagents are harmful to the environment and must be disposed as chemical waste, and light beams and refract and incur error.

According to Le Chatelier's Principle, when a stress is induced into a system, the system will react in a way to compensate the stress [4]. In a balanced chemical reaction, the amount of reactants inputted is equivalent to the amount of products yield. This means that for a given sample/system if a stress is imposed in the form of a reactant then the system will shift to use up that reactant by combing it with other compounds and producing new chemicals with the same mass as the original reactants. By creating a standardized, balanced reaction with one fixed reactant and one unknown reactant with varying concentration but contains the desired chemical compound (in this case nitrate, phosphate, or sulfate), the amount of nutrients in any unknown sample can be determined [4,7-9,14-18]. This process will only work for a specific fixed reactant that will yield a solid precipitate; thus, it is coined the key reactant/reagent [14]. Based upon the amount of fixed reactant added and the color of the solid precipitate at equilibrium, standardized reaction using stoichiometry can be used to find the concentration of the unknown nutrient. In an chemical from aqueous environment. ions compounds dissociate into the solution. This enables the key reagent to react with the desired chemical compound. As long as the solid precipitate is formed, the reaction is complete [8]. This concept

may seem confusing at first but it will become apparent in the methodology.

This study attempts to apply Beer-Lambert's Law, Le Chatelier's Principle, Law of Conservation of Mass, stoichiometry, and solubility rules to create a different approach to detecting nitrates, sulfates, and phosphates in water [4, 7, 16]. Specifically, this study contains two phases, which can be thought of as two experiments. Phase linvolves the development of a possible novel method to detect nutrients. According to solubility rules, Strontium sulfate is not soluble in water, Dicalcium phosphate is not soluble in water, and most carbonate compounds are insoluble in water [7]. Therefore, it is hypothesized that by using a 1 molar solution of Strontium nitrate  $(Sr(NO_3)_2)$  to vield Strontium sulfate, a 1 molar solution of Calcium chloride (CaCl<sub>2</sub>) to yield Dicalcium phosphate, a 1 molar solution of Sodium carbonate  $(Na_2CO_3)$  to yield a carbonate compound, and stoichiometry a value can be derived for the amount of sulfate, phosphate, and nitrate, respectively, in a water sample. Phase 2 involves evaluating the novel method's accuracy compared to the accuracy of a SMART Colorimeter. LaMotte<sup>®</sup> 2 It is hypothesized that the readings from the novel method are extremely accurate due to the key reagents used and how the reactions performed are double displacements reactions that run to completion.

# Methodology

To create the novel method (Phase 1), known reactions were ran to determine the specific hue that was formed upon reacting with a nutrient compound. That specific coloration or hue is unique to each chemical reactions and chemical reactants and will not be produced unless equilibrium is achieved and the reaction went to completion for that one specific reaction [7-8]. By identifying key reagents that will produce hues and then running completed, controlled reactions to produce the hues, the reactions are known to be completed when that specific hue is exhibited during the reaction. Next by using the key reagents on any unknown sample to attain the hue, all possible nutrients will have bound to the key reagent and completed the reaction. Finally by measuring the amount of key reagent added and using stoichiometry, one can determine the amount of nutrients present in the sample. The key reagents are really a set of unique chemical compounds that will yield a measurable precipitate when they react with nitrates, sulfates, and phosphates. It should be noted that additional criteria for the key reagents include high environmental friendliness and high activity. Additionally, the key reagent must also yield a soluble product to maximize ease to distinguish the nutrient precipitate/ hue formed. For example, it would be extremely difficult to identify the nutrient precipitate if one precipitate was creamy white and the other was pearl white. To identify the key reagents, a sample pool of 12 possible chemical compounds were taken and three key reagents were isolated based on precipitate formed, environmental friendliness, and position on the chemical activity series; one key reagent for nitrate, one for sulfate, and one for phosphate. In total, there were three stages of selection to identify 3 key reagents from the possible pool of 12. The 12 starting chemical compounds were thought to be possible key reagents after careful literature review [1-19]. The 12 starting chemical compounds are as follows:  $Sr(NO_3)_2$  Ca(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>  $Pb(NO_3)_2$ ,  $BaCl_2$ ,  $AgNO_3$ ,  $Cu_2SO_4$ ,  $K_2CO_3$ , NaNO<sub>3</sub>, and CaCO<sub>3</sub>.

After considering 12 possible key reagents out of a plethora of chemical compounds, they had to be tested to determine if they would yield a precipitate when reacted with nitrate, sulfate, or phosphate. To do this, each of the twelve chemical compounds were reacted with a nitrate compound, a sulfate compound, and a phosphate compound. MgSO<sub>4</sub> was used as the reagent for all sulfate reactions.  $Sr(NO_3)_2$  was used as the reagent for all nitrate reactions.  $Na_2HPO_4$  was used as the reagent for all phosphate reactions. To illustrate the reactions carried out, below are stock examples of the chemical reactions where X, Y, and Z are all possible key reagents.

 $X + MgSO_4 =$  sulfate precipitate + soluble byproduct

 $Y + Sr(NO_3)_2 = soluble \ nitrate \ by product + \\ insoluble \ by product$ 

 $Z + Na_2HPO_4 = phosphate precipitate + soluble byproduct$ 

Note that nitrates are always soluble [8]. Because of this, the key reagent for nitrates will actually yield a soluble nitrate product and another insoluble product. The only change will be that the stoichiometry calculations will be slightly different to account for this discrepancy.

After running a combination of 34 reactions where each of the twelve reagents were reacted with the three nutrient compounds (original 36 reactions minus MgSO<sub>4</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> for sulfate and nitrate reactions respectively as they were the designated nutrient compounds), it was determined that NaNO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were unsuitable to be key reagents as they did not precipitate desirable products. At the end of the first round of selection, the remaining possible key reagents were as follow: Sr(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, BaCl<sub>2</sub>, AgNO<sub>3</sub>, Cu<sub>2</sub>SO<sub>4</sub>, and CaCO<sub>3</sub>.

Next, the remaining possible key reagents were furthered filtered based on their impact to the environment. This was accomplished by reviewing each compound's MSDS on Sigma-Aldrich, a for profit chemical manufacturing company [1]. Compounds that have an adverse effect on the environment were removed from the pool. Compounds that had little to no impact on the environment were selected for one final round of review. This process ensures that the key reagents were environmentally safe as the study objective is to detect chemical contaminants in the environment and not to add excess chemical contaminants into the environment. At this point, the following chemical compounds remain  $Sr(NO_3)_2$ ,  $CaCl_2$ ,  $Na_2CO_3$ , and  $CaCO_3$ .

The final stage of selection involved determining the chemical compounds' location on the activity series. The key reagents must be as reactive as possible. To put this into perspective, let us say that in an unknown sample there is an unknown compound that creates a similar hue when reacted with the nutrients. To reduce faulty readings, the key reagent must be more reactive than the unknown compound. Thus by finding key reagents that are extremely reactive and are at or near the top of the chemical activity series, this step will decrease incurred error [18]. Na<sub>2</sub>CO<sub>3</sub>, and CaCO<sub>3</sub> yield similar hues for nitrate detection; however, because sodium is more reactive than calcium, Calcium carbonate was eliminate. This resulted in the following key reagents:  $Sr(NO_3)_2$ , CaCl<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub> for sulfate, phosphate, and nitrate detection, respectively.

Upon identifying the key reagents, reactions were ran to determine the standardized hues produced with the key reagents. These hues became the base images for all future reactions to indicate when the reaction ran to completion. To produce the base images, the following reactions were carried out,

\* Sulfate Detection:  $Sr(NO_3)_2 + MgSO_4 \rightarrow Mg(NO_3)_2 + SrSO_4$ 

\* Phosphate Detection:  $CaCl_2 + Na_2HPO_4 - CaHPO_4 + 2NaCl$ 

\* Nitrate Detection:  $Na_2CO_3 + Sr(NO_3)_2 \rightarrow 2NaNO_3 + SrCO_3$  The novel method reaction works only if  $Sr(NO_3)_2$  is the key reagent for sulfate detection because it produces  $SrSO_4$  (precipitate) if  $CaCl_2$  is the key reagent for phosphate detection because it produces  $CaHPO_4$ (precipitate) and if  $Na_2CO_3$  is the key reagent for nitrate detection because it produces a soluble  $NaNO_3$  in addition to a precipitate. A 1 M solution of  $Sr(NO_3)_2$  was prepared by mixing 21.163 g  $Sr(NO_3)_2$  with 100 mL of distilled water. A 1 M solution of CaCl<sub>2</sub> was prepared by mixing 11.098 g CaCl<sub>2</sub> with 100 mL of distilled water. A 1 M solution of Na<sub>2</sub>CO<sub>3</sub> was prepared by mixing 10.598 g Na<sub>2</sub>CO<sub>3</sub> with 100 mL of distilled water. One M solution of MgSO<sub>4</sub> was prepared by mixing 12.038 g MgSO<sub>4</sub> with 100 mL of distilled water. One M solution of Na<sub>2</sub>HPO<sub>4</sub> was prepared by mixing 14.196 g Na<sub>2</sub>HPO<sub>4</sub> with 100 mL of distilled water. One M solution of Ba(NO<sub>3</sub>)<sub>2</sub> was prepared by mixing 10.598 g Ba<sub>2</sub>CO<sub>3</sub> with 100 mL of distilled water.

Five mL of  $Sr(NO_3)_2$  was added to 5 mL of MgSO<sub>4</sub> to make a base image (Figure 3). Five mL of Na<sub>2</sub>HPO<sub>4</sub> was added to 5 mL of CaCl<sub>2</sub> to create a base coloration (Figure 4). Five mL of Na<sub>2</sub>CO<sub>3</sub> was added to 5 mL of  $Sr(NO_3)_2$  to create a base coloration (Figure 5). Next, following unit analysis and stoichiometry were carried out to determine a quantitative value of nutrients formed. Rough sample calculations are depicted in figure 1. Percent composition was incorporated at the end to derive the final mass of desired nutrient. Note that nitrates are always soluble; thus, the hue produced by nitrate testing is the carbonate compound and not nitrates.

 $= \int_{a}^{b} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} + \frac{1}{A_{a}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} + \frac{1}{A_{a}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} + \frac{1}{A_{a}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} + \frac{1}{A_{a}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}}} \int_{a}^{b} \frac{de^{-\frac{1}{2}}}{de^{-\frac{1}{2}}} \int_{a}^{b} \frac$ 

Figure 1: Sample calculations to determine nutrients



Figure 2: Lab setup to determine base colorations



Figure 3: Sulfate base image



Figure 4: Phosphate base image



Figure 5: Nitrate base image

Although the reactions ran to create the base image had known reagents, these reactions are what will actually occur in nature, where X's represent unknown compounds in nature:

\* Sulfate Detection:  $Sr(NO_3)_{2(aq)} + XSO_{4(aq)} \rightarrow X(NO_3)_{2(aq)} + SrSO_{4(s)}$ 

\* Phosphate Detection:  $XHPO_{4(aq)} + CaCl_{2(aq)} \rightarrow CaHPO_{4(s)} + XCl_{(aq)}$ 

\* Nitrate Detection:  $Na_2CO_{3(aq)} + X(NO_3)_{2(aq)} \rightarrow 2NaNO_{3(aq)} + XCO_{3(s)}$ 

### Study Site

The Metedeconk River is a 90 mile long freshwater river with little to no salt that flows through nine towns and two counties. Currently, the Metedeconk River is home to 52 species of fishes and 79 species of bird, most of which are endangered [12]. This river is where the Brick Township Municipal Utilities Authority, NJ (designated water sanitation plant for Brick Township, NJ and Point Pleasant Township, NJ) draw their water supply. In fact, the Brick Municipal Utilities Authority water treatment plant (Brick MUA Lab) houses some of the largest and most accurate equipment like analytical ion chromatography to detect for nutrients.

To evaluate the capabilities of the novel method in a real world scenario (Phase 2), 48 water samples were gathered from the Metedeconk River, Brick NJ and from a designated Brick, NJ tap water source over six months. Samples were collected once a week on Wednesday from August 15, 2012 to January 23, 2013. This accounts for how water quality may vary over time and yield different measurements. To limit variability, samples were always gathered on Wednesdays. This totaled 46 samples, not 48 samples as Hurricane Sandy struck New Jersey on November 29-30, 2013, which was the day before a schedule sampling date. To clarify, the Brick MUA tap water gathered is not the tap water that residents would receive as the nutrient levels may be nonexistent. The Brick MUA tap water gathered went through a preliminary filter at the Brick MUA plant to remove sediments.

After 60 minutes upon collection, the water samples were tested for nutrients on the LaMotte® SMART 2 Colorimeter. The LaMotte® SMART 2 Colorimeter was calibrate and samples were ran for nitrates. sulfates. and phosphates using the operator's instructions for each test [17]. Colorimeters cannot read turbid samples [10]. Due to Hurricane Sandy, sample #12 was extremely turbid and had to be filtered with a vacuum pressure pump attached to a filter flask attached to a funnel (Figure 9).

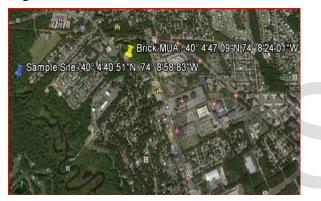


Figure 6: Satellite image of the sampling site in the Metedeconk River and the Brick MUA

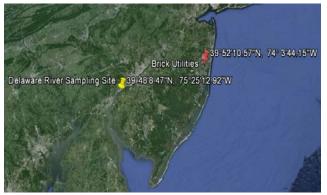


Figure 7: Satellite image of the Brick MUA and Delaware River sampling site in relation to N.J.



Figure 8: LaMotte SMART 2® colorimeter to detect nutrient levels



Figure 9: Vacuum pump setup to remove suspended particles

Ten mL of the samples were taken and measured for nutrients with the novel method, and key reagents were added via a micropipette. By using a micropipette to add key reagents, it alleviates human error and creates extremely accurate readings. To determine accuracy of the novel method compared to the colorimeter, detailed lab results were obtained from the Brick MUA Lab for comparison. In other words, the Brick MUA Lab results are the control, while the novel method and the colorimeter are variables to be tested for efficiency.

Overall efficiency was evaluated on the basis of cost, accuracy, and speed (Phase 2). Overall efficiency is summarized and outlined in table 1. Data regarding cost of the test were obtained from Brick MUA, LaMotte®, and Carolina® Supply Company. A Colorimeter costed \$925.00 from LaMotte®. Each nitrate reagent cost \$60.00 and runs about 50 test; this averages to about **\$19.70** per nitrate test. Each phosphate reagent cost \$50.00 and runs about 40 test; this averages to about \$24.38 per phosphate test. Each sulfate reagent cost \$50.00 and runs about 50 test; this averages to about \$19.50 per sulfate test [10]. Brick MUA utilizes large scale computers, ion monitoring sensors, and man power to measure the nutrients, which totals to about \$50.00 per test. The cost to purchase Strontium nitrate, Calcium chloride, and Sodium carbonate (key reagents) are \$5.90/lb, \$8.50/lb, and \$9.25/lb per respectively. A pound makes about (21) 100 mL 1 Molar solutions of Strontium nitrate (enough for about 1,100 test); (41) 100 mL 1 Molar solutions of Calcium chloride (enough for about 1500 test); and (43) 100 mL 1 Molar solutions of Sodium carbonate (enough for about 1700 test). The average cost per test for each of the nutrients evaluated was approximately \$0.004 [3]. The time it took all three methods (Brick MUA Lab, Colorimeter, and novel method) to determine the amount of nutrient in a sample was obtained from Brick MUA, LaMotte® and through experimentation. Brick MUA Lab results took two hours to development, the Colorimeter took 10-15 minutes for the colors to develop, and the novel method base image appeared instantaneously upon addition of the key reagents. Accuracy data was obtained from Brick MUA and through experimentation.

# Statistical Analysis

Data collected were analyzed using t-test pair two samples for mean with an alpha value of 0.05 or less used for significance between data sets. Statistical difference means that the data did not occur by chance and are good representations of the actual data. Results were averaged and plotted onto a line graphs for comparison with a 5% standard error.

#### Results

All measurements were taken to two decimal places with alpha/p-values to four decimal places. Sulfate readings in the Metedeconk River ranged from 104.00 ppm to 288.00 ppm for the colorimeter, from 150.00 ppm to 292.00 ppm for the novel method, and from 157.00 ppm to 187.00 ppm for the Brick MUA lab (Figure 10). Sulfate readings from the Brick MUA tap water ranged from 15.00 ppm to 28.00 ppm for the colorimeter, from 16.17 ppm to 39.79 ppm for the novel method, and from 17.91 ppm to 43.30 ppm for the Brick MUA Lab (Figure 11). Phosphate readings in the Metedeconk River ranged from 10.00 ppm to 23.00 ppm for the colorimeter, from 13.66 ppm to 34.80 ppm for the novel method, and from 12.70 ppm to 33.10 ppm for the Brick MUA lab (Figure 12). Phosphate readings for Brick MUA tap water ranged from 0.17 ppm to 0.45 ppm for the colorimeter, from 0.07 ppm to 52 ppm for the novel method, and from 0.11 ppm to 0.51 ppm for the Brick MUA lab (Figure 13). Nitrate readings in the Metedeconk River ranged from 7.00 ppm to 22.00 ppm for the colorimeter, from 10.34 ppm to 29.75 ppm for the novel method, and from 11.05 ppm to 30.83 ppm for the Brick MUA lab (Figure 14). Nitrate readings for Brick MUA tap water ranged from 7.00 ppm to 15.00 ppm for the colorimeter, from 7.97 ppm to 17.91 ppm for the novel method, and from 7.79 ppm to 19.61 ppm for the Brick MUA lab (Figure 15). Note that the x-axis on the graphs below depict sampling days where each date represents consecutive Wednesday from August 15, 2012 to January 23, 2013.

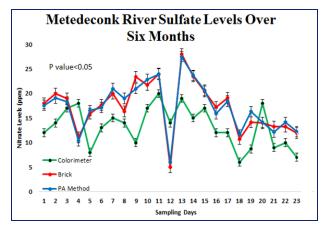


Figure 10: Metedeconk River sulfate levels (ppm;  $\pm$  5% Standard Error) from 8/15/12 to 1/23/13

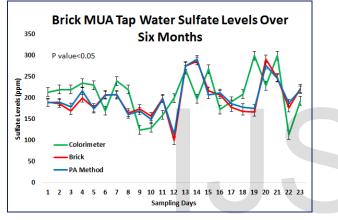


Figure 11: Brick MUA tap water sulfate level

```
(ppm; <u>+</u> 5% Standard Error) from 8/15/12 to 1/23/13
```

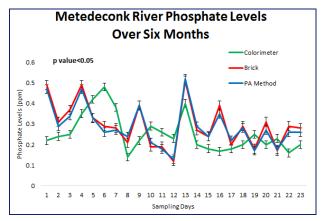


Figure 12: Metedeconk River phosphate levels (ppm;  $\pm$  5% Standard Error) from 8/15/12 to 1/23/13

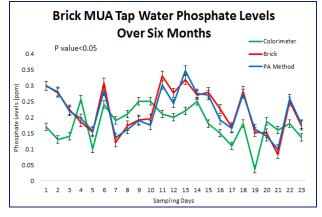


Figure 13: Brick MUA tap water phosphate level (ppm;  $\pm$  5% Standard Error) from 8/15/12 to 1/23/13

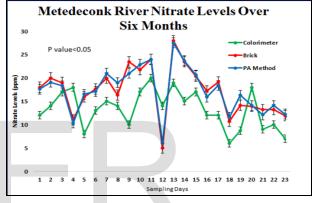


Figure 14: Metedeconk River nitrate levels (ppm;  $\pm$  5% Standard Error) from 8/15/12 to 1/23/13

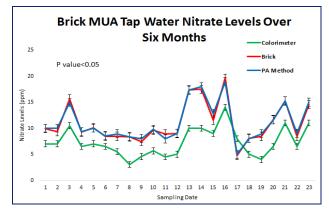


Figure 15: Brick MUA tap water nitrate levels (ppm;  $\pm$  5% Standard Error) from 8/15/12 to 1/23/13

Calculated percent error using the Brick MUA lab results as the accepted reading showed that for the Metedeconk River sulfate detection: the colorimeter had an average error of 18.17%, while the average error for the novel method was 2.84%,

phosphate detection: the average error for the colorimeter was 35.19%, while it was 4.78% for the novel methods, and nitrate detection: the average error for the colorimeter was 32.65%, while it was 5.49% for the novel method (Table 1). For the Brick MUA tap sulfate detection: the colorimeter had an average error of 19.84%, while the average error for the novel method was 3.90%, phosphate detection: the average error for the colorimeter was 29.66%, while it was 5.93% for the novel methods, and nitrate detection: the average error for the novel methods, while it was 5.93% for the novel methods, and nitrate detection: the average error for the novel method.

Results obtained from two tailed t-test indicate that the p-values for all readings involving colorimeter vs novel method and colorimeter vs Brick MUA were under 0.05 indicating statistical difference. The p-values involving novel method vs Brick MUA was over 0.05 indicating statistical similarity.

Overall, the novel method proved to be 10 times faster, 970 times more cost efficient, and 6 times more accurate. The novel method demonstrated to be 180 times faster, 12,500 times more cost efficient, and within a 5% accuracy compared to the Brick lab (Tables 1-3).

Calculated percent error using the Brick MUA lab results as the accepted reading showed that for the Metedeconk River sulfate detection: the colorimeter had an average error of 18.17%, while the average error for the novel method was 2.84%, phosphate detection: the average error for the colorimeter was 35.19%, while it was 4.78% for the novel methods, and nitrate detection: the average error for the colorimeter was 32.65%, while it was 5.49% for the novel method (Table 1). For the Brick MUA tap sulfate detection: the colorimeter had an average error of 19.84%, while the average error for the novel method was 3.90%, phosphate detection: the average error for the colorimeter was 29.66%, while it was 5.93% for the novel methods, and nitrate detection: the average error for the

colorimeter was 16.37%, while it was 3.70% for the novel method.

Results obtained from two tailed t-test indicate that the p-values for all readings involving colorimeter vs novel method and colorimeter vs Brick MUA were under 0.05 indicating statistical difference. The p-values involving novel method vs Brick MUA was over 0.05 indicating statistical similarity.

Overall, the novel method proved to be 10 times faster, 970 times more cost efficient, and 6 times more accurate. The novel method demonstrated to be 180 times faster, 12,500 times more cost efficient, and within a 5% accuracy compared to the Brick lab (Tables 1).

Table 1: Efficiency comparison among the three methods

Method	Speed	Accuracy	Cost (per test)
Colorimeter	10 mins	72.69%	\$3.88 (3.88 x 10 <sup>1</sup> )
Brick Lab	180 mins	Control	\$50.00 (\$5.00 x 10 <sup>2</sup> )
PA Method	1 min	96.17%	\$0.004 (\$4.00 x 10 <sup>-3</sup> )

# Discussion

Based on the results, a distinct coloration using key reagents was produced to measure the amount of nutrients in a 10 mL water sample (Figure 3, 4, and 5). This support the hypothesis of Phase 1 that by using Strontium nitrate to yield Strontium sulfate (note the 1:1 solution ratio is characteristic of the molar ratio in Figure 3), Calcium chloride to yield Dicalcium phosphate (note the 2:1 solution ration is characteristic to the molar ratio in Figure 4), Sodium carbonate to yield a carbonate compound (note the 2:1 solution ration is characteristic to the molar ratio in Figure 4), and mole ratios and unit analysis, a quantitative value for the amount of sulfate, phosphate, and nitrate can be determined. Results also indicate that the novel method proved to be much more accurate compared to the colorimeter supporting the hypothesis of Phase 2 that the novel method readings would be more accurate compared to the colorimeter (Figure

10-15). Colorimeters use light rays to determine the amount of contaminants in a sample. Light rays can be diffracted by finger smudges or microscopic cracks in the vials that house the water sample thus resulting in faulty readings [11]. It may seem that the novel method may be erroneous because each drop of key reagent may vary in volume and individuals with shaky hands may add excessive drops. However, this is not an issue because surface tension of liquids will hold each droplet together and ensure that they have the same volume [9]. Additionally, error can also be eliminated by using a micropipette set to the desired volume of reagents.

Key reagents will not bind to other ions and incur faulty readings because ions dissociate in water [9]. The key reagent will bind to the desired nutrient and other ions as well. However, continuous addition of the key reagent until the base image is achieved ensures that most of the nutrients are bound to the key reagent. The base image will always be produced because equilibrium will always establish itself in the water sample [4]. The key reactants are specific for their nutrient and because they must fit three criteria. A) The cation must always be insoluble in a compound with the desired chemical contaminant, B) The anion must always be soluble regardless of the element it is bonded to, and C) The key reagent to be added to the sample must be a 1 molar solution to allow for mole ratios and unit analysis. Even if the key reagents bind to other aqueous compounds that are not the desired nutrient, error will not be incurred because the reaction will not produce the desired base image. These criteria ensure that one of the products will precipitate to allow for unit analysis.

NaCl diffracts and reflects light from the colorimeter [11]. This may have contributed to high percent error for the Metedeconk River that is an estuary, which is a combination of salt and fresh water where salt water inflow is greater than fresh water inflow. Although the samples were obtained from a definite freshwater location, salt intrusion

may have occurred. This hints at the potential for the novel method to be used in saline water. Developing a method for detection in saline waters was not the original objective. As a future study, the method can be tested on ocean water with more trials for nitrate, sulfate, and phosphate detection. A projected hypothesis to why the novel method is accurate in saline waters is because ions dissociate in aqueous environments and the key reagents binds to the nutrient ions and are not affected by NaCl. Furthermore, other future research studies involving the novel method may include using the knowledge from this study to create novel methods to detect for other contaminants including calcium, magnesium, heavy metals, xenobiotics, and even pathogens. Theoretically, the novel method should incur no error as all nutrient ions are bound to the key reagents; however, the novel method incurred an averaged 3.83% error. The error could have been a result of the instruments used or a limitation due to rounding during calculations. Further testing can elucidate the cause of the 3.83% error incurred by the novel method.

Hurricane Sandy was a post-tropical storm that struck the Jersey Shore on November 29, 2012 to November 30, 2013 carrying wind gust speeds of over 60 mph and heavy rain [13]. Sample #12 was gathered on November 7, 2013, eight days after Hurricane Sandy hit the Metedeconk River. The storm stirred up the river and made it turbid. High turbidity cannot be tested on the colorimeter or the novel method. Thus, the sample had to be filtered to remove sediments. Sediments contain pockets that will retain ions and nutrients known as cation exchange capacity [2]. Thus, when the sediments were filtered so were nutrients. This resulted in low readings eight days after Hurricane Sandy when normal nutrient readings are expected to be high due to excessive runoff from heavy rain and wind.

The proposed novel method makes it easy for individuals and water monitoring organizations like Clean Ocean Actions, NJ and the Barnegat Bay Partnership, NJ to test for nutrients. For example, a test kit could be created revolving around the novel method that could come prepackaged with 1 Molar solutions of the key reagent, pipettes, sampling vials, a chart depicting the base image, and a table that shows nutrient calculations. Because the novel method is cost efficient and extremely accurate, the novel method is viable for consumers to test their ponds, lakes, drinking water, etc. This may promote citizen science in the future. Furthermore, the novel method can adopted by nonprofit water quality monitoring organizations as a cost efficient solution to accurately detect nutrient levels in water systems. Overall, the novel method could be useful to both consumers and the industry alike.

Costs for both the novel method, Brick MUA, and Colorimeter were based on cost estimates from Carolina®, Brick MUA, and LaMotte®. Cost estimates are subjected to change without warning as dictated by the supplies; thus, cost calculations may be inaccurate. It should be noted that when if the cost calculations are inexact, the novel method is still more cost efficient compared to both the Brick MUA and the colorimeter by at least two orders of magnitude.

In all the tests, novel vs Brick MUA lab the p-value was less than 0.05, and colorimeter vs Brick MUA lab was over 0.05 (Figures 10-18). This means that colorimeter readings were not a good representation of neither the novel method nor the Brick lab. However, the novel method is a good representation of the Brick lab. Graphically, this can be depicted as error bars with 5% standard deviation.

# Conclusion

The novel method involves a double displacement of Strontium nitrate and any sulfate compound to yield Strontium sulfate (precipitate), Calcium chloride and any phosphate compound to yield Calcium hydrogen phosphate (precipitate), and Sodium carbonate with any nitrate compound to yield Sodium nitrate (precipitate). By adding the key reagents to any sample to obtain the base coloration, the reactions have gone to completion [4]. By measuring the amount of key reagent inputted and using mole ratio conversions, the amount of a nitrates, phosphates, and sulfates present in a sample can be determined. Overall, the novel method demonstrated to be significantly more accurate by an average of 5-6 times, 3,000 times cheaper, 10 times faster, and 100 times more energy efficient. Additionally, the novel method is environmentally friendly, which is important for any testing conducted out in the field. This suggests that the novel method could be an effective mean to detect nitrate, sulfates, and phosphates in solution. Meanwhile, the colorimeter is still a viable form of testing for nutrients as it cheaper and faster than the Brick MUA Lab.

# Acknowledgements

Many thanks go out to the following people and organization for their continued support: John Wnek, Marine Academy of Technology and Environmental Science, and Rob Karl of the Brick MUA.

# Resources

- Aderemi, P., Man, H., Soom, M., Mohammed, T., & Oluwakunmi, A. (2014). Groundwater Quality of Shallow Wells on Nigerian Poultry Farms. Polish Journal Of Environmental Studies, 23(4), 1079-1089.
- 2. Aquafina. (2011). Hydro-7<sup>TM</sup> Process.
- 3. Bienkowski, B. (2013). New report: Unregulated contaminants common in drinking water. *Environmental Health News*.
- 4. Burney, J. A., Kennel, C. F., & Victor, D. G. (2013). Getting serious about the new realities of global climate change. Bulletin Of The Atomic Scientists, 69(4), 49-57. doi:10.1177/0096340213493882
- 5. Center for Disease Control and Prevention. (2012). Commercially Bottled Water.
- 6. Center for Disease Control and Prevention.
- (2012). Water Treatment.

International Journal of Scientific & Engineering Research, Volume 5, Issue 11, November-2014 ISSN 2229-5518

7. Dasani. (2011). The Purification Process.

- 8. Deer Park. (2011). Deer Park-Born Better.
- 9. Epa.gov. (2011). Drinking Water Contaminants.
- Halliday, E., McLellan, S. L., Amaral-Zettler, L. A., Sogin, M. L., & Gast, R. J. (2014). Comparison of Bacterial Communities in Sands and Water at Beaches with Bacterial Water Quality Violations. Plos ONE, 9(3), 1-9. doi:10.1371/journal.pone.0090815.
- 11. Mercola, J. (2010).
  - Http://www.huffingtonpost.com/drmercola/thyroidhealth\_b\_472953.html. *Avoid This If You Want To Keep Your Thyroid Healthy*.
- 12. Mernild, S. H., Liston, G. E., & Hiemstra, C. A. (2014). Northern Hemisphere Glacier and Ice Cap Surface Mass Balance and Contribution to Sea Level Rise. Journal Of Climate, 27(15), 6051-6073. doi:10.1175/JCLI-D-13-00669.
- 13. Mishra, S., & Nandeshwar, S. (2013). A STUDY TO ASSESS WATER SOURCE SANITATION, WATER QUALITY AND WATER RELATED PRACTICES AT HOUSEHOLD LEVEL IN RURAL MADHYA PRADESH. National Journal Of Community Medicine, 4(4), 599-602.

14. Nestle. (2012). Leading Water Brands -Aquafina, Dasani, Evian and Nestle© Bottled Water.

- 15. Parreira, S. (2014). Model Behavior: Evaluating Instrumentation And Control In The Coagulation Process. *Water Online*.
- 16. Poland Spring. (2011). Poland Spring-Born Better.
- 17. Primus, S. (2014). The UV Uprising: How UV Disinfection Will Claw Its Way To Prominence. *Water Online*.
- 18. Rosa G, Majorin F, Clasen T, et al. Assessing the Impact of Water Filters and Improved Cook Stoves on Drinking Water Quality and Household Air Pollution: A Randomised

Controlled Trial in Rwanda. Plos ONE [serial online]. March 2014;9(3):1-9.

- Steffen, S. (2001). Smart 2 colorimeter operator's manual. (2 ed., Vol. 2, p. 51). Chestertown: LaMotte Company.
- 20. USGS. (2012). A National Assessment of Changes in Chloride, Dissolved Solids, and Nitrate in Groundwater.
- 21. Water.org. (2012). The Water Crisis.
- 22. Westerling, K. (2014). EPA Drinking Water Agenda: What's On Tap? *Water Online*.
- 1. Aldrich, S. (2012). MSDS Search. MSDS Search and Product Safety Center.
- 2. Aprile, F., & Lorandi, R. (2012). Evaluation of Cation Exchange Capacity (CEC) in Tropical Soils Using Four Different Analytical Methods. *Journal Of Agricultural Science*
- 3. Carolina®. (2013). *Elements, compounds, and mixtures*.
- 4. Clark, J. (2002). Le chatelier's principle.
- 5. "Drinking Water Contaminants". (2012). Water Contaminants. Epa.gov
- 6. "Effects of Pollution." *Water*. Nrdc.org, n.d. Web. 25 Aug. 2012.
- 7. Fosbol, P. (2013) "General Solubility Rules." Researchgate.net
- Ho, P.C., Palmer, D.A.: Ion association of dilute aqueous sodium hydroxide solutions to 600 degrees C and 300 MPa by conductance measurements. J. Solution Chem. 25, 711– 729 (1996)
- 9. Hunter PR, MacDonald AM, Carter RC (2010) Water Supply and Health. PMed 7(11):
- 10. LaMotte (2012). "SMART 2 Colorimeter." *Smart 3 Colorimeter*.
- 11. "Metedeconk River". (2012). *Metedeconk River*. Bbp, ocean.edu
- 12. Nutt, A. (2013). One Year After Hurricane Sandy. *NJ.com*
- 13. Pacific Institute. (2013). Waste water.

- 14. Rowland, F., & Tang, Y. (1968). Upper limits for the single-step double-displacement reaction in recoil tritium systems. *The Journal of Physical Chemistry*, 72(2), 707-713.
- 15. Ryther, J. H., & Dunstan, W. H. (1979). Nitrogen, phosphorus, and eutrophication in the coastal marine environment. *Science AAAS*, *171*(3975), 1008-1013.
- 16. Sheffield Hallam University (2013)."Introduction." *Beer's Law Theoretical Principles.*
- 17. Steffen, S. (2001). Smart 2 colorimeter operator's manual. (2 ed., Vol. 2, p. 51). Chestertown: LaMotte Company.
- Tro, N. (2010). Chemistry: A Molecular Approach (2nd Edition) (2nd ed., pp. 1-1224). Prentice Hall.
- 19. "What Is a Colorimeter?" (2012) *WiseGEEK*. Wisegeek.org.