The Effect of the Salinity of Water and its PH Value on the Concentration of Dissolved Oxygen in Regular Tap Water in Singapore Based on Winkler Titration Method

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ABSTRACT

In today’s world, humans have breached several limits in contaminating our already-fragile ecosystems and biospheres, affecting land, water, air, flora and fauna, and producing pollutants in copious amounts due to industrial development, urbanisation and excessive use of fossils fuels due to surging population levels, while wildlife is in sharp decline. Having identified the fact that concentration of dissolved oxygen in water is vital to maintain a health ecosystem in water, the author decides to explore a topic concerning measurements and analysis of certain environmental parameters where chemical knowledge, skills and a problem-solving approach can be employed. This investigation is aimed at determining the relationship between the salinity of water, and its pH value, on the oxygen concentration in regular tap water in Singapore, measured by Winkler method. Observation from the tests, dissolved oxygen is maximum at extremes of pH, viz 6.40 at pH 5 and 5.64 at pH 9; however, at pH 7, lower levels 4.96 were detected, since the growth of bactericeria leads to the decreased oxygen. Thus, pH>7 or if pH< 7, a high salinity, a low quantity of bacteria, high DO is produces, and low BOD is recorded.

Keywords: Salinity of Water; PH value; Winkler Titration Method; Concentration of Dissolved Oxygen

1. INTRODUCTION

Without oxygen, water is void of life. The act of humans dumping waste can lead to the degradation of oxygen value within water since microbes interact with waste, consuming oxygen in the process. Many biological processes are reliant upon oxygen; without which, cellular activity would be impossible. Agricultural run-off containing, for example, nitrates, phosphates, etc., can trigger algal bloom causing a threat called eutrophication [1]. The algae will flourish thanks to the water’s eutrophication, causing damages to people’s daily water supply and fishery, even the ecosystem in water [2]. With these questions in mind, the author formulated the following investigation whereby the effects of pH and salt on the oxygen content in water is monitored using the Winkler Titration method. The ability to collect sea water samples for the analysis would have been preferable, however, this was not possible, and thus regular tap water was utilised for the study.

This topic is a highly sensitive one with global implications; there is a consensus that as humans, we do not want lakes and ponds without fish and other marine creatures. The factors found to decrease oxygen must be investigated and followed up with action for controlling the situation, which is critical.

2. METHODOLOGY

2.1. The Winkler Method

This is a titration analytical method used to quantify dissolved oxygen within water samples suspected of displaying values lower than those of normal standards [3]. Titration is utilised in order to determine dissolved oxygen (DO) found within the water sample. The sample bottle is fully filled with water, eliminating space for air, in order to reduce the impact of air on the results. The DO utilised within the sample is "fixed" by adding a set of chemical reagents which form an acidic compound;
this is subsequently titrated utilising a neutralising substance which causes an end-point colour change.

Transition metals possess variable oxidation states, owing to the closeness of 4s and 3d orbitals with respect to the close energy levels they comprise. The DO (denoted by O2(g)) is fixed with the addition of a manganese (II) salt such as MnSO4. Oxygen oxidizes Mn (II) to Mn(IV). The reaction of O2 combined with salt within the basic solution causes oxidation of Mn(II) to higher oxidation states, such as Mn(IV), as illustrated by the equations below:

\[ 2\text{Mn}^{2+}(aq) + \text{O}_2(g) + 4\text{OH}^-(aq) \rightarrow 2\text{MnO}_2(s) + 2\text{H}_2\text{O}(l) \]

(1). Acidified iodide ions, I-, are added to the solution, and are oxidized by the Mn (IV) to I2:

\[ \text{MnO}_2(s) + 2\text{I}^-(aq) + 4\text{H}^+(aq) \rightarrow \text{Mn}^{2+}(aq) + \text{I}_2(aq) + 2\text{H}_2\text{O}(l) \]

(2). Titrate the produced iodine with sodium thiosulfate:

\[ 2\text{S}_2\text{O}_3^{2-}(aq) + \text{I}_2(aq) \rightarrow 2\text{I}^-(aq) + \text{S}_4\text{O}_6^{2-}(aq) \]

Therefore, 4 mol of S2O32– are utilised; thus, when thiosulfate moles are determined for each 1 mole of O2 in the water, it is divided by a factor of 4 to obtain oxygen moles.

2.2. Hypothesis

As the salinity in the water increases, the available dissolved oxygen concentration should increase correspondingly. High concentrations of the salt should inhibit/ prevent the growth of microorganisms. As microbes decrease, there should be a lower consumption of dissolved oxygen in the water; therefore, high residual oxygen should be detected.

It is understood that the ideal pH value for the survival of bacteria is 6.5-7.0 [4], which is close to neutral, and thus, they are able more easily to propagate. As a result, the water will have a lower oxygen concentration due to the ability of microbes to survive, which consume oxygen and decrease its concentration [5]. If the water were too acidic or basic, it would result in higher residual/remainder of oxygen concentration [6]. Consequently, the survival of microorganisms would be suppressed and the oxygen in the water difficult to consume; thus, higher residual oxygen would be the result.

2.3. Variables

Then, the author discusses the effect of salinity of water on the oxygen concentration in a water sample.

| Variable type | Variable name          | Controlling/ Measuring method                          | Possible effect on the result                                      |
|---------------|------------------------|-------------------------------------------------------|-------------------------------------------------------------------|
| Independent   | Salinity               | Adjusted at 0, 10, 20, 30, 40 g in 250 cm³             | -                                                                 |
| Dependent     | Oxygen concentration   | Winkler’s method                                      | -                                                                 |
| Controlled    | pH                     | No acid or base added.                                | For a fair test                                                   |
|               | Temperature            | Temperature/air condition of lab is maintained throughout experiments. | Temperature has a direct effect on the oxygen concentration in water[7]; higher temperature results in oxygen concentration decrease, as gases dissolve less at high temperature due to gases diffusing out. |
|               | Same volume of the sample | 250 mL                                               | Constant volume for all trials to enable fair comparison of results |
Table 2. Effect of pH of water on the oxygen concentration

| Variable type | Variable name | Controlling/Measuring method | Possible effect on the result |
|---------------|---------------|------------------------------|------------------------------|
| Independent   | pH            | pH sensor of Vernier company | Different pH values can affect microbial growth[6]: if the solution is too acidic or basic, the survival of microorganisms would be suppressed, and the oxygen in the water would be difficult to consume. |
| Dependent     | Oxygen concentration | Winkler’s method | |
| Controlled    | Temperature   |                              | Temperature has an effect on the oxygen concentration in water[7]. |
|               | Same volume of the sample |              | For fair and reliable result all other variables to be kept fixed/constant. |
|               | Salinity      | No salt added                | So that amount of substrate for bacteria to act upon remains same. |
|               | Amount of soy milk | 2 drops of soy milk added using the same dropper every time | |

Table 3. Apparatus and chemicals

| Burette (±0.05 mL) and stand | 10 ml measuring cylinder (±0.1 mL) | cheese cloth |
|-------------------------------|-----------------------------------|--------------|
| 250 mL volumetric flask       | 250 ml measuring cylinder         | pipettor     |
| 20 ml pipette (±0.10 mL)      | 250 ml conical flask              | blender      |

Table 4. Chemicals

| CHEMICALS                | QUANTITY | CONCENTRATION |
|--------------------------|----------|---------------|
| manganese sulfate        | 2 mL     | 0.5 M         |
| Iodine solution          | 2 mL     | 0.005 mol/L   |
| Starch indicator solution| 2 mL     | 0.5%          |
| alkali-iodide-azide      | 2 mL     |               |
| concentrated sulfuric acid| 2 mL    | 1 M           |
| Sodium thiosulfate       | 2 litres | 0.025 mol/L   |
| NaOH                     | 500 mL   | 0.1 mol/L     |
| HCl                      | 500 mL   | 0.1 mol/L     |
2.4. Lab safety and risk assessment

A lab coat is worn at all times. Gloves are worn when handling sulfuric acid due to its highly corrosive properties on contact; if contact occurs with skin, it is rinsed with adequate amounts of cool water and medical attention is sought.

2.5. Environmental considerations/implications

Waste is disposed of in the sink, with adequate water in order to dilute the concentrations of chemicals used. Sulfuric acid solution requires draining with soap solution to neutralise the acid. No organic solvents/heavy metal waste were produced.

3. EXPERIMENTAL PROCESS

3.1. Preparing different pH solutions with constant/controlled salinity

(1). No NaCl is added to the 250 cm³ sample water. Diluted HCl (0.1 M) is utilised in order to prepare the solution at a pH of 5, due to its acidity.

(2). This method is repeated to obtain solutions with a pH of 6, 7, 8, and 9.

(3). For pH 7 no acid or base is required.

(4). In relation to pH 8 and 9 NaOH basic solution is utilised.

(5). Acid or base is introduced via burettes; drops and pH levels are checked simultaneously and stopped when the required pH is achieved.

3.2. Preparing different salinity solutions with constant/controlled pH

(1). Place 0 g of NaCl in 250 cm³ sample water.

(2). Repeat the above process with 10, 20, 30, and 40 g salt, respectively.

(3). It is unnecessary to make it acidic or basic, thus there is no requirement to add HCl or NaOH for this set.

3.3. Producing the respective solutions

(1). Make 0.005 mol L⁻¹ of iodine solution

a). Weigh 2.00 g of potassium iodide into a 100 mL beaker.

b). Weigh 1.30 g of iodine and combine it with the beaker containing potassium iodide.

c). Add a few about 10 mL of distilled water and swirl for a few minutes until iodine is dissolved.

d). Transfer iodine solution to a 1L volumetric flask.

(2). Make 0.5% starch indicator solution

a). Weigh 0.25 g of soluble starch and add it to 50 mL of near-boiling water contained within a 100 mL conical flask.

b). Stir to dissolve and cool before using.

(3). Make 0.0250 mol/L Sodium thiosulfate

a). Weigh out 6.2 g of hydrate sodium thiosulfate of in a clean, dry beaker.

b). Add enough deionized water to dissolve the solid, stirring with a glass rod.

c). Transfer the solution with rinsing to a 1000 cm³ volumetric flask using a funnel.

d). Rinse the beaker and glass rod with deionized water and add to the volumetric flask.

e). Fill to the mark by adding deionized water until the bottom of the meniscus is on the mark.

f). Secure the flask with a stopper and invert to mix thoroughly.

3.4. Winkler Method to determine concentration of dissolved oxygen

(1). Take a 250 mL volumetric flask, stoppered bottle full of the sample water, with 2 drops of soy milk added to each sample.

(2). Add 2mL of MnSO₄ to the collection bottle by inserting a pipette slightly below the liquid surface. Squeeze the pipette gradually to prevent bubbles entering through the pipette in order to avoid errors within the readings.

(3). Transfer 2 mL alkali-iodide-azide chemical similarly.

(4). Use the stopper to secure the bottle. Mix the entire sample water by inverting the bottle multiple times.

(5). If any oxygen is detected, a brownish-orange, milky, semi solid-like precipitation will be visible.

(6). Place 2 mL of sulfuric acid solution into the sample, holding a pipette slightly above the surface of the water. Dissolve the flocs by securing the solution with the stopper and inverting carefully for a few times. Now the sample is "fixed".

(7). Continue by spraying distilled water along the plug, then cover the bottle with aluminum foil and affix it utilising a rubber band; finally, store it in a dark and cool place. The solution may be stored for up to 8 hours.

(8). Using the conical flask, titrate the water sample with aq sodium thiosulfate to pale straw/light yellow colour.
(9). Then add 2 mL of fresh starch solution to form a blue colour.

(10). Continue the titration, observing carefully until the water becomes clear; as the endpoint approaches, the blue colour will disappear suddenly. This change occurs within a single drop.

(11). The identical methodology is employed for Trial 2, for each independent variable, and then the average of the raw data produced in Trial 1 and 2 is extrapolated for data processing.

4. RESULTS

4.1. Raw data collection

Table 5. Effect of Salinity as an independent variable

| Mass of salt/g | Sodium thiosulfate volume/ cm3 /±0.10 |
|---------------|---------------------------------------|
| Trial 1       | Trial 2                               | Average    |
| 0             | 5.60                                  | 5.80       | 5.70       |
| 10            | 6.20                                  | 5.90       | 6.05       |
| 20            | 6.20                                  | 6.40       | 6.30       |
| 30            | 6.90                                  | 6.80       | 6.85       |
| 40            | 7.20                                  | 7.20       | 7.20       |

Table 6. Processed data table for the effect of salinity

| Salinity/g | Average Na2S2O3 V cm3 | V/dm3 | n | n/O2 | c=n/V | m/g | c in mg/dm3 or ppm |
|------------|-----------------------|-------|---|------|-------|-----|-------------------|
| 0          | 5.70                  | 0.00570 | 0.00014250 | 0.0000356250 | 0.00014250 | 0.00456 | 4.56              |
| 10         | 6.05                  | 0.00605 | 0.00015125 | 0.0000378125 | 0.00015125 | 0.00484 | 4.84              |
| 20         | 6.30                  | 0.00630 | 0.00015750 | 0.0000393750 | 0.00015750 | 0.00504 | 5.04              |
| 30         | 6.85                  | 0.00685 | 0.00017125 | 0.0000428125 | 0.00017125 | 0.00548 | 5.48              |
| 40         | 7.20                  | 0.00720 | 0.00018000 | 0.0000450000 | 0.00018000 | 0.00576 | 5.76              |

4.2. Graphical analysis

Figure 1. The effect of salinity
Table 7. Effect of pH as an independent variable

| pH | Sodium thiosulfate volume/cm³/(±0.05)+(±0.05) |
|----|---------------------------------------------|
|    | Trial 1 | Trial 2 | Average |
| 5  | 8.10    | 7.90    | 8.00    |
| 6  | 7.20    | 7.30    | 7.25    |
| 7  | 6.10    | 6.30    | 6.20    |
| 8  | 6.70    | 6.70    | 6.70    |
| 9  | 7.10    | 7.00    | 7.05    |

4.3. Data processing

Table 8. Processed data table for the effect of pH

| pH | Average V of Na₂S₂O₃ soln/cm³ | V/dm³ | n=cV | n/O₂  | c =n/V | m/g  | c/ ppm |
|----|--------------------------------|-------|------|-------|--------|------|--------|
| 5  | 8.00                           | 0.0080 | 0.00020000 | 0.0000500000 | 0.00020000 | 0.00640 | 6.40   |
| 6  | 7.25                           | 0.00725 | 0.00018125 | 0.0000453125 | 0.00018125 | 0.00580 | 5.80   |
| 7  | 6.20                           | 0.00620 | 0.00015500 | 0.0000387500 | 0.00015500 | 0.00496 | 4.96   |
| 8  | 6.70                           | 0.00670 | 0.00016750 | 0.0000418750 | 0.00016750 | 0.00536 | 5.36   |
| 9  | 7.05                           | 0.00705 | 0.00017625 | 0.0000440625 | 0.00017625 | 0.00564 | 5.64   |

4.4. Graphical analysis

Figure 2. The effect of salinity
The calculation of Sample DO uses the general formulae:

\[ n = c \times V \]  \hspace{1cm} (1)

Where \( c \) is concentration in moldm\(^{-3} \) and \( V \) is volume in dm\(^{3} \).

\[ m = n \times M_r \]  \hspace{1cm} (2)

Where \( M_r \) is relative molar mass:

- \( c \) of sodium thiosulfate = 0.025 M;
- \( V \) of sodium thiosulfate = 8.0 cm\(^{3} \);
- \( V \) of sodium thiosulfate = 0.008 dm\(^{3} \);
- \( n \) of sodium thiosulfate = \( c \times V = 0.0002 \) mol;
- \( n(O_2) = (\text{mol of sodium thiosulfate}/4) = 0.00005 \) mol;
- 0.00005 mol in 250 mL water sample
  \[ = 0.0002 \text{ mol in 1 dm}^{3} \]
  \[ m = n \times M_r = 0.0002 \times 32 \]
  \[ = 0.0064 \text{ g/litre} = 6.4 \text{ mg/litre} = 6.4 \text{ ppm} \]

Uncertainty propagation: Volume uncertainty is from burette readings, which is 0.10 mL; thus uncertainty percentage = \((0.10/8.0) \times 100 = 1.25\% \)

Fresh drinking tap water has DO of 6.5 ppm

Above sample calculation is based on five days’ incubation time.

5. DISCUSSION

Based on the results, and as observed in the Figures, dissolved oxygen is maximum at extremes of pH, viz 6.40 at pH 5 and 5.64 at pH 9; however, at pH 7, lower levels 4.96 were detected, as it allows for bacterial growth, which is responsible for decreased oxygen. Therefore, pH > 7 or if pH < 7, meaning less bacteria, high DO remains, thus, low BOD is recorded. With high salinity there is a lower quantity of bacteria as a result of salt content suppressing bacterial growth and multiplication, and thus high DO is produced, resulting in low BOD.

6. EVALUATION

6.1. Random errors

The colour-changes are not highly reliable due to the fact that the variation occurs rather quickly, making exact endpoint detection difficult and less reliable.

There is a small uncertainty (just 0.10 mL) within the burette solution; consequently, there is no major random error with respect to volume readings.

6.2. Systematic errors

During the transference of solution, a small proportion of the sample remains in the original container, although this occurs in very small amounts; thus leading to systematic error.

Because of warm conditions in the lab room warm, a small amount of oxygen might be escaping from the system, resulting in the detection of less oxygen.

6.3. Assumptions

These are factors assumed to have no effect on results but which could potentially affect the results; they decrease the reliability of results.

It is assumed that temperature, sunlight/UV did not impact the results. In addition, it is assumed that oxygen did not escape the system when the reactions were in process.

6.4. Weaknesses

The colour changes were insufficient to detect endpoints distinctly.

7. CONCLUSION

According to the results, dissolved oxygen is maximal at extreme pH values, i.e. 6.40 at pH 5 and 5.64 at pH 9; However, at a pH of 7, a lower level of 4.96 is detected because it allows bacteria to grow, which is what causes oxygen to decrease. Therefore, the pH value >; 7 or if pH < 7, meaning fewer bacteria, high DO still exists.

Complex sets of redox reactions occurred making it difficult to determine if a complete reaction transpired or if any secondary reactions occurred which would obscure the true result values. Unfortunately, there are no true values with which to compare results; however, to a large extent, a clear trend pattern could be identified: that pH close to 7 leads to lowest DO and higher salinity leads to higher DO available. Further exploration might incorporate the way in which the above variables affect different wastes released in water, for example, agricultural rain water run-off may contain a high amount of nitrates dissolved in fertilizer; thus, it could aggravate algal growth, which can be measured utilising the Winkler method in order to discover which fertilizer salts increase BOD; and to what extent. Accordingly, fertilizer composition should be modified to decrease environmental impact. The precise and optimum values of pH and salinity levels required to maintain a high enough DO to sustain aquatic life can be calculated and applied to produce healthy ecosystems.
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