RATIO METRIC METHOD FOR OZONE ABSORPTION CROSS SECTION MEASUREMENT

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A thesis submitted in fulfilment of the requirements for the award for the degree of Doctor of Philosophy (Electrical Engineering)

Faculty of Electrical Engineering
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JULY 2015
To my beloved family for unconditional support through ups and downs
ACKNOWLEDGEMENTS

I would like to express my gratitude to Universiti Teknologi Malaysia (UTM) and Ministry of Higher Education (MOHE) Malaysia for supporting this research work under Research University Grant (RUG) Scheme grant no: 05J60 and grant no: 04H35, Fundamental Research Grant Scheme (FRGS) grant no: 4F317, and UTM Zamalah Fellowship. In addition, I thank my main supervisor, Assoc. Prof. Dr. Mohd Haniff bin Ibrahim for constructive feedback on my writings, academic advice and financial support to purchase equipments for experiment. I am grateful to my cosupervisor, Dr. Nor Hafizah binti Ngajikin for commenting my writings and financial support to purchase equipments for experiment. I thank Dr. Asrul Izam bin Azmi for his time and effort spent to review my writings. I show appreciation to Assoc. Prof. Dr. Sevia Mahdaliza bin Idrus for financial support to purchase equipments for experiment. I appreciate colleagues Michael David, Maslina Yaacob, Mohd Rashidi Salim and Nabihah Hussin for constructive criticisms. In short, I extend my appreciation to people that have helped to me at various occasions to ensure successful outcome of this study.
ABSTRACT

Ultraviolet absorption spectroscopy has been practised for ozone concentration measurement because the method of measurement is fast and reliable. Ratiometric method corrects intensity drift of light source for improvement of measurement stability. However, ozone absorption cross section may not be determined via ratiometric method because of limitation of existing Beer–Lambert law. Absorption cross section defines strength of absorption, which is an important parameter for calculation of ozone concentration. Firstly, optical path length of gas cell that suits dynamic range of ozone monitor in this work (less than 1000 ppm) is determined. Based on spectralcalc.com simulation, gas cells of optical path lengths of 5 cm, 10 cm and 20 cm are optimized for concentration measurement from 494.1 ppm to 988.1 ppm, 247.0 ppm to 494.1 ppm and 123.5 ppm to 247.0 ppm respectively. Secondly, Beer–Lambert law deviation is observed when long gas cell of optical path length 10 cm is used to measure high ozone concentration from 357 ppm to 971 ppm. Typically, ozone is sampled using strong absorption wavelength for high sensitivity measurement. When strong absorption wavelengths cause saturation, linearity of measurement is preserved by sampling ozone using weak absorption wavelength 279.95 nm. Thirdly, temperature and pressure stability of ozone absorption cross section are verified using spectralcalc.com simulation. Finally, a novel equation is established based on Beer–Lambert law for measurement of ozone absorption cross section via ratiometric method. The equation is verified for ozone concentration measurement from 450 ppm to 989 ppm using short gas cell of optical path length 5 cm, sampling wavelength 260.99 nm and reference wavelength 377.05 nm. The equation is attractive to researchers in areas of absorption spectroscopy and optical gas sensor because ratiometric method is gaining popularity for high stability ozone concentration measurement.
ABSTRAK

Spektroskopipi penyerapan ultraurungi sering diguna untuk mengukur kepekatan ozon kerana cara pengukuran ini cepat dan boleh dipercayai. Kaedah metrik nisbah meningkatkan kestabilan pengukuran kerana keamatan cahaya yang kurang stabil dipertimbangkan. Keratan rentas penyerapan ozon tidak dapat dikira melalui kaedah metrik nisbah kerana kekurangan hukum Beer–Lambert yang sedia ada. Keratan rentas penyerapan ozon adalah parameter penting untuk pengiraan kepekatan ozon. Pertama, panjang sel gas yang bakal mengukur julat kepekatan ozon yang boleh diukur oleh alat pengukur ozon (kurang dari 1000 ppm) dikenal pasti. Hasil simulasil spectralcalc.com menunjukkan kepekatan ozon yang bakal diukur oleh sel gas 5 cm, 10 cm dan 20 cm, adalah 494.1 ppm ke 988.1 ppm, 247.0 ppm ke 494.1 ppm dan 123.5 ppm ke 247.0 ppm. Kedua, pelencangan hukum Beer–Lambert diperhatikan apabila sel gas 10 cm digunakan untuk pengukuran kepekatan ozon dari 357 ppm ke 971 ppm. Biasanya, panjang gelombang yang kuat diserap oleh ozon digunakan untuk pengukuran yang peka. Apabila panjang gelombang yang kuat diserap oleh ozon menyebabkan ketepuan, hubungan linear pengukuran dikekalkan dengan menggunakan panjang gelombang yang lemah diserap oleh ozon 279.95 nm. Ketiga, kestabilan keratan rentas penyerapan ozon pada suhu dan tekanan berlainan disahkan melalui simulasispectralcalc.com. Akhirnya, persamaan baru diperoleh dari hukum Beer–Lambert untuk mengira keratan rentas penyerapan ozon melalui kaedah metrik nisbah. Persamaan tersebut disahkan melalui pengukuran kepekatan ozon dari 450 ppm ke 989 ppm menggunakan sel gas 5 cm, panjang gelombang sampel 260.99 nm dan panjang gelombang rujukan 377.05 nm. Persamaan tersebut menyumbang kepada bidang spektroskopipi penyerapan dan pengukuran gas melalui kaedah optik kerana kaedah metrik nisbah semakin kerap digunakan untuk pengukuran kepekatan ozon yang stabil.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>i</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
<td></td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xvii</td>
<td></td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xviii</td>
<td></td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xx</td>
<td></td>
</tr>
</tbody>
</table>

1 INTRODUCTION 1
1.1 Introduction to Ozone and Its Applications 1
1.2 Review of Ozone Sensors 4
1.3 Problem Formulation 7
1.4 Motivation of Research 8
1.5 Objectives of Research 9
1.6 Scope of Research 10
1.7 Overview of Thesis 11

2 THEORETICAL BACKGROUND FOR ABSORPTION BASED OZONE SENSOR 14
2.1 Introduction 14
2.2 Derivation of Beer–Lambert Law for Concentration Measurement
2.3 Beer–Lambert Law for Ratiometric Method Calculation
2.4 Twyman–Lothian Perspective for Disobedience of Beer–Lambert Law at High and Low Transmittance
2.5 Limitations of Beer–Lambert Law
2.6 Prerequisites of Beer–Lambert Law
2.7 Review of Ozone Absorption Cross Section
2.8 Review of Sensor Performance Specifications
2.9 Sensitivity for Selection of Maximum Absorption Wavelength
2.10 Summary

3 INSTRUMENTATION FOR ABSORPTION BASED OZONE SENSOR
3.1 Introduction
3.2 Review of Sensor Instruments
   3.2.1 Optical Components
   3.2.2 Gas Components
   3.2.3 Gas Cell Construction for Ozone Application
   3.2.4 Gas Cell Diameter and Sensor Sensitivity
3.3 Gas Cell Fabrication Decision
3.4 Summary

4 OPTICAL PATH LENGTH OPTIMIZATION FOR HIGH OZONE CONCENTRATION MEASUREMENT
4.1 Introduction
4.2 Concentration Measurement Range Optimization for Specific Optical Path Length
   4.2.1 Simulation Methodology
   4.2.2 Simulation Result of Maximum and Minimum Absorption Wavelength
4.2.3 Simulation Result of Maximum Absorption Cross Section 64
4.2.4 Simulation Result of Concentration Measurement Range at Specific Optical Path Length 67
4.3 Limitation of Long Gas Cell for High Ozone Concentration Measurement 68
  4.3.1 Simulation of Absorption Cross Section Spectrum 69
  4.3.2 Experimental Methodology using Long Gas Cell 70
  4.3.3 Experimental Result of Sensor Linearity and Recommendations 72
4.4 Summary 76

5 CHARACTERIZATION OF OZONE ABSORPTION CROSS SECTION 77
  5.1 Introduction 77
  5.2 Simulation of Temperature Dependence of Absorption Cross Section 78
    5.2.1 Simulation Result of Temperature Dependence 78
  5.3 Simulation of Pressure Dependence of Absorption Cross Section 81
    5.3.1 Simulation Result of Pressure Dependence 82
  5.4 Ratiometric Method for Maximum Absorption Cross Section Determination 84
    5.4.1 Experimental Methodology using Short Gas Cell 85
    5.4.2 Experimental Result of Maximum and Minimum Absorption Wavelength 87
    5.4.3 Experimental Result of Real Time Ozone Concentration Measurement 89
    5.4.4 Experimental Result of Maximum Absorption Cross Section 91
  5.5 Summary 94
6 CONCLUSIONS, CONTRIBUTIONS AND FUTURE WORK

6.1 Conclusions 95
6.2 Contributions 96
6.3 Recommendations for Future Work 98

REFERENCES 100

Appendices A–C 116–134
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Physical Characteristics of Ozone Gas</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>Comparison of Ozone Absorption Cross Section among Hartley, Huggins, Huggins Chappuis Minimum and Chappuis Band</td>
<td>26</td>
</tr>
<tr>
<td>2.2</td>
<td>Performance Specifications of Absorption Based Ozone Sensor in Previous Work</td>
<td>31</td>
</tr>
<tr>
<td>3.1</td>
<td>Comparison of Optical Components between This Work and Previous Work</td>
<td>38</td>
</tr>
<tr>
<td>3.2</td>
<td>Comparison of Gas Components between This Work and Previous Work</td>
<td>44</td>
</tr>
<tr>
<td>3.3</td>
<td>Comparison of Ozone Gas Cell Construction between This Work and Previous Work</td>
<td>50</td>
</tr>
<tr>
<td>3.4</td>
<td>Details of Gas Cell Fabrication</td>
<td>55</td>
</tr>
<tr>
<td>3.5</td>
<td>Selection of Experimental Instruments for This Work</td>
<td>57</td>
</tr>
<tr>
<td>4.1</td>
<td>Comparison of Sampling and Reference Wavelengths among This Simulation and Previous Experiments</td>
<td>64</td>
</tr>
<tr>
<td>4.2</td>
<td>Comparison of Maximum Absorption Cross Section among This Simulation and Previous Experiments</td>
<td>66</td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison of Dynamic Range among This Simulation and Previous Experiments for Ozone Concentration Measurement via Ultraviolet Absorption Spectroscopy</td>
<td>67</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.4</td>
<td>Comparison of Linearity among Selected Sampling Wavelengths</td>
<td>74</td>
</tr>
<tr>
<td>4.5</td>
<td>Comparison of Absorption Cross Section between This Experiment and Simulation</td>
<td>75</td>
</tr>
<tr>
<td>5.1</td>
<td>Temperature Dependence Comparison among Maximum Absorption Cross Section in This Simulation and Previous Experiments</td>
<td>81</td>
</tr>
<tr>
<td>5.2</td>
<td>Comparison of Ozone Absorption Cross Section among This Experiment and Previous Experiments</td>
<td>93</td>
</tr>
<tr>
<td>A.1</td>
<td>Comparison of Ozone Sensing Techniques</td>
<td>117</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Scope of research of this study</td>
<td>11</td>
</tr>
<tr>
<td>2.1</td>
<td>Graph of absorbance versus transmittance based on theoretical calculation from Equation 2.6</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>Model to illustrate exponential reduction of light intensity after passing through ozone of equal concentration in a fixed volume cylindrical gas cell</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>Twyman–Lothian curve based on transmittance error 0.10 % (Hughes, 1963)</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Ozone absorption cross section spectrum simulated based on spectralcalc.com gas cell simulator at temperature 300 K, pressure 1 atm, ozone concentration 500 ppm and optical path length 5 cm</td>
<td>25</td>
</tr>
<tr>
<td>3.1</td>
<td>Ocean Optics DH-2000 deuterium tungsten halogen light source in operation. The instrument is connected to an optical fibre.</td>
<td>41</td>
</tr>
<tr>
<td>3.2</td>
<td>Ocean Optics QP400-025-SR premium solarisation resistant fibre of 25 cm length and 400 µm diameter with protection cap on for storage</td>
<td>42</td>
</tr>
<tr>
<td>3.3</td>
<td>Ocean Optics HR4000CG-UV-NIR high resolution spectrometer in operation. The instrument is connected to an optical fibre and USB connection to computer.</td>
<td>43</td>
</tr>
<tr>
<td>3.4</td>
<td>Ocean Optics 74-UV collimating lens ready for connection to optical fibre and gas cell</td>
<td>44</td>
</tr>
<tr>
<td>3.5</td>
<td>Longevity Resources corona discharge ozone generator EXT50. Input to the generator is pure oxygen supply via vinyl tube. Output from the generator is ozone via silicone tube.</td>
<td>47</td>
</tr>
<tr>
<td>3.6</td>
<td>Purified oxygen supply at 99.999 % purity. The oxygen</td>
<td></td>
</tr>
</tbody>
</table>
supply is connected to pressure regulator to control speed of oxygen flow to ozone generator. Vinyl tube is used for oxygen transportation.

3.7 2B Technologies ozone monitor model 106-M is warming up for experiment

3.8 Brass male pneumatic fitting for silicone tube of 4 mm internal diameter and 6 mm external diameter

3.9 A set of 3/8 UNF X 24 Majesta hand tap for threading of aluminium gas cell to fit SMA 905 connector of Ocean Optics 74-UV collimating lens

3.10 From left to right, prefabricated aluminium rod of 0.64 cm internal diameter, fabricated aluminium gas cells of length 6.3 cm, 11.3 cm and 21.3 cm. The gas cell is fitted with brass pneumatic fittings for gas inlet and outlet. Both sides of gas cell will be fitted to Ocean Optics 74-UV collimating lens for light input and output. Connections are tighten with PTFE tape to prevent gas leakage.

4.1 Graphic user interface of spectralcalc.com gas cell simulator for wavelength selection

4.2 Graphic user interface of spectralcalc.com gas cell simulator for selection of gas, isotope, volume mixing ratio (VMR), optical path length, pressure, temperature and line list database

4.3 Transmittance spectrum of ozone obtained via spectralcalc.com gas cell simulator at wavelength from 240 nm to 270 nm, optical path length 5 cm, temperature 300 K, pressure 1013.25 mbar and ozone concentration from 35.64 ppm to 2102.70 ppm

4.4 Transmittance spectrum of ozone obtained via spectralcalc.com gas cell simulator at wavelength from 360 nm to 400 nm, optical path length 20 cm, temperature 300 K, pressure 1013.25 mbar and ozone concentration 247.0 ppm

4.5 Graph of concentration versus natural logarithm of transmittance obtained from this simulation at maximum absorption wavelength 255.442 nm, temperature 300 K, pressure 1 atm and optical path length 5 cm, 10 cm and 20 cm

4.6 Graphic user interface of spectralcalc.com line list browser for selection of gas, wavenumber, pressure, temperature and line list database
4.7 Ozone absorption cross section spectrum simulated via spectralcalc.com line list browser at temperature 300 K and pressure 0 torr

4.8 Experimental setup for ozone concentration measurement via ultraviolet absorption spectroscopy using long gas cell of 10 cm optical path length

4.9 Transmissive aluminium gas cell of 0.64 cm internal diameter and 10 cm optical path length. The gas cell is fitted with brass pneumatic fittings for gas inlet and outlet. The gas cell is fitted to Ocean Optics 74-UV collimating lens for light input and output. Connections are tighten with PTFE tape to prevent gas leakage.

4.10 Graph of natural logarithm of transmittance (sensor output) versus actual ozone concentration (commercial ozone monitor output) based on experimental result at optical path length 10 cm and selected sampling wavelengths

5.1 Graph of absorption cross section versus wavelength at temperature from 200 K to 300 K and pressure 0 torr obtained from simulation via spectralcalc.com line list browser

5.2 Graph of maximum absorption cross section versus temperature at pressure 0 torr obtained from simulation via spectralcalc.com line list browser

5.3 Ozone absorption cross section spectrum simulated based on spectralcalc.com gas cell simulator at optical path length 0.20 m, temperature 300 K, pressure from 0.1 atm to 3 atm and concentration 123.5 ppm

5.4 Graph of maximum absorption cross section versus pressure simulated using spectralcalc.com gas cell simulator at maximum absorption wavelength 255.442 nm, optical path length 0.20 m, temperature 300 K, and concentration 123.5 ppm

5.5 Transmissive aluminium gas cell of 0.64 cm internal diameter and 5 cm optical path length

5.6 Experimental block diagram for ozone concentration measurement using ultraviolet absorption spectroscopy and short gas cell of 5 cm optical path length

5.7 Transmittance spectrum of ozone obtained through experiment at wavelength from 210.03 nm to 409.95 nm, optical path length 5 cm and ozone concentration from 452 ppm to 976 ppm
5.8 Graph of actual ozone concentration (commercial ozone monitor output) and sensor output versus time obtained through experiment using maximum absorption wavelength 260.99 nm, minimum absorption wavelength 377.05 nm and optical path length 5 cm

5.9 Graph of minimum absorption wavelength intensity (sensor output) versus time obtained through experiment at optical path length 5 cm and concentration from 450 ppm to 989 ppm

5.10 Graph of sensor output versus actual ozone concentration (commercial ozone monitor output) obtained through experiment using maximum absorption wavelength 260.99 nm, minimum absorption wavelength 377.05 nm and optical path length 5 cm
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIPM</td>
<td>Bureau International des Poids et Mesures or International Bureau of Weights and Measures</td>
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<tr>
<td>DH</td>
<td>Deuterium halogen</td>
</tr>
<tr>
<td>DUV</td>
<td>Deep ultraviolet</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drug Administration</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>HITRAN</td>
<td>High resolution transmission</td>
</tr>
<tr>
<td>HR</td>
<td>High resolution</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LPM</td>
<td>Litres per minute</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>OSHA</td>
<td>Occupational Safety and Health Administration</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>ppt</td>
<td>Parts per trillion</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>USD</td>
<td>United States Dollar</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>VMR</td>
<td>Volume mixing ratio</td>
</tr>
</tbody>
</table>
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Absorbance of light (no unit)</td>
</tr>
<tr>
<td>$A_g$</td>
<td>Cross sectional area of gas cell in m$^2$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>Concentration of ozone in second system that varies in temperature, pressure or volume from first system</td>
</tr>
<tr>
<td>$c_s$(ppm)</td>
<td>Standard gas concentration given by commercial gas monitor in ppm by volume</td>
</tr>
<tr>
<td>$c$(g m$^{-3}$)</td>
<td>Density of ozone in g m$^3$</td>
</tr>
<tr>
<td>$c$(g Nm$^{-3}$)</td>
<td>Density of ozone at pressure 1 atm and temperature 273.15 K in g Nm$^{-3}$</td>
</tr>
<tr>
<td>$c$(mol m$^{-3}$)</td>
<td>Concentration of ozone in mol m$^3$</td>
</tr>
<tr>
<td>$c$(ppm)</td>
<td>Concentration of ozone in ppm by volume</td>
</tr>
<tr>
<td>$c$(wt%)</td>
<td>Concentration of ozone in percentage by weight</td>
</tr>
<tr>
<td>$I$</td>
<td>Light intensity in count</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Output intensity of absorbing wavelength passing ozone at zero concentration in count</td>
</tr>
<tr>
<td>$I_{0r}$</td>
<td>Output intensity of non absorbing wavelength passing ozone at non zero concentration in count</td>
</tr>
<tr>
<td>$I_t$</td>
<td>Output intensity of absorbing wavelength passing ozone at non zero concentration in count</td>
</tr>
<tr>
<td>$I_s$</td>
<td>Forward scattering contribution of absorbing wavelength in count</td>
</tr>
<tr>
<td>$k$</td>
<td>Absorption coefficient of ozone in m$^{-1}$</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Constant used to relate $I_0$ and $I_{0r}$ in ratiometric calculation</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant, $1.362595903 \times 10^{-28}$ atm m$^3$ K$^{-1}$ molecule$^{-1}$</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of sample in m</td>
</tr>
<tr>
<td>$l_s$</td>
<td>Optical path length in m</td>
</tr>
<tr>
<td>$N$</td>
<td>Number density in molecule m$^3$</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s constant, $6.02214199 \times 10^{23}$ molecule mol$^{-1}$</td>
</tr>
</tbody>
</table>
$n_{(cm^{-1})}$ - Wavenumber in cm$^{-1}$
$n_f$ - Mole fraction of ozone (no unit)
$n_m$ - Amount of ozone gas in mol
$n_T$ - Total amount of gas in mol
$P$ - Total pressure of gas in atm
$p$ - Partial pressure of ozone in atm
$r$ - Norm of residual
$R$ - Ideal gas constant, $8.205746 \times 10^{-5}$ atm m$^3$ mol$^{-1}$ K$^{-1}$
$S$ - Forward scattering correction factor (no unit)
$t$ - Time in s
$T$ - Absolute temperature in K
$T_r$ - Transmittance of light (no unit)
$T_{rr}$ - Constant used to relate $I_r$ and $I_{0r}$ in ratiometric calculation
$V$ - Total volume of gas in m$^3$
$v$ - Volume of ozone in m$^3$
$V_m$ - Molar volume of ozone in m$^3$ mol$^{-1}$
$y_i$ - A data point in a graph
$y_{ibest}$ - A data point at best fit line
$\Delta c$ - Error of ozone concentration
$\Delta c/c$ - Relative error of ozone concentration
$\Delta T_r$ - Absolute error of transmittance
$\varepsilon$ - Molar absorption coefficient in m$^2$ mol$^{-1}$
$\varepsilon_{10}$ - Decadic molar absorption coefficient in m$^2$ mol$^{-1}$
$\lambda$ - Wavelength in nm
$\rho$ - Ozone density at 1000000 ppm in g m$^{-3}$
$\sigma$ - Absorption cross section of ozone in m$^2$ molecule$^{-1}$
$\sigma_{\text{experiment}}$ - Absorption cross section in this experiment
$\sigma_{\text{simulation}}$ - Absorption cross section in this simulation via spectralcalc.com line list browser
$\sigma_{\text{this}}$ - Absorption cross section in this work
$\sigma_{\text{previous}}$ - Absorption cross section in previous work
$\sigma_{200K}$ - Absorption cross section at temperature 200K
$\sigma_{300K}$ - Absorption cross section at temperature 300K
$\omega$ - Molar mass of ozone, 48 g mol$^{-1}$
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Summary of Ozone Sensing Techniques</td>
<td>117</td>
</tr>
<tr>
<td>B</td>
<td>Conversion Fundamentals, Relationships and Variations in Beer–Lambert Law</td>
<td>125</td>
</tr>
<tr>
<td>C</td>
<td>List of Publications</td>
<td>131</td>
</tr>
</tbody>
</table>
1.1 Introduction to Ozone and Its Applications

Ozone (triatomic oxygen, O\textsubscript{3}) is described to be good up high, but bad nearby (United States Environment Protection Agency, 2003). Ozone at stratosphere protects the earth from harmful ultraviolet sun rays. On ground level, ozone pollutes the air. Ozone is generated from anthropogenic emissions such as organic volatile compound and oxides of nitrogen in presence of sunlight (Arif and Abdullah, 2011; Cooper \textit{et al.}, 2010; Weschler, 2000; Yadav \textit{et al.}, 2014). At industrial and urban areas in Peninsular Malaysia, high concentration of ground level ozone is recorded from April to June because of dry weather (Rajab \textit{et al.}, 2011). In wet weather, rain cleanses nitrogen oxides in the air, which hinders formation of ozone (Rajab \textit{et al.}, 2010). Ozone has distinctive pungent smell. However, inhalation of ozone causes pulmonary disease (Jakpor, 2009). Based on OSHA standard, a worker should not expose to ozone more than 0.1 ppm in 8 hours (United States Department of Health and Human Services and United States Department of Labour, 1978). Based on Malaysian industry code of practice on indoor air quality, acceptable ozone exposure limit is 0.05 ppm in 8 hours (Department of Occupational Safety and Health, 2010). Nonetheless, ozone is generated purposely for benefit of humankind. Safe application of ozone in enclosed environment is strongly recommended.

Table 1.1 summarizes physical characteristics of ozone gas. Firstly, ozone has strong oxidizing property. This feature is often applied in disinfection technology. Secondly, the gas is invincible at low concentration, but is pale blue at high
concentration. The pale colour is a useful feature to measure ozone concentration using visible wavelength (O’Keeffe et al., 2007; O’Keeffe et al., 2005a; O’Keeffe et al., 2005b; O’Keeffe et al., 2005c; Teranishi et al., 2013). Thirdly, ozone is unstable in nature, as it will revert to oxygen. In a sealed container, ozone half life ranges from 39 minutes to 25.4 hours, which is dependent on air flow rate, temperature and humidity (McClurkin et al., 2013). In ventilated indoor environment, ozone half life ranges between 7 minutes and 10 minutes, which is mainly dependent on outdoor air exchange and surface removal (Weschler, 2000). Ozone lifespan is long when air is still, cold and dry (McClurkin et al., 2013). Moving ozone molecules interact among themselves to dissociate to oxygen (McClurkin et al., 2013). The higher the temperature, the faster the ozone dissociation to oxygen (Yagi and Tanaka, 1978). Ozone reacts with water to form hydroxyl radical, which accelerates ozone destruction (Campbell, 1986; Chen et al., 2011; Mikoviny et al., 2007; Pekárek, 2008; Skalný et al., 2008). Ozone lifespan is greatly reduced when it is in contact with large surface area such as carpet and fleece (Weschler, 2000). Since ozone has limited lifespan, ozone cannot be transported and should be generated on site.

Table 1.1: Physical Characteristics of Ozone Gas

<table>
<thead>
<tr>
<th>Details</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Ozone (triatomic oxygen)</td>
</tr>
<tr>
<td>Atomic view (Tejerina, 2009)</td>
<td><img src="image" alt="Ozone atomic view" /></td>
</tr>
<tr>
<td>Chemical symbol</td>
<td>O₃</td>
</tr>
<tr>
<td>Description</td>
<td>Toxic and strongly oxidizing</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless at low concentration. Pale blue at high concentration.</td>
</tr>
<tr>
<td>Smell</td>
<td>Pungent</td>
</tr>
<tr>
<td>Stability</td>
<td>Unstable. Quick breakdown to oxygen.</td>
</tr>
<tr>
<td>Molecular weight, $\omega$</td>
<td>48 g mol$^{-1}$ (Department of Occupational Safety and Health, 2010)</td>
</tr>
<tr>
<td>Density, $P\omega/(RT)$</td>
<td>2141 g m$^{-3}$ at pressure 1 atm and temperature 273.15 K.</td>
</tr>
<tr>
<td></td>
<td>1962 g m$^{-3}$ at pressure 1 atm and temperature 298.15 K.</td>
</tr>
<tr>
<td>Boiling temperature</td>
<td>$-112 \degree C$ at pressure 1 atm (Department of Occupational</td>
</tr>
<tr>
<td>Safety and Health, 2010)</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td>Explosive risk</td>
<td></td>
</tr>
<tr>
<td>Concentration exceeds 10 % by volume (Koike et al., 1999)</td>
<td></td>
</tr>
</tbody>
</table>

Ozone, ultraviolet and chlorine disinfection technologies have begun since early 20th century (Sonntag and Gunten, 2012). Usually, ozone and ultraviolet light are used simultaneously to treat wastewater (Rivas et al., 2009) and pack food (Naitou and Takahara, 2008). Ozone kills 99 % surface virus at 47 to 223 min mg m$^{-3}$ doses (Tseng and Li, 2008). Ozone dose is product of ozone concentration and contact time (Tseng and Li, 2008). Similarly, UV-C rays damage genes of micro-organisms. For example, either 0.38 mg dm$^{-3}$ ozone concentration, or 270 J dm$^{-3}$ ultraviolet dose at wavelength 254 nm disinfects seawater completely (Penru et al., 2013). Unlike light travelling in straight line, ozone sanitizes hard to reach areas such as food. Exposure of 0.7 $\mu$L L$^{-1}$ of gaseous ozone for 3 minutes preserves red bell peppers better than liquid chlorine (Horvitz and Cantalejo, 2012). This is because chlorine leaves behind toxic residues such as trihalomethanes (Gottschalk et al., 2010). In short, ozone is an environmentally friendly alternative for disinfection purpose.

Ozone has been approved by Food and Drug Administration (FDA) for food contact since 2001 (Lake, 2001). Today ozone is applied to reduce bacteria, pesticide residue and microbial spoilage for long term storage of fruits and vegetables (Tiwari and Muthukumarappan, 2012). This is effective if ozone is applied at high relative humidity environment above 80 % (Tiwari and Muthukumarappan, 2012). However, appropriate gaseous ozone concentration is required for this application. This is because extreme concentration of ozone degrades sensory quality of fruits, especially aroma (Tiwari and Muthukumarappan, 2012). Exposure of tomatoes to 0.025 g m$^{-3}$ gaseous ozone for 2 hours daily for 16 days extends lifetime of tomatoes (3 of 22 damaged) compared to tomatoes without treatment (12 of 22 damaged) or treatment at 0.045 g m$^{-3}$ (6 of 22 damaged) (Venta et al., 2010). Likewise, 0.3 ppm ozone exposure for 420 minutes reduces Bacillus cereus count in processed rice by 1.63 log (Shah et al., 2011). Exposure of $8 \pm 0.2$ ml s$^{-1}$ ozone flow rate below 20 minutes enriches antioxidant contents (phenol and flavonoid) of honey pineapple and banana (pisang mas) (Alothman et al., 2010). However, vitamin C content diminishes. Pyrimethanil is
a fungicide used in vineyard (Gabriolotto et al., 2009). To remove pyrimethanil from grapes, exposure of grapes to 0.3 µL L\(^{-1}\) ozone concentration for 36 days (51.6 % removal) is more effective than air (14.5 % removal) (Karaca et al., 2012). Similar trend is observed in aqueous ozone treatment. For example, 0.075 ppm and 0.15 ppm aqueous ozone concentrations preserve strawberry for 3 weeks, but 0.25 ppm aqueous ozone concentration deteriorates strawberry (Aday et al., 2014). Not much differences are observed for ozone exposure times between 2 minutes and 5 minutes (Aday et al., 2014). In short, ozone sanitizes, preserves, improves nutrition and reduces fungicide of fruits and vegetables at appropriate concentration.

### 1.2 Review of Ozone Sensors

Ozone has played an important role for disinfection applications; thus, ozone sensor is required to monitor ozone concentration. Ozone has been measured from different perspectives. All sensors have their own advantages and drawbacks; therefore, selecting suitable type of sensor for specific application is important. Examples of sensing method include the optical absorption spectroscopy (Aoyagi et al., 2012; Degner et al., 2009; Degner et al., 2010; O’Keeffe et al., 2005a; O’Keeffe et al., 2005b; O’Keeffe et al., 2005c; O’Keeffe et al., 2007; O’Keeffe et al., 2008; Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008; Teranishi et al., 2013), cavity ringdown laser absorption spectroscopy (Washenfelder et al., 2011), Fabry–Perot interferometry (Puschell et al., 2005), interferometric photoacoustic spectroscopy (Köhring et al., 2012), metal oxide semiconductor (Aguir et al., 2002; Arshak et al., 2007; Carotta et al., 2011; Chien et al., 2010; Ghaddab et al., 2012; Martins et al., 2004; Wagner et al., 2011; Wang et al., 2011), carbon (Park et al., 2009; Sano and Ohtsuki, 2007), dye (Maruo, 2007; Maruo et al., 2009; Maruo et al., 2010; Miwa et al., 2009), decomposition heat (Nakagawa et al., 2001) and soft sensor (Zhang et al., 2010). Summary to compare the measurement techniques is attached in Appendix A.

Optical absorption spectroscopy works based on the principle that every gas absorbs light at specific wavelength. In this study, optical absorption spectroscopy is
selected to measure ozone concentration. Advantages of optical absorption spectroscopy over other measurement techniques for ozone concentration measurement are discussed as follow:

Firstly, strength of absorption based sensor is short response time. For example, response time between 0.7 s and 60 s is typically reported in absorption spectroscopy (Aoyagi et al., 2012; Degner et al., 2009; Degner et al., 2010; Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008; O’Keeffe et al., 2005a; O’Keeffe et al., 2007; Teranishi et al., 2013). Similarly, soft sensor has fast response time (0.58 s) (Zhang et al., 2010). Other sensors typically require longer time for ozone measurement. For example, carbon nanohorn sensor requires response time of 1400 s (Sano and Ohtsuki, 2007). Reported response times for metal oxide semiconductor sensors are 45 s (Chien et al., 2010), 240 s (Arshak et al., 2007), few minutes (Carotta et al., 2011) and 40 minutes (Ghaddab et al., 2012). Early work of dye sensor in glass substrate requires a week to respond to presence of ozone (Maruo, 2007). After that, response time of dye sensor in paper substrate is improved to few hours (Maruo et al., 2009; Maruo et al., 2010; Miwa et al., 2009). Thus, absorption based sensor is suitable for real time measurement.

Secondly, absorption based sensor is reliable for long lasting operation. This is because light interacts with ozone without physical contact. Metal oxide semiconductor sensor requires oxidation of sensing material by ozone (Chien et al., 2010). Dye sensor is disposable, as measurement is irreversible (Maruo, 2007; Maruo et al., 2009; Maruo et al., 2010; Miwa et al., 2009). Absorption based sensor can be used repeatedly. Deuterium lamp operates up to 1000 hours (Ocean Optics, 2009); whereas, LED operates beyond 10000 hours (Aoyagi et al., 2012). Absorption based sensor is often designed for operation in harsh environment (Degner et al., 2009; Degner et al., 2010; O’Keeffe et al., 2005a; O’Keeffe et al., 2005b; O’Keeffe et al., 2005c; O’Keeffe et al., 2007; Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008). Thus, absorption based sensor is robust because it can be used repeatedly at minimal maintenance.
Thirdly, absorption based sensor is capable to measure moderate to high ozone concentration. For example, concentration measurement from 25 g m\(^{-3}\) to 126 g m\(^{-3}\) (12821.48 ppm to 64620.25 ppm at temperature 300 K and pressure 1 atm) has been reported in visible absorption spectroscopy (O’Keeffe et al., 2005a; O’Keeffe et al., 2007). Not many sensors are able to measure such high concentrations. The closest sensor for comparison is decomposition heat sensor, which measures 0 g m\(^{-3}\) to 100 g m\(^{-3}\) (0 ppm to 51285.91 ppm at temperature 300 K and pressure 1 atm) (Nakagawa et al., 2001). Other sensors are designed for moderate to low concentration measurement. For example, concentration measurement from 0.03 g m\(^{-3}\) to 0.97 g m\(^{-3}\) (15.39 to 497.47 ppm at temperature 300 K and pressure 1 atm) has been reported in ultraviolet absorption spectroscopy (O’Keeffe et al., 2005c; O’Keeffe et al., 2007). This dynamic range is higher than metal oxide semiconductor sensors, which dynamic ranges are reported to be from 0 to 500 ppb (Arshak et al., 2007), 20 ppb to 2.4 ppm (Wagner et al., 2011) and 10 ppb to 200 ppm (Wang et al., 2011). Small ozone concentration measurement from 26 ppt to 250 ppb is reported in cavity ringdown laser absorption spectroscopy (Washenfelder et al., 2011).

Fourthly, absorption based sensor is immune to electromagnetic interference. This is an important safety feature for ozone monitoring in high voltage environment (Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008). Light is transferred through fibre optics, which does not impose fire hazard. Risk of fire is reduced when absorption based ozone sensor is used to detect spark in switchboard (Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008). Metal oxide semiconductor sensors rely on conductivity (Aguir et al., 2002; Carotta et al., 2011; Martins et al., 2004), resistivity (Chien et al., 2010) or resistance (Arshak et al., 2007; Ghaddab et al., 2012; Wang et al., 2011; Wagner et al., 2011) for ozone concentration measurement. Similarly, carbon sensors rely on resistance (Park et al., 2009; Sano and Ohtsuki, 2007) to measure ozone concentration. Interference of electrical signal may avoided if absorption based sensor is used.

Fifthly, absorption based sensor operates without the need of additional heating. Heating of sensor requires additional cost and energy. For example, sensor that measure decomposition heat of ozone works at high temperature 680 K (Nakagawa et al., 2001).
al., 2001). Early work of metal oxide semiconductor ozone sensor requires high working temperature from 470 K to 720 K (Aguir et al., 2002). Similarly, carbon nanotube sensors require annealing in furnace at 300 °C (Ghaddab et al., 2012) or 350 °C (Park et al., 2009). Thus, absorption based sensor is favourable for ozone concentration measurement because it can be operated at ambient temperature.

Disadvantage of absorption based ozone sensor is requirement of large amount of start up capital for purchase of optical instruments. Optical components that work in ultraviolet region are more expensive than visible region. For example, polymethyl methacrylate (PMMA) plastic optical fibre for visible light transmission is more cost effective than solarization resistant fibre for ultraviolet light transmission (O’Keeffe et al., 2007). The benefit of choosing ultraviolet wavelength over visible wavelength for ozone concentration measurement is the ability to differentiate small amount of concentration. Resolution of ultraviolet absorption based sensor at 0.05 g m\(^{-3}\) (O’Keeffe et al., 2005c; O’Keeffe et al., 2007) is higher than visible absorption based sensor at 5 g m\(^{-3}\) (O’Keeffe et al., 2005b) and 10 g m\(^{-3}\) (O’Keeffe et al., 2005c). Optical instrument purchase may be regarded as worthwhile investment for new research opportunities.

Based on the review, absorption based ozone sensor is found to be fast, reliable, safe to use and able to work at ambient temperature. Although absorption based ozone sensor may require high start up cost, it is a worthwhile investment for high ozone concentration measurement.

1.3 Problem Formulation

From 2005 to 2012, researchers have adopted two methods to measure ozone concentration via ultraviolet absorption spectroscopy. Typically, researchers measure ozone concentration by non ratiometric method (O’Keeffe et al., 2008; Degner et al., 2009; Degner et al., 2010; Aoyagi et al., 2012). In this method, researchers compare intensities of absorbing wavelength that passes through ozone and does not pass
through ozone. Absorption cross section may be calculated using existing Beer–Lambert law when transmittance value is known. However, broadband light source typically experiences drift in output power of less than 0.01 % per hour (Ocean Optics, 2009). The drift in intensity affects stability of measurement. Alternatively, ratiometric method has been gaining popularity for ozone concentration measurement (O’Keeffe et al., 2005a; O’Keeffe et al., 2005b; O’Keeffe et al. 2005c; O’Keeffe et al., 2007; Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008). In this method, researchers measure ozone concentration by comparing intensities of absorbing wavelength and non absorbing wavelength that pass through ozone. Ratiometric method helps to improve stability of measurement (O’Keeffe et al., 2007), minimize system disturbances (O’Keeffe et al., 2005b; O’Keeffe et al., 2007), reduce particulate interference (O’Keeffe et al., 2005a; O’Keeffe et al. 2005c), correct reference intensity drift (Maria et al., 2008) and achieve linearity (Maria and Bartalesi, 2012). However, absorption cross section may not be calculated using existing Beer–Lambert law via ratiometric method, as transmittance value is not known. This is the reason absorption cross section is not explicitly reported in previous experiment via ratiometric method calculation (O’Keeffe et al., 2005a; O’Keeffe et al., 2005b; O’Keeffe et al. 2005c; O’Keeffe et al., 2007; Maria and Bartalesi, 2012; Maria and Rizzi, 2009; Maria et al., 2008). Based on literature review, measuring absorption cross section based on ratiometric method calculation may be considered as a novel technique. This is because a novel equation is to be established based on existing Beer–Lambert law for ratiometric method to calculate absorption cross section. The equation contributes to existing knowledge and benefits future researchers.

1.4 Motivation of Research

Measurement of ozone absorption cross section has attracted attention of researchers because the parameter is important for calculation of ozone concentration. Ultraviolet and visible absorption cross sections serve as vital reference for measuring atmospheric ozone gas via remote sensing (Orphal and Chance, 2003). Although ozone absorption cross section may be simulated online from spectralcalc.com based on HITRAN 2008 database, the simulation results are correct for ideal case at specific
temperature and pressure only. Actual experimental condition may not be similar to simulation or previous experimental conditions; thus, determination of absorption cross section parameter for each experiment ensures high accuracy calculation of ozone concentration. Increasing trend of adopting ratiometric method calculation for ozone concentration calculation has accelerated the need to determine absorption cross section through this method. Proper selection of sampling wavelength and optical path length help to preserve linearity of ozone concentration measurement. Verification of temperature and pressure dependence on ozone absorption cross section is important to ensure these parameters have minimal effect to ozone absorption cross section measurement.

1.5 Objectives of Research

Based on formulation of problem and motivation of research, the objectives of this research are stated as follow:

1. To optimize range of ozone concentration measurement for specific optical path length of gas cell.

2. To illustrate deviation of Beer–Lambert law and propose a solution to maintain linearity of measurement.

3. To determine temperature and pressure stability of ozone absorption cross section.

4. To determine maximum ozone absorption cross section through ratiometric method at specific temperature and pressure.
1.6 **Scope of Research**

To achieve the objectives of this study, scope of research is divided into several categories as follow: theoretical study, preliminary simulation and experiment.

Theoretical study:

1. Mathematical relationships relevant to the study are derived and verified with literature. For example, a novel equation is established based on Beer–Lambert law for ozone absorption cross section measurement through ratiometric method. Relevant equations and relationship of conversion among units of concentration are derived in Appendix B. The concentration units are arranged to show variations of Beer–Lambert law and relations among important parameters. Mathematical relations established in this work are useful for future researchers to calculate desired parameters.

Simulations and experiments:

2. Simulate maximum absorption wavelength, maximum absorption cross section and practical dynamic range of ozone concentration measurement at optical path length 5 cm, 10 cm and 20 cm using spectralcalc.com gas cell simulator. This is to select optical path length of gas cell that suits ozone concentration measurement range of equipments in this work.

3. Perform experiment to determine linearity of Beer–Lambert law using gas cell of 10 cm optical path length. This is to illustrate deviation of Beer–Lambert law and propose a solution to prevent sensor saturation.

4. Simulate maximum absorption wavelength and maximum absorption cross section at temperature from 200 K to 300 K via spectralcalc.com line list browser. This is to verify temperature stability of wavelength used to measure ozone concentration.
5. Simulate maximum absorption wavelength and maximum absorption cross section at pressure from 0.1 atm to 3 atm via spectralcalc.com gas cell simulator. This is to verify pressure stability of wavelength used to measure ozone concentration.

6. Perform experiment to determine maximum absorption cross section via ratiometric method calculation. This is to improve stability of measurement, as ratiometric method corrects intensity drift of light source.

Further details are illustrated in Figure 1.1.

![Figure 1.1](image)

**Figure 1.1** Scope of research of this study

### 1.7 Overview of Thesis

Ratiometric method has been used to improve stability of measurement of ozone concentration in ultraviolet absorption spectroscopy. The method compensates
intensity drift of light source. However, ozone absorption cross section may not be determined via ratiometric method based on existing Beer–Lambert law. Absorption cross section defines strength of absorption, which is important for calculation of ozone concentration in ultraviolet absorption spectroscopy. Thus, this thesis proposes a novel technique to determine maximum ozone absorption cross section via ratiometric method. To achieve the objectives of this study, theoretical study, three simulations and two experiments have been conducted. These activities are organized into six chapters in this thesis as described below:

In chapter 1, ozone is introduced by discussing its physical properties and applications to highlight the need to measure ozone concentration. After that, ozone sensors are reviewed. Ultraviolet absorption spectroscopy is selected for ozone concentration measurement because the method is fast, reliable, safe to use, and able to measure high concentration at ambient temperature. Chapter 1 describes the need to conduct this study and highlights the approach that will be used for new knowledge creation.

Next, in chapter 2, theoretical background of absorption based ozone sensor is discussed. For example, equations are derived based on Beer–Lambert law for ozone concentration measurement in ppm by volume. In addition, Beer–Lambert law is modified so that a new equation may be applied for measurement of absorption cross section via ratiometric method. Conditions for Beer–Lambert law deviation is thoroughly discussed and supported by Twyman–Lothian equation. Hence, guidelines for adherence of Beer–Lambert law are discussed. In addition, characteristics of ozone absorption cross section are reviewed at different wavelengths and temperature. This is to justify the reason a particular wavelength is chosen for ozone concentration measurement. Performance specifications of absorption based ozone sensor are reviewed to obtain general relation among optical path length, dynamic range and response time. Chapter 2 describes fundamental measurement principles that are applicable at later part of this study.

Subsequently, in chapter 3, instrumentation for absorption based ozone sensor is reviewed. The review is important to decide equipments to be purchased and used in
this work. The review is categorized into optical components, gas components, and gas cell construction. Based on the review, gas cell is fabricated using ozone compatible materials. Details of fabrication will be discussed.

After that, in chapter 4, gas cell optical path length is optimized for high concentration measurement below 1000 ppm. This is because concentration up to 1000 ppm can be verified using 2B Technologies ozone monitor 106-M in this work. Spectralcalc.com gas cell simulator is used to relate optical path length and ozone concentration based on the assumption that transmittance lies between 0.25 and 0.5. The assumption is to avoid deviation of Beer–Lambert law as discussed in chapter 2. Next, experiment is conducted to illustrate limitation of long gas cell of 10 cm optical path length for high concentration below 1000 ppm. Extent of Beer–Lambert law deviation is characterized. After that, a solution is proposed to maintain linearity of measurement. As a result, short gas cell of 5 cm optical path length is applied in the next chapter for high concentration measurement below 1000 ppm.

Next, chapter 5 contains two simulations and one experiment to characterize ozone absorption cross section. Spectralcalc.com simulations are applied to verify temperature and pressure dependence on maximum ozone absorption cross section. After that, experiment is conducted to verify equation derived in chapter 2 to determine maximum ozone absorption cross section via ratiometric method. Significance of ratiometric method to compensate light source intensity drift is illustrated.

Finally, chapter 6 contains conclusions of study. Contributions of the study is discussed. Since research is a continuous effort, future work is suggested. Interested readers may refer to appendices for summary of ozone sensing techniques, conversion relations among concentration units and list of publications of this work.
REFERENCES


