# Practical Range of Ozone Concentration Simulation for Transmissive Gas Cells

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***Abstract***

Gas cells of different length have been previously designed for measurement of ozone through ultraviolet absorption spectroscopy, but each gas cell is used for measurement of single range of concentration only. In current work, practical ranges of ozone concentration measurement for transmissive gas cells between 0.05 m and 0.50 m are theoretically calculated and verified via SpectralCalc.com gas cell simulator. Selections of optical path length and concentration range to be considered practical are justified. Gas cell of optical path length 0.05 m is found to be practical for measurement between 3.57 ppm and 471.61 ppm. Decrease of range of concentration measurement is observed when optical path length is increased from 0.05 m to 0.25 m. However, further increase of optical path length beyond 0.25 m has small effect on reduction of dynamic range of concentration.

***Keywords:*** Concentration, Transmissive Gas Cell, Optical Path Length, Ozone, Range, Simulation, Ultraviolet Absorption Spectroscopy

## Introduction

Ozone is a colourless oxidizing gas, but has a pungent smell. In nature, ozone exists at stratosphere to absorb harmful ultraviolet radiation from reaching the earth. In practice, ozone is generated on site at different concentration for specific application. For example, 0.025 g $m^{-3}$ to 0.045 g $m^{-3}$ of ozone is applied for preservation of tomatoes (Venta M. B. *et al*., 2010); whereas, 10 g $m^{-3}$ to 50 g $m^{-3}$ of ozone (Rivas J. *et al*., 2009) is used for wastewater recycling. The concentration difference between these two applications is more than 400 times. Therefore, there is a need to design an ozone sensor for specific range of concentration measurement.

Gas cells of length between 5 cm and 63 cm have been designed for ozone concentration measurement through absorption spectroscopy (Aoyagi Y. *et al*., 2012; Degner M. *et al*., 2009, 2010; Maria L. D. *et al.*, 2008; Maria L. D. and Bartalesi D., 2012); O'Keeffe S. *et al*., 2005a, 2005b, 2007, 2008; Teranishi K. *et al.*, 2013). Some of the previous work utilize transmissive type gas cell (Aoyagi Y. *et al*., 2012; O'Keeffe S. *et al*. 2005a, 2005b, 2007; Teranishi K. *et al*., 2013). Gas cell has specific optical path length for specific range of measurement of ozone concentration only. Therefore, objective of current work is to determine practical range of ozone concentration that is measurable using transmissive gas cells between 5 cm and 50 cm. Current work is useful for researchers or ozone analyzer manufacturers to design transmissive gas cell for specific range of ozone concentration measurement.

## Theoretical Analysis

### *Transmissive Gas Cell*

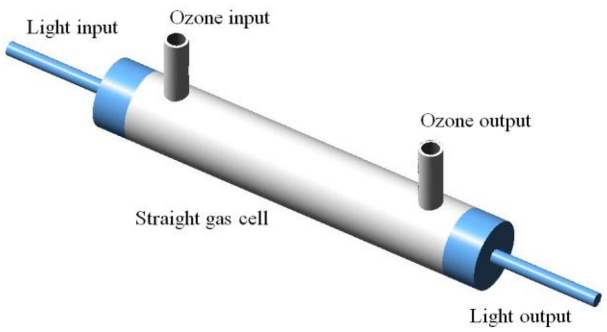


*Figure 1. Transmissive gas cell modelled using Zemax Part Designer. Light from optical fiber interacts with ozone sample in a straight gas cell.*

Figure 1 shows transmissive gas cell in current work. It consists of a cylindrical gas cell that contains sample ozone gas. Intensity of light decays exponentially as it passes through sample gas for specific length. This may be theoretically explained through Beer–Lambert law.

### *Beer–Lambert Law*

In ultraviolet absorption spectroscopy, ozone concentration may be obtained based on well-established Beer–Lambert law as shown in Equation 1. Interested readers may refer to the literature (Campbell I. M., 1986; Clark B. J. et al., 1993; Hughes H. K., 1963) for more information of this law. Equation 1 shows ozone concentration is dependent on optical path length and transmittance of light through gas cell.

$$c_{(\mathrm{ppm})} = -1000000RT/(\sigma N_A P l_s)\times\ln(I_t/I_0) \qquad (1)$$
$$T_r = I_t/I_0 \qquad (2)$$

$c_{(\mathrm{ppm})}$ = ozone concentration in ppm by volume
$I_0$ = input intensity to ozone sample in count
$I_t$ = output intensity from ozone sample in count
$l_s$ = optical path length in m
$N_A$ = Avogadro's constant, $6.02214199\times10^{23}$ molecule $mol^{-1}$

$P$ = pressure in atm
$R$ = ideal gas constant, $8.205746\times10^{-5}$ atm $m^3$ $mol^{-1}$ $K^{-1}$
$T$ = absolute temperature in K
$T_r$ = transmittance
$\sigma$ = absorption cross section in $m^2$ $molecule^{-1}$

*Practical Range of Ozone Concentration Selection*

Transmittance, $I_t/I_0$ from 0.516 to 0.995 is previously achieved (O'Keeffe S. *et al*., 2007). This is calculated based on information in the paper. At maximum detection limit 0.97 mg/l, $I_0$ = 370 count, $I_t$ = 191 count; therefore, $I_t/I_0$ = 0.516. At minimum detection limit 0.03 mg/l, $I_0$ = 370 count, $I_t$ = 368 count; therefore, $I_t/I_0$ = 0.995. Hence, transmittance, $I_t/I_0$ between 0.516 and 0.995 is assumed to be practical to achieve and used in current work for calculation of ozone concentration.

*Practical Optical Path Length Selection*

Optical path length between 5 cm and 50 cm are selected for current work analysis, because gas cells within 50 cm are shown to have fast response time of a few seconds (Aoyagi Y. *et al*., 2012; Degner M. *et al*., 2009, 2010; O'Keeffe S. *et al*., 2005b, 2007; Maria L. D. *et al*., 2008; Teranishi K. *et al*., 2013). Reflective gas cell of 63 cm is shown to respond slowly at 60 s (Maria L. D. and Bartalesi D., 2012). Ultraviolet absorption spectroscopy is considered to have low absorption sensitivity compared to cavity enhanced absorption spectroscopy (Gomez A. L. and Rosen E. P., 2013), especially for very short gas cell of less than 5 cm. Short optical path length results in small light intensity decrease when light passes through sample. Therefore, transmissive gas cells between 5 cm and 50 cm are considered to be practical for analysis in current work.

## Methodology

*Theoretical Calculation*

Firstly, calculation of ozone concentration up to two decimal places are done through Beer–Lambert law in Equation 1 based on following input parameters:

$\sigma = 1.147\times10^{-21}$ at peak absorption wavelength 253.65 nm (Hearn A. G., 1961)
$N_A = 6.02214199\times10^{23}$ molecule $mol^{-1}$
$P$ = 1 atm
$R = 8.205746\times10^{-5}$ atm $m^3$ $mol^{-1}$ $K^{-1}$
$T$ = 300 K
$l_s$ = 0.05 m, 0.10 m, 0.15 m... 0.50 m
$I_t/I_0$ = 0.516, 0.995

*SpectralCalc.com Simulation*

Secondly, simulation is done using gas cell simulator of SpectralCalc.com to verify calculation result. Following parameters are input to the simulator to obtain output transmittance at peak absorption wavelength 255.442 nm.

$N_A = 6.02214199\times10^{23}$ molecule $mol^{-1}$

$P$ = 1013.25 mbar
$R$ = 8.205746×$10^{-5}$ atm $m^3$ $mol^{-1}$ $K^{-1}$
$T$ = 300 K
$l_s$ = 0.05 m, 0.10 m, 0.15 m... 0.50 m
$c_{(ppm)}$ = as calculated in two decimal places
Waveband = 0.24 µm to 0.27 µm
Line list = HITRAN2008
Gas = $O_3$

## RESULTS AND DISCUSSIONS

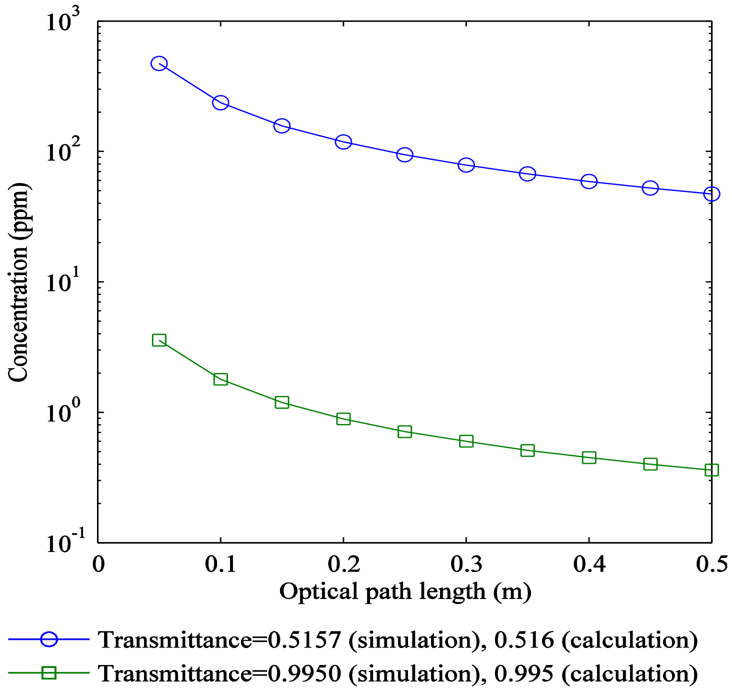


*Figure 2. Practical range of ozone concentration measurement for optical path length between 0.05 m and 0.50 m based on theoretical calculation and SpectralCalc.com simulation*

Figure 2 shows practical range of ozone concentration measurement for optical path length between 0.05 m and 0.50 m. Results obtained are in close agreement between theoretical calculation (transmittance from 0.516 to 0.995) and SpectralCalc.com simulation (transmittance from 0.5157 to 0.9950). Four observations may be made in Figure 2.

Firstly, practical values from Figure 2 may be extracted for concentration range interpretation in Table 1. Table 1 is useful for prediction of ozone concentration measurement for gas cell of specific optical path length. For example, optical path length of 0.05 m is practical for concentration measurement from 3.57 ppm to 471.61 ppm.

*TABLE 1. PRACTICAL CONCENTRATION RANGE FOR TRANSMMISIVE GAS CELLS OF OPTICAL PATH LENGTH BETWEEN 0.05 M TO 0.50 M*

| Optical path length (m) | Dynamic range of concentration (ppm)[a, b] |
|---|---|
| 0.05 | 3.57 to 471.61 |
| 0.10 | 1.79 to 235.80 |
| 0.15 | 1.19 to 157.20 |
| 0.20 | 0.89 to 117.90 |
| 0.25 | 0.71 to 94.32 |
| 0.30 | 0.60 to 78.60 |
| 0.35 | 0.51 to 67.37 |
| 0.40 | 0.45 to 58.95 |
| 0.45 | 0.40 to 52.40 |
| 0.50 | 0.36 to 47.16 |

a. Based on theoretical calculation using transmittance from 0.516 to 0.995
b. Based on SpectralCalc.com simulation to obtain transmittance from 0.5157 to 0.9950

Secondly, constant gap space exists between two lines in Figure 2. Existence of gap between the lines may be theoretically explained by division of two sets of Equation 1. All parameters are kept constant except transmittance, $I_t/I_0$. In theory, concentration at transmittance 0.5157 is more than concentration at transmittance 0.9950 by a factor of ln(0.5157)/ln(0.9950) or 132.1. Based on simulation result at optical path length 0.05 m, concentration at transmittance 0.5157 (471.61 ppm) is more than concentration at transmittance 0.9950 (3.57 ppm) by a factor of 132.1.

Thirdly, shift of concentration measurement is observed when optical path length is changed. The higher the optical path length, the lower the range of ozone concentration measurement as shown in Table 1. This will be further elaborated below.

Fourthly, the shift of concentration is evident from optical path length 0.05 m to 0.25 m only. For example, dynamic range of concentration at 0.05 m optical path length (3.57 ppm to 471.61 ppm) is very much more than dynamic range of concentration at 0.25 m optical path length (0.71 ppm to 94.32 ppm). Further increase of optical path length beyond 0.25 m results in small decrease in concentration measurement. For example, dynamic range of concentration at 0.25 m optical path length (0.71 ppm to 94.32 ppm) is slightly more than dynamic range of concentration at 0.05 m optical path length (0.36 ppm to 47.16 ppm).

Finally, trend of concentration shift observed in current work is consistent with previous work. For example, 4 cm gas cell may measure up to 100 ppm of ozone; whereas, 40 cm gas cell may measure up to 10 ppm of ozone (Degner M. *et al*., 2009, 2010). This shows comparison with previous work are in close agreement. In short, optical path length is shown to affect range of ozone concentration measurement, especially optical path length between 0.05 m and 0.25 m.

## Conclusion and Recommendation

In conclusion, practical ranges of ozone concentration measurement have been theoretically calculated and verified via SpectralCalc.com gas cell simulator. Simulation result shows shift of range of concentration measurement when optical path length is varied. The higher the optical path length, the lower the dynamic range of concentration. Transmissive gas cell of optical path length 0.05 m is strongly recommended for measurement of ozone concentration from 3.57 ppm to 471.61 ppm. To reduce range of ozone concentration measurement, optical path length should be increased up to 0.25 m for measurement between 0.71 ppm and 94.32 ppm. Further increase of optical path length beyond 0.25 m is found to have small effect on reduction of range of concentration measurement.

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