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Wide Range Analysis of Absorption Spectroscopy Ozone Gas Sensor

Maslina Yaacob[a,b*], Mohd Rashidi Salim[b], Tay Ching En Marcus[b], Micheal David[b], Nabihah Hussin[b], Mohd Haniff Ibrahim[b], Nor Hafizah Ngajikin[b], Asrul Izam Azmi[b]

[a]Department of Communication Engineering, Faculty of Electrical and Electronic Engineering, Universiti Tun Hussien Onn Malaysia, Parit Raja, 86400 Batu Pahat, Malaysia
[b]Light wave Communication Research Group (LCRG), Faculty of Electrical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: maslinay@uthm.edu.my
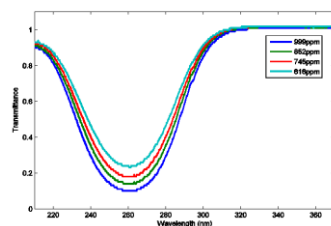
Graphical abstract

Figure 5 Transmittance measurements for various ozone concentration at range of wavelength from 210 nm to 370 nm.

Abstract

A wide range analysis of spectroscopic ozone gas sensor is conducted in order to obtain specific affected wavelength when 616 ppm to 999 ppm of ozone concentration is released into 5 cm gas cell of transmission type. It is observed that by employing different wavelength in ultraviolet region based on spectroscopic ozone detection, obvious differences of transmittance value are obtained for each particular wavelength. Consideration with Twyman-Lothian equation, specific wavelength at 239 nm, 240 nm, 241 nm, 242 nm, 278 nm, 279 nm, 280 nm, 281 nm is proven to achieve wide range of ozone detection when low relative error of concentration is achieved by value of transmittance in range between 0.25 and 0.5.

Keywords: Absorption spectroscopy, optical fiber sensor, wide range, concentration, ozone, ultraviolet, transmittance, relative error, wavelength

■1.0 INTRODUCTION

The ability of ozone to disinfect polluted water was recognized in 1886 by de Meritens [1]. Therefore, much work have been done by number of engineers and scientists to develop electrical equipment to test ozone's application for disinfection of drinking water. In most water treatment plants, ozonation is used to achieve a variety of treatment goals. The purpose of ozonation including disinfection and algae control, oxidation of inorganic pollutants, oxidation of organic micropollutants, oxidation of organic macropollutants and improvement of coagulation [1]. Table 1 shows the summary of ozone application in drinking water treatment. From this table illustrates that the demand for wide range of ozone concentration sensor to measure accurately various dose of ozone during drinking water treatment.

Besides, ozone gas monitoring is important in many fields such as rubber testing, semiconductor processes, biotechnology processes, research laboratories, package food [2] and preserve fruit juice [3]. Again, with increasing the use of ozone, there is a greater demand for a wide range of ozone monitoring system must to be developed.

In the past couple of years, the existing technology for ozone monitoring system can be classified into three types namely electrochemical [4], semiconductor [5, 6, 7] and optical sensor based absorption spectroscopy. Among the three types of ozone monitoring system, the optical sensor based absorption spectroscopy offer vast advantages such as good long term stability, good selectivity [8] and fast response. Current available optical sensor in monitoring ozone is based on absorption in UV spectrum due to high absorption by ozone in this spectrum. In addition, the optical fibers sensor enables the sensing system to make measurement in harsh environment because of their robust nature and low susceptibility to chemical and electromagnetic interference since it is constructed from glass and ceramic components.

The previous work has been reported for ultraviolet based optical sensor in determining the concentration of ozone in the range of 0 to1 mg/L and visible based sensor to measure high concentration over a wide range of 25 to 126 mg/L by O'Keefe, *et al.* [8]. However, the work presented here focusing on wide range analysis to improve the range of ozone concentration detection of present developed ultraviolet based sensor. This analysis considering Twyman-Lothian equation to improve the sensor's capability to achieve wide range of ozone concentration detection.

Table 1 Summary of ozone application in drinking water treatment [1]

| Control of:	Point of Application	Ozone Dose
Iron and manganese	Pre, Inter	Med
Colour	Inter	Med-High
Taste and odour	Inter	High
Particles	Pre	Low
Algae	Pre, Inter	Low-Med
Pathogens	Pre, Post	Med-High
Cl_2 by-products	Inter, Pre	Low-High
Biodegradables	Inter	Med

■2.0 OZONE ABSORPTION THEORY

Many atmospheric gas molecules are transparent in ultraviolet and visible region. Ozone is one of these gaseous that have significant absorption in these spectrums. Ozone absorbs radiation in the ultraviolet and visible region due to major electronic transition within ozone molecule. As ozone absorbs ultraviolet radiation, valence electrons are excited from one energy level to a higher energy level. The energy differences between electronic levels in most molecules vary from 125 to 650 kJ/mole [9].

However, atom in a molecule also undergo rotation and vibration among each other at room temperature. The energy levels for these rotation-vibration transition are quite closely spaced and can be considered as being packed on top of each electronic levels. As electronic and rotation-vibration transition may undergo excitation simultaneously, this leads to superposition of rotation-vibration levels on electronic level. Thus, ultraviolet absorption spectrum over a wide range of wavelength is produced instead of sharp lines.

In addition, each wavelength of light has a certain energy related with it. If that particular amount of energy is ideal for making transition, then that wavelength will be absorbed. In fact, there are so many possible transition exist inside the molecule. Different type of transition needs different amount of energy. From this, it is clear explains why the different amount of absorption appear at different wavelengths due to particular transition that involved.

Each gasses have it own atomic structure. These gasses contain different number of electron. This indicates that different gasses need different amount of energy to be absorbed due to different number of electron to perform electronic transition. In ultraviolet absorption, this phenomenon explain why a different gasses have a different absorption spectrum since different electron needs a different amount of energy before it can perform electronic transition.

However, it has been widely reported by previous researcher to present ozone characteristic using absorption cross section. Absorption cross section represents probability of absorption process to happen.
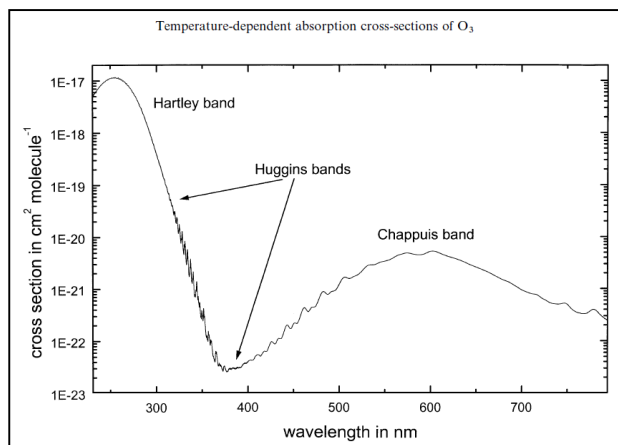
Figure 1 Absorption cross-section of ozone spectrum at 293K for complete coverage of 231nm to 794 nm range [10]

For ozone, absorption cross section can be monitor in ultraviolet and visible region as shown in Figure 1. From the graph, wavelength with the largest magnitude of absorption cross section will experience maximum absorbance. Two wavelength region, which are Hartley band and Chappuis band have been reported to have large value of absorption cross section in ultraviolet and visible region, respectively. Work done by Burrows *et al*. [10] shows that absorption cross section of ozone in the Hartley band is found to be $\sigma=1150\text{x}10^{-20}$ cm^2molecule^{-1} with peak absorption at 253.65 nm. There is also a second peak observed in Chappuis band at 611.97 nm with absorption cross section is found to be $\sigma = 47000$ x 10^{-24} cm^2molecule^{-1}.

Absorbance is useful information to be apply in order to obtain concentration of gasses. The relationship between absorbance and concentration of an absorbing species can be calculated by using Beer-Lambert law. This law is described in detail by many chemistry textbook and journal [11]

$$A = -\ln(T_r) = \varepsilon c l \qquad (1)$$

$$T_r = \frac{I_{(\lambda)}}{I_{o(\lambda)}} \qquad (2)$$

A	is absorbance
$I_{(\lambda)}$	is the transmitted intensity when ozone passes through.
$I_{o(\lambda)}$	is the incident intensity at zero ozone concentration.
ε	is molar absorptivity of the species (m^2 mol^{-1})
c	is concentration of the species (mol m^{-3})
l	is optical path length (m)
T_r	is transmittance of light

Ozone concentrations is normally read in parts per million, *ppm*. Equation (3) is the derivation from the Beer-Lambert law which gives ozone concentration in ppm and was previously described [12, 13, 14].

$$c_{ppm} = -\frac{1000000RT}{\sigma N_A Pl} In\left(\frac{I_{(\lambda)}}{I_{o(\lambda)}}\right) \qquad (3)$$

c_{ppm}	is concentration of the species (ppm)
R	is ideal gas constant, 8.205746×10^{-5} (atm m^3 mol^{-1} K^{-1})
T	is absolute temperature (K)
σ	is absorption cross section of the species (m^2 $molecule^{-1}$)
N_A	is Avogadro's constant, $6.02214199 \times 10^{23}$ (molecule mol^{-1})
P	is pressure (atm)
l	is optical path length (m)
$I_{(\lambda)}$	is the transmitted intensity at certain ozone concentration
$I_{o(\lambda)}$	is the incident intensity at zero ozone concentration

Equation (3) shows concentration is dependent on several parameters. It is also noticeable from Equation (3) that these parameters can be measured in real time. Thus, calculation of the ozone concentration can be calculated accurately using these parameters. However, Beer-Lambert law has limitations. Based on Twyman-Lothian equation, high error of relative error of concentration is observed at high transmittance or low transmittance. For example, disobedience of the law at low transmittance due to stray light [15]. Typical transmittance for low relative error of concentration measurement is from 0.25 to 0.50 [16]. The relationship between the relative error of concentration and the transmittance can be describe as follow [17]:

$$\frac{\Delta c}{c} \times 100 = \frac{\Delta T_r}{T_r In T_r} \times 100 \qquad (4)$$

$\Delta c /c$	is relative error of concentration (%)
ΔT_r	is absolute error of transmittance
T_r	is transmittance of light

We estimate the relative error in concentration $\Delta c/c$ by assuming that $c=c_s$ is regarded as a conventional true value and $\Delta c/c$ corresponds to $(c_{ppm}-c_s)/c_s$, where c_{ppm} and c_s are ozone concentrations obtained by calculation from the results during experiment and measurement from ozone monitor, respectively. Figure 2 shows graph of relative error of concentration versus transmittance. The curve is plotted based on calculation using Equation (4) and absolute transmittance error, $\Delta T_r = 0.001$. From the graph, it is observed low relative error of concentration is achieved for transmittance value of 0.25 to 0.50.
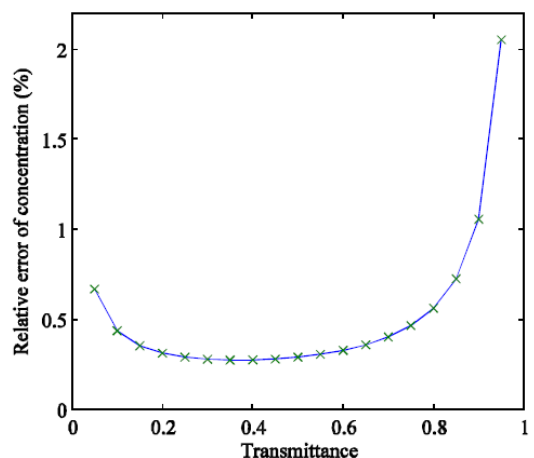

Figure 2 Twyman-Lothian curve based on absolute transmittance error 0.001 [15]

■3.0 EXPERIMENTAL SET UP

The sensor, as assembled in laboratory, is shown in Figure 3. The optical fiber sensor set up consists of two Ocean Optics QP400-025-SR 400 μm diameter premium solarization resistant fiber of 25 cm length. The use of solarization resistant fiber is needed to prevent fiber damage due to ultraviolet radiation. These fibers are the illuminating fiber, which is connected to the light source and a read fiber, connected to a spectrometer. These two fibers are connected to Ocean Optics 74-UV collimating lens at each end of the aluminium gas cell. The use lens is to focus parallel light beam to and from gas cell. The gas cell is fabricated at 6.4 mm internal diameter and 5 cm length.
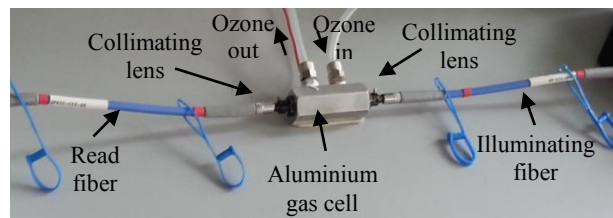

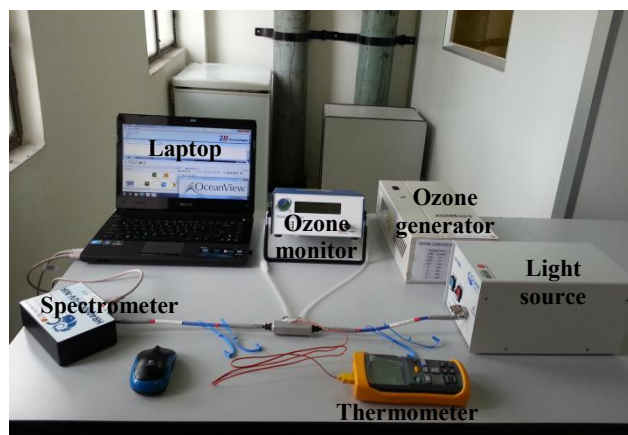**Figure 3** Optical fiber ozone sensor

Figure 4 Experimental set up

Figure 4 shows complete experimental set up for testing of ozone sensor. The experiment set up are described as follow. The Longevity Resources ozone generator EXT50 generates the ozone from high purity oxygen (99.995%) based on corona discharge principle and passes it through the gas cell via silicon tube. The Ocean Optics DH-2000 deuterium tungsten halogen light source is used throughout these experiments to deliver ultraviolet wavelength from 210nm to 410nm. The Ocean Optics HR4000CG-UV-NIR high resolution spectrometer is used to detect the fiber transmission for further analysis. The spectrometer is interfaced with the laptop using Ocean Optics Ocean View software. Ocean View is a specifically designed program to acquire the data from spectrometer in real time. The 2B Technologies ozone monitor was connected to the output of the gas cell for ozone concentration measurement and ozone destruction. The ozone concentration reading are recorded in laptop using 2B Technologies Data Display Application software. Digital thermometer is attached to the gas cell for temperature measurement.

■4.0 RESULTS AND DISCUSSION

The ozone is flowed into the gas cell with decreasing concentration from 999 ppm to 616 ppm and the light intensity from 210 nm to 370 nm is recorded by spectrometer for each concentration. Equation (2) along with recorded measured intensity is utilized to calculate transmittance for each concentration. Then the transmittance is plotted on graph as shown in Figure 5. It is clearly shown that maximum absorption wavelength is observed at 260.453 nm with great reduction of transmittance value when 616 ppm to 999 ppm of ozone concentration is flowed into the gas cell. Wavelength 260.453 nm is the most sensitive wavelength for ozone concentration measurement in this work due to the smaller value of transmittance. However, wavelength 260.453 nm is not recommended for wide range ozone concentration measurement due to the high relative error of concentration based on Twyman-Lothian equation.
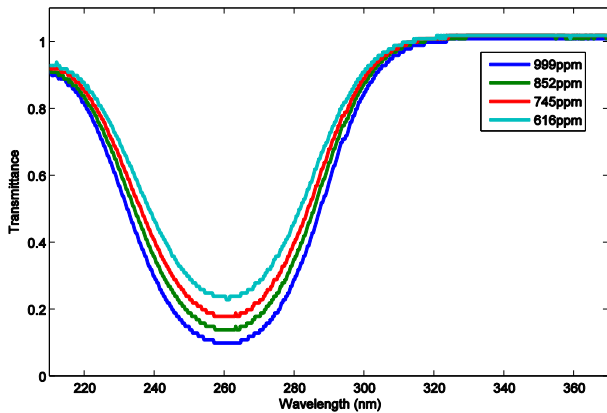

Figure 5 Transmittance measurements for various ozone concentration at range of wavelength from 210 nm to 370 nm

To conduct further wide range analysis of concentration, ultraviolet region is divided in to two set of wavelength. First set data consist of wavelength range from 225 nm to 260 nm while second set data consist of wavelength region from 260 nm to 310 nm.

First analysis is done towards 12 wavelengths starting from 225 nm to 260 nm. Graph of transmittance versus concentration for

these wavelengths are shown in Figure 6. From the graph, the transmittance decreased as the ozone concentration is increased from 616 ppm to 999 ppm for the whole wavelengths. Thus, this result follows the Beer Lambert Law. Besides, it is clearly can be seen that different wavelength have a different value of transmittance for the same concentration of ozone. From this information, wide range analysis is conducted by considering transmittance value between 0.25 to 0.5. This transmittance value will provide the low relative error of concentration. The low relative error of concentration are achieved by specific wavelengths which include 239 nm, 240 nm, 241 nm and 242 nm. This particular wavelength is suggested for wide range ozone concentration measurement particularly for range 616 ppm to 999 ppm.

For better understading, graph of range of concentration versus wavelength is plotted as shown in Figure 7. The graph is plotted particularly for transmittance range from 0.25 to 0.5 due to low relative error consideration. Again, it is shown that wide range of concentration is achieved at 239 nm, 240 nm, 241 nm, 242 nm with highest value of range of 383 ppm.
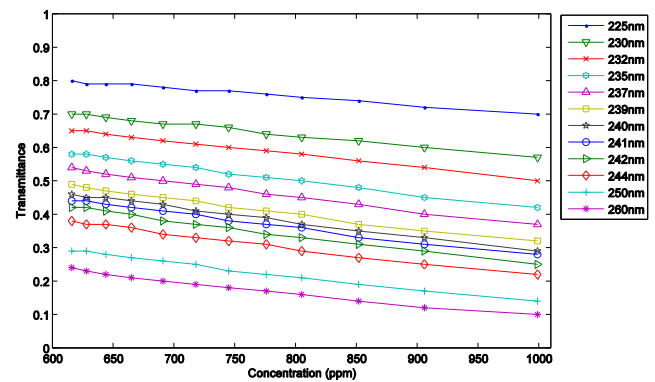

Figure 6 Transmittance measurement for wavelength from 225 nm to 260 nm used for wide range analysis of ozone concentration
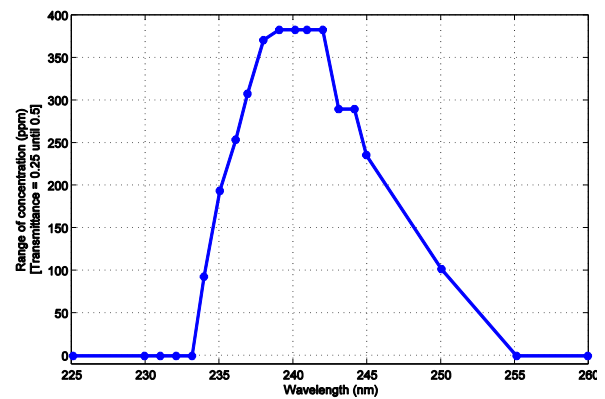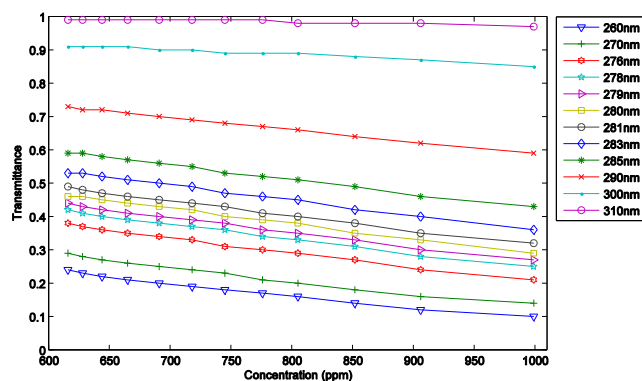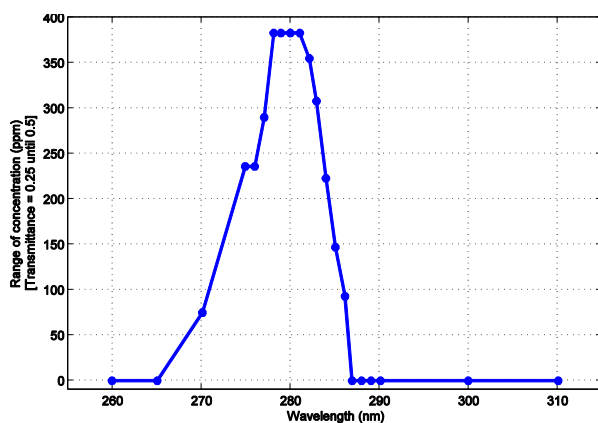

Figure 7 Range of ozone concentration at different wavelength from 225 nm to 260 nm for transmittance range from 0.25 to 0.5

Second analysis is done towards 12 additional wavelengths within range from 260 nm to 310 nm as shown in Figure 8. Based on the graph, wavelengths at 278 nm, 279 nm, 280 nm and 281 nm are the best to be suggested for wide range ozone concentration measurement due to low relative error of concentration. Again, Figure 9 shows a graph of ozone concentration at different wavelength from 260 nm to 310 nm for transmittance range from 0.25 to 0.5. From the graph, it clearly shown that wide range of

concentration is achieved at 278 nm, 279 nm, 280 nm and 281 nm with highest value of range at 383 ppm.

Figure 8 Transmittance measurement for wavelength from 260 nm to 310 nm used for wide range analysis of ozone concentration

Figure 9 Range of ozone concentration at different wavelength from 260 to 310 nm for transmittance range from 0.25 to 0.5

Compared to maximum absorption wavelength at 260.453 nm, transmittance value of 0.24 is obtained when 616 ppm of ozone concentration is flowed into the gas cell. This wavelength failed to fulfill the consideration based on Twyman-Lothian equation to achieve low relative error of concentration.

From these experiments, it can be shown that wide range ozone measurement can be realized if the operating wavelength is farther from the gas absorption peak due to low relative error of concentration consideration. Care has to be taken while selecting these wavelengths, considering lesser light absorption capability for extreme cases. This scenario is proven by observing transmittance behavior at 300 nm and 310 nm. Visually, it can be deduced that light absorption by the ozone gas molecules seems to be weaken at these wavelengths, which are farther from peak absorption of 260.453 nm.

In addition, our experiment set up has limitation to generate ozone below than 661 ppm. This is because of high flow rate of oxygen needs to supply to ozone generator in order to generates lower concentration. Precaution needs to be taken by not performing experiment at high flow rate to keep instrument safe and remain working properly. Thus analysis below 616 ppm cannot be done. Besides, our monitor is certified to measure ozone concentration below 1000 ppm which further limit the range of concentration to be considered from 616 ppm to 999 ppm.

■5.0 CONCLUSION

Wide range analysis of ozone concentration was successfully conducted via absorption spectroscopic technique based on fiber optic extrinsic sensor in ultraviolet region. Experimental results show that wide range of ozone concentration from 616 ppm to 999 ppm can be achieved by observing transmittance of specific wavelength at 239 nm, 240 nm, 241 nm, 242 nm, 278 nm, 279 nm, 280 nm and 281 nm. Twyman-Lothian equation has been considered in these analyses to reduce relative error of concentration. In addition, peak absorption is found to be 260.453 nm at temperature experiment environment of 298.54 K.

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