

Original Article

# Color Detection Algorithm for Measuring Ozone Concentrations using Indigo Method

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**Abstract** - Water ozone offers a variety of beneficial uses and critical functions. Ozone is significant in water treatment and other applications for a number of reasons. Ozone measurement is important for several reasons, particularly in applications where ozone is used or present. Some important measurement factors for ozone in water are safety, process control, compliance with regulations, equipment maintenance, environmental monitoring, research and studies. An international supplier list of indigo trisulfonate is provided with the indigo method for determining ozone, developed for Standard Methods for Drinking Water Analysis. Many nations will require this novel, straightforward method for ozone analysis because existing techniques are typically non-selective when used on actual drinking waters or wastewater. This study succeeded in measuring ozone concentrations in doses ranging from 0 - 0.4 mg/L.

**Keywords** - Color detection, Indigo, Oxidizing, Ozone, Water treatment.

## 1. Introduction

Ozone is a powerful oxidizing agent that can be used for water treatment, including drinking water. When ozone is introduced into water, it reacts with various contaminants and microorganisms, providing several benefits:

**Disinfection:** Ozone is a highly effective disinfectant and can kill a wide range of microorganisms, including bacteria, viruses, and protozoa. It is particularly effective against chlorine-resistant pathogens such as *Cryptosporidium* and *Giardia*. Ozone disinfection helps ensure the safety of drinking water by reducing the risk of waterborne illnesses.

**Oxidation of Organic Compounds:** Ozone has strong oxidation properties and can break down organic compounds present in water. It can effectively remove contaminants such as pesticides, pharmaceuticals, industrial chemicals, and taste- and odor-causing compounds. Ozone reacts with these substances, breaking them down into simpler, less harmful compounds or mineral byproducts [1].

**Taste and Odor Control:** Some drinking water sources may contain natural or man-made substances that impart unpleasant tastes and odors. Ozone treatment can effectively eliminate these compounds, improving the overall taste and odor of the water.

**Color and Turbidity Reduction:** Ozone can help in reducing the color and turbidity (cloudiness) of water. It

oxidizes and breaks down the organic particles responsible for these characteristics, producing clearer and aesthetically pleasing water.

**Reduction of Disinfection Byproducts (DBPs):** When chlorine is used as a primary disinfectant, it can react with naturally occurring organic matter in water, forming disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). Ozone can help reduce the formation of DBPs by oxidizing the precursors before they react with chlorine, leading to lower levels of potentially harmful byproducts.

**Short Residual Life:** Unlike chlorine, which leaves a residual disinfectant in water, ozone breaks down rapidly, leaving no residual disinfectant in the treated water. This eliminates concerns about residual disinfectants and associated taste and odor issues.

Ozone is actually abundant in the atmosphere [2]. It is important to note that ozone is not typically used as a standalone treatment for drinking water. It is often used in conjunction with other treatment processes, such as filtration or chlorination, to provide comprehensive water treatment. Additionally, ozone generation and application require careful monitoring and control to ensure its safe and effective use. It is important to note that while ozone offers numerous benefits, its application in water treatment requires careful control and monitoring to ensure its effective and safe use. Proper design,



operation, and maintenance of ozone systems are essential to maximize their advantages.

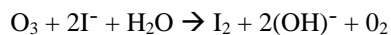
Instead of the usual two oxygen atoms bonded together, ozone has three. It is made artificially when UV light causes oxygen to split into three parts and reassemble. On contact, ozone kills bacteria, fungi, viruses, algae, and other microorganisms. It also converts dangerous compounds into less toxic, simpler molecules. Ozone destroys the cell membranes of bacteria to cause their death. Healthy cells' built-in defenses prevent them from being harmed. Ozone should be utilized within the first 5–10 minutes to ensure its strength because it has a half-life of 20 minutes. Due to the infections it eliminated dying off, it can initially make you feel low on energy. Particularly vulnerable are malignant cells. 1 ug/ml of diluted ozone in water has anti-microbial properties. It enhances white blood cells' phagocytic (pathogen-eating) activity. Doctors in various parts of the world have documented various cases of progress in curing HIV, the disappearance of AIDS symptoms, progress in healing tumors, and curing many systemic infections such as hepatitis, staphylococcal infections, and meningitis using this drug (usually given intravenously). One should take vitamin E and other supplements to assist the glutathione detoxification system while utilizing ozone therapy. Monocytes and lymphocytes are both activated by ozone. It enhances the brain's oxygenation. By increasing the major cycle for the release of energy from glucose, the citric acid cycle enhances oxygenation and metabolism. Numerous gastrointestinal and gynecological issues are treated with ozonated water in Russia and Cuba. In order to prevent blood cell membranes from adhering together and losing their ability to absorb oxygen and transfer it to tissues, ozone modifies their electrical charge [3].

The solubility of ozone in various solvents has been measured by methods for connecting solvents containing ozone to water contaminated with compounds present and causing contaminants. [4].

## 2. Literature Review

The residual ozone concentration at the exit of the contact towers must be larger than 0.4 mg/L to achieve the correct water disinfection. Therefore, a very sensitive method for measuring ozone levels in water between 0 and 1.5 mg/L must be available.

The iodometric approach is still the most used technique when no additional oxidants are present. It is based on ozone's capacity to remove iodine from alkaline iodide solutions using the following equation:



For confirming the O<sub>3</sub> sensitivity coefficient, indigo solution breakdown and a straightforward initial absorbance

approach are provided [5]. Measuring ozone levels in drinking water typically involves specialized equipment and testing methods. Here are a few common approaches used to measure ozone concentrations:

- **Dissolved Ozone Test Kits:** Test kits are available that allow for on-site measurement of dissolved ozone in water. These kits typically include test strips or reagent-based tests that change color in the presence of ozone. The color change can be compared to a color chart to estimate the ozone concentration. While these kits provide a quick and convenient method, they may have limitations regarding accuracy and precision.
- **Photometric Analysis:** Photometric analysis involves using a spectrophotometer or a photometer to measure the absorbance of ozone at a specific wavelength. This method relies on the principle that ozone absorbs light at specific wavelengths, and the extent of absorption is proportional to the ozone concentration in the water sample. Photometric analysis provides more accurate and quantitative results compared to test kits.
- **Electrochemical Sensors:** Electrochemical sensors are commonly used to measure ozone concentrations. These sensors work by detecting the electrochemical reactions that occur when ozone is present in water. The sensor produces an electrical signal that can be correlated to the ozone concentration. Electrochemical sensors are often integrated into ozone monitoring systems for continuous measurement.
- **Titration:** Titration is a chemical analysis technique used to determine the concentration of a substance in a solution. In the case of ozone, a titration method called iodometric titration can be employed. It involves adding a known concentration of iodide ion to the ozone-rich water sample and titrating it with a standardized sodium thiosulfate solution until the iodine is completely consumed. The amount of sodium thiosulfate used can be used to calculate the ozone concentration.

It is important to note that accurate ozone measurement requires proper calibration, quality control, and adherence to standardized testing procedures. Additionally, ozone levels in drinking water can vary depending on factors such as treatment processes, contact time, and water quality, so regular monitoring is necessary to ensure compliance with regulatory standards and to maintain safe drinking water.

In 2014, J Nobbs and C. Tizaoui conducted a study to measure ozone concentration using the modified indigo method in nonaqueous solvents to analyze dissolved ozone in nonaqueous liquid phases. The indigo method for analyzing aqueous ozone was adapted. Vegetable oil and the solvent decamethylcyclopentasiloxane 245 were used to test the procedure. When the molar absorptivity of indigo trisulfonate molecules at 600 nm was re-examined, a number of moles of the substance was found, which corresponded to the value considered as a standard. The solubility of ozone in DCA 245

satisfies Henry's rule, with a certain constant with a weight in a liter in the gas phase, according to the correlation between liquid form and gas form on ozone measurement. With gas and liquid form volume measured in weight, the solubility of ozone in vegetable oils. These results prove that Henry's rule has been fulfilled in the study [6].

Goitybell Martinez, in 2005, conducted a study entitled: "Measurement of Peroxidic Species in Ozonized Sunflower Oil" to measure weighted ozone in flower oil. Different techniques were used to evaluate the peroxidic species in ozonized sunflower oil, including iodometry and fox test. An iodometric test in ozonized sunflower oil was used to calculate the required reaction time, which ranged from two minutes to 36 hours. After 24 hours of reaction time, peroxide values reached their maximum levels. A linear association was found between the amount of hydroperoxides identified by the fox test and the amount of peroxide determined by the iodometric assay at two minutes [7]. This study has succeeded in measuring the presence of ozone in sunflowers accurately.

Residual ozone concentration, or C, was measured with a drinking water ozone disinfection system for quality assurance on virus removal data. The standard method for measuring ozone is the indigo trisulfonate colorimetric technique. The accuracy of the Standard Method currently written is based on certain ITS quality assurance considerations, even though its implementation is quite simple. The ozone measurement guarantee process is carried out periodically to ensure the removal of remaining viruses. The Standard Method is rather rigid because it is based on predetermined material and sample volumes. Instead of being conducted in accredited laboratories by analytical chemists, operating staff frequently carry out tests in plant settings. The ITS method is given a strategy that is more adaptable, of good quality, and easy to use in this work. This manuscript aims to continuously improve existing ozone measurements by examining a number of topics related to the ITS method, such as the influence of time, weather such as temperature, vendors, measurement results and use of measurement results. Results are presented that show what happens when certain conditions are ignored. For instance, an ITS solution kept on a shelf for a few days can result in a slight underestimation of ozone residual, whereas keeping it for a few weeks can result in a significant underestimation [8].

In 1992, Mary E. Williams conducted a study titled "Measuring Ozone by Indigo Method: Interference of Suspended Material" to measure ozone using the indigo method. The efficiency of four ozone-trapping agents for monitoring O<sub>3</sub> concentrations in the air was tested using a badge-style passive monitor. They were p-acetamidophenol (p-ATP), indigo carmine, 3-methyl-2-benzothiazolinone acetone azine (MBTH), and sodium nitrite (NaNO<sub>2</sub>) [9].

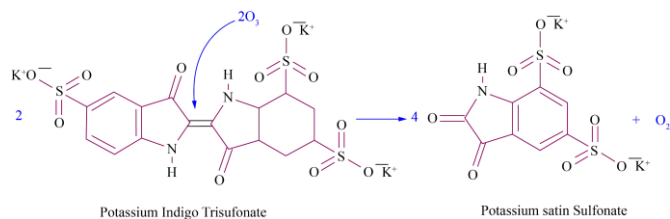
In 2009, Yasuko Y. Maruo conducted research using paper to measure ozone by detecting ozone using indigo

carmine. Paper containing indigo carmine is reacted with ozone. The reflectance results on the treated paper can be examined to identify the presence of ozone. The residue on the paper resulting from the yellowish-white reaction is a material for measuring ozone levels. If a color changes due to this reaction, the measurement can be calculated and processed using an adapted photoelectric meter. Cellulose sheets, humectants, acids, and indigo carmine are required to obtain accurate results. If there is a high enough ambient ozone concentration, the color of the ozone detector paper changes drastically from blue to white. The glycerol content in the immersion solution is needed to produce an optimal response. Apart from that, it also requires humectant content, which will significantly affect the presence of ozone [10].

### 3. Method

For routine monitoring of ozone or chlorine dioxide in various types of drinking water, the sulfonated form of indigo shows certain noteworthy properties that make it appealing [11].

- As redox and/or pH indicators, indigo trisulfonate and indigo disulfonate are commercially available in calcium and sodium versions. These goods' purity is sufficient for creating reagent solutions [12].
- Like certain water pollutants, sulfonated indigo is extremely soluble in water, making it simple to generate concentrated stock solutions. The dye also has little potential to interfere with measurements through absorption processes.
- When kept in a dark location with a low pH, indigo reagent stock solutions last for months.
- Indigo, trisulfonate, and indigo disulfonate have comparatively high molar absorption coefficients of around 20,000 L/(mol·cm) and absorb at 600 and 610 nm, respectively, as shown in Figure 1. Natural waters' intrinsic colors do not interfere in this spectral region. In this range, photometers and even the human eye are fairly accurate [9].
- The absorption changes strictly linearly with the amount of the oxidizing agent at each wavelength in the absorption band (550 to 650 nm). Only substances without visible spectrum absorptions are produced when ozone and chlorine dioxide interact.
- Ozone or chlorine dioxide reacts swiftly with the one functional group that makes up an indigo molecule. This -C=C-double bond is what gives indigo its chromophoric structure, as shown in Figure 1. It interacts with both oxidants with a rate constant of more than 10<sup>7</sup> L/(mol·sec), which is extremely high. Such a number belongs to the category of the highest known reaction rate constants. In the case of ozone and particularly in the reactions of chlorine dioxide. There are very few contaminants in the reagent solution that ozone or chlorine dioxide will not eat away at a similar reaction rate, competing with the color removal process.



- At best, the generated oxidation products react very slowly with ozone and chlorine dioxide. This means that a momentary localized excess, as might happen with each ozone addition, does not result in a zero-sum demand for the oxidant. However, organic molecules of the sort that are produced during the indigo reaction serve as carriers of a radical chain reaction, which could lead to a catalytic disintegration of ozone and make ozone determination easier. The pH of the solution used to measure ozone is kept low (pH 3) to prevent this chain reaction. When it comes to chlorine dioxide, the first created chlorite ion undergoes a delayed reaction that results in the production of chlorine dioxide once more, interfering with the analysis. As a result, chlorine dioxide is measured at a higher pH (pH > 4).

Both gaseous and aqueous ozone might be determined using a modified version of the indigo method that Bader and Hoigné created for aqueous ozone analysis. Using a gas-tight syringe filled with a predetermined amount of indigo reagent, samples of gas or water were extracted. The revised method

offered a more reliable foundation for determining gaseous and aqueous ozone, enabling more precise estimations of the ozone mass balance [13].

Figure 2 shows a schematic diagram of the plasma discharge setup by Muhammad Farooq, Muhammad Ibrahim Khan and Najeeb Rehman. According to research by Bader and Hoigné (1982) [14], ozone linearly in acidic liquid with discolors of indigo trisulfonate (also called “reagent of indigo”) with greater liquid volume. The distinctive absorbance of indigo reagent at 600 nm is easier to quantify in actual water samples than the ultraviolet can absorb. In addition, the destruction coefficient value,  $e$ , at 15.6 mm, is much higher than that of ozone at 260 nm, which is only about 2,900 mol concentration, thereby increasing the measurement accuracy [12]. Ozone is transmitted to the water phase of the tilapia when it comes into contact with ozone, which is not a liquid, and this causes the tilapia reagent to change color. Because ozone and indigo are immiscible phases, the difference in the absorption level between samples of indigo solutions that do not react and those that react with ozone can be used to measure the amount of ozone present in nonliquid substances. The following list of chemicals is used to create the indigo technique for use with nonliquid substances. The resistivity of Milli-Q water (Millipore Corp.), used to create all aqueous solutions, was 18.2 MΩ.cm. The nonaqueous solvents utilized were decamethylcyclopentasiloxane 245 and vegetable oil (Costcutter, UK). All other chemicals were at least reagent grade.

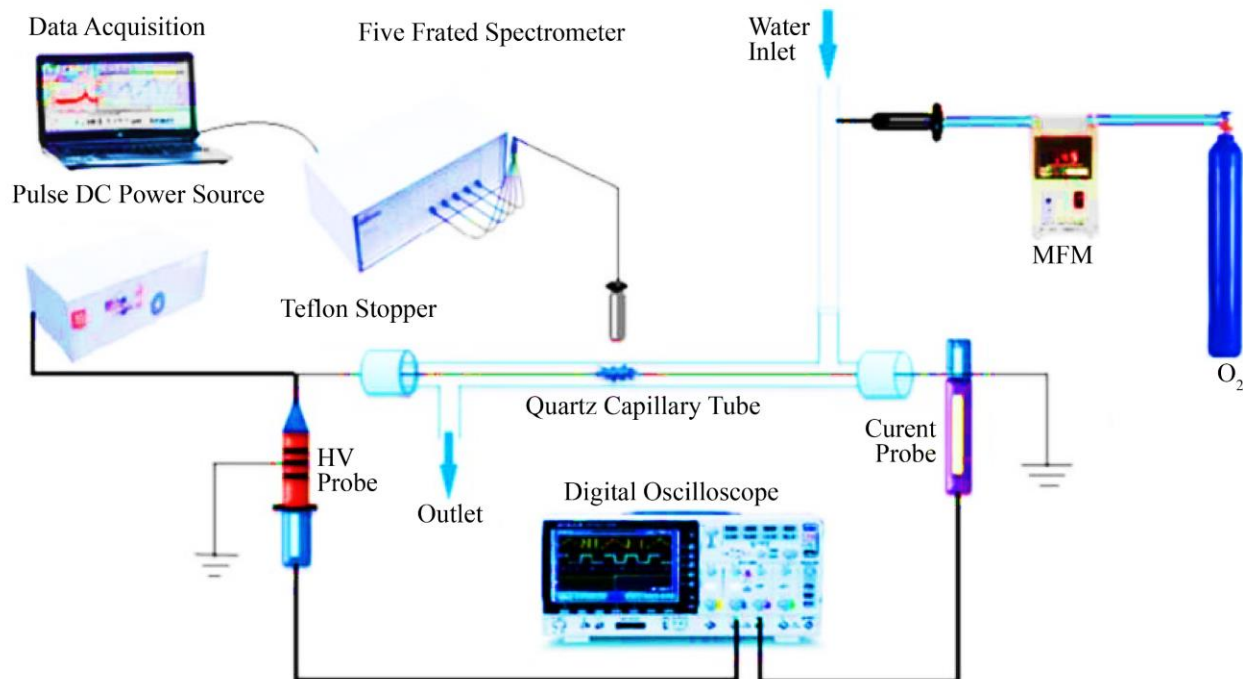


Fig. 2 Block diagram of plasma discharge [11]

At 600 nm, the IR2 absorbance was calculated. Equivalent amounts of the nonaqueous phase and several samples of the same indigo solution are combined at a specified rate for a specified time. The substance is then transferred to several funnels, where the liquid is allowed to stand for a certain time before a second IR2 absorption measurement is carried out. Centrifugation was then used to separate the liquid phases further. It is assumed that any observed decrease in absorption results from the transfer of the substance from a liquid to a nonliquid state.

Indigotrisulfonate is used to measure residual ozone using Standard Methods 4500-O3B, which assumes that the molar absorptivity is 20,000 M<sup>-1</sup> cm<sup>-1</sup> and the constant sensitivity coefficient is 0.42 L mg<sup>-1</sup> cm<sup>-1</sup>. For several sources of indigo, data are presented that demonstrate significant variations in molar absorptivity and, as a result, in the computed sensitivity coefficients. The sensitivity coefficient must be measured frequently due to the change in molar absorptivity (up to 15%). It is suggested to alter a straightforward estimate to account for decaying indigo reagents. With the current Standard Method technique, a modified equation is provided. However, it is advised that the dried indigo reagent be periodically calibrated for the most accurate results [15].

Advanced Oxidation Technology (AOT) is used in the Non-Thermal Plasma (NTP) method to degrade organic molecules in water. This work extensively evaluated the kinetics of indigo carmine degradation using several substances, and the outcomes were compared. Identifying and measuring the transient of O, OH, and NO was possible. This process is produced by releasing NTPs in the gas-liquid portion and byproducts (such as NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and NO<sub>3</sub> which are stabilized by the liquid. These species contribute to changes in the water's chemical properties, including a pH drop.

### 3.1. Color Detection

The calculation of the visual method is as follows:

$$\text{Mg O}_3/\text{L} = (100 - V_A)/100 \cdot k \quad (1)$$

Where:

V<sub>A</sub> = mL of the reference solution's volume in cylinder A.

k = A spectrophotometric study of ozone was used to calibrate the conversion factor for the indigo stock solution. If the absorbance is 0.19/cm after a 100-fold dilution, the value is approximately 0.10 mg O<sub>3</sub> / L.

Each pixel in the Red-Blue-Green image consists of three series of values. The values processed during image processing will only look for pixels whose Red, Green and Blue values are within a certain range. The range value is specified within the mandatory range of R-B-G values for the specific color to be identified. One of the three primary colors (red, green, or blue) will be identified using a very easy technique that will be discussed.

```
Mat RedDetectBGR(Mat img, int min_thresh, int max_thresh){
//the result image matrix is initialized
Mat result(img.rows,img.cols,CV_8UC1);

int i,j,r = img.rows, c = img.cols;
for(i=0;i<r;i++){
//loop through all rows
for(j=0;j<c;j++){
//loop through all columns
Vec3b colours = img.at<Vec3b>(i,j);
//extract 3 channel pixel information in a vector
if(colours[2]>=min_thresh && colours[1]<max_thresh
&& colours[0]<max_thresh)
//enforce condition on uchar value of each channel
result.at<uchar>(i,j) = 255;
//particular pixel is made white
else
result.at<uchar>(i,j) = 0;
//particular pixel is made black
}
}
return result;
}

int main(){
string fname;
cout<<"Enter name of file:";
cin>>fname;

Mat image = imread(fname);
int minthresh = 80, maxthresh = 100;

string win_name = "Colour-extracted image";
namedWindow(win_name,CV_WINDOW_NORMAL);
imshow("Original image",image);
createTrackbar("Low Threshold",win_name,&minthresh,255);
createTrackbar("High Threshold",win_name,&maxthresh,255);

while(1){
Mat result = RedDetectBGR(image,minthresh,maxthresh);
imshow(win_name,result);
char ch = waitKey(33);
if(ch==27)
break;
}
image.release();
destroyAllWindows();
return 0;
}
```

Fig. 3 Color detection pseudocode

For each pixel that is processed, whether the range of values with a larger value indicates a greater number of colors present will be determined. The RGB value is greater than a certain threshold value and whether there are values in the other two series that are less than the specified threshold value. If a pixel meets these requirements, it is assumed to be the appropriate color, and is assigned white in the resulting image. Black pixels are retained in all other cases. The color resulting from the chemical reaction will be detected using the software. Figure 3 is pseudocode for color detection.

## 4. Results

Using a pipette or plastic dispenser, fill 25 mL of Indigo Reagent into two identical 200 mL measuring tubes (tube A and tube B). A reference tube A filled with water was used for the comparison sample. Tube B is filled with a substance containing ozone. When adding the sample to cylinder B, ensure that no degassing occurs and that completely discolored areas can be removed quickly by the coalescing and mixing process. Pour a portion of the color comparison solution into tube A into a beaker. After that, pour it back into the tube until the liquid is the same color when viewed from above.



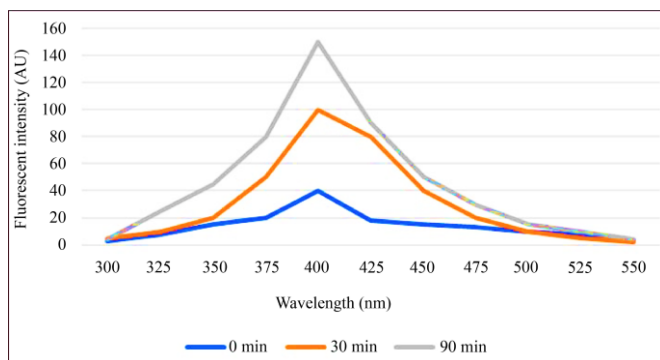


Fig. 4 Indigo wavelength

Figure 4 displays the emission spectra of an indigo-trisulfonate solution before, after, and after 90 minutes of ozone sampling. The wavelength of excitation was 245 nm.

Figure 5 displays the standard curve for the ozone-induced reagent discoloration experiment using tap water (pH 7.5) and an expected range of 0.05–0.5 mg/L. Each sample was given individual doses of a solution containing concentrated ozone.

The direct ultraviolet reference ( $\epsilon$  258 nm = 2,900 mol zat) was used to concurrently determine the concentration and the absorbance  $A$  of residual indigo. The method of ozone addition and the somewhat less accurate reference method used to determine ozone are the two factors that cause the biggest mistake.

Simultaneously adding ozone to two sample flasks during duplicate measurements using the indigo method resulted in an average variation of sc 1 to 1.5% within the pair.

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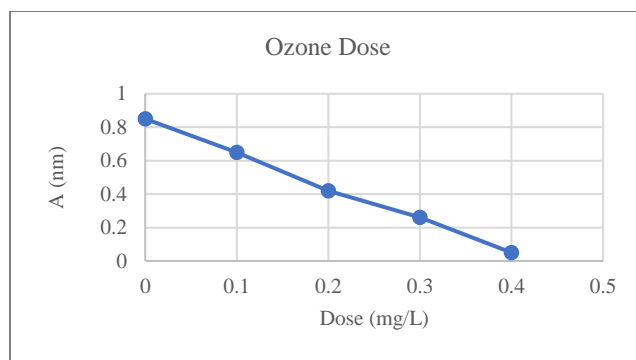


Fig. 5 Result

## 5. Conclusion

The technique described here was created and tested for the kinds of waters that are frequently utilized in Indonesia. In some locations, bromide might be more significant. In these circumstances, a technique for masking the HOBr should be developed (or compensating for HOBr by utilizing a blank in which ozone is selectively eliminated). This approach is based on a chromophoric compound-specific stoichiometric measure of discoloration. However, the purity of the reagent and photolytic degradation of the reagent prior to use can affect the amount of chromophoric chemical per weight of indigo-trisulfonate-reagent. As a result, the indigo method should not be applied as a technique where the leftover color is "titrated" with the ozone-containing substance until it vanishes.

## Acknowledgments

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