Sampling frequency effect on the absorption cross section of ozone in the Visible Spectrum

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Effect of sampling frequency on variation of absorption cross section for ozone gas measurement is reported. Signal smoothing on ozone gas absorption cross section in the visible spectrum is investigated theoretically and experimentally. Aluminium gas cell of length 0.5 m is used for ozone detection at scan to average between 1 and 100 using Ocean View software. Percentage variations between 0.17% and 11.93% are recorded in comparison with theoretical absorption cross section for ozone detection at wavelength 603 nm.

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1. Introduction

Noise in signals is a form of contamination which limits accuracy and further complicates data interpretation and decision making process [1-3] . In ozone gas measurements based on absorption spectroscopic method, tools for data acquisition and data analysis technique have been applied as shown in previous work [4-10]; however, there has been little emphasis on the analysis of moving average points on detected signals. Generally, moving average as a smoothing technique introduces lag [11], such as delay in both rise and fall times of sensor. Consequently, sensor's speed of response is negatively affected. Ocean View software version 1.3.4, has minimum of 1 point scan to average. It can also be as high as thousands of points scan to average. Signals acquired at 10 and 100 points scan to average at integration time of 100 milliseconds (ms) will have corresponding sampling frequencies (f_s) 1 and 0.1 Hz respectively according to equations 1 and 2.

In this work transmittance values were obtained using spectrometer while concentration measurements were obtained with 2B Technologies 106-M model ozone monitor. The monitor has default minimum sampling time of 10 seconds (s). The aim of this paper is to investigate effect of transmittance at different scan points to average on absorption cross section of ozone gas in the visible spectrum. Both concentration and transmittance values are primarily used for absorption cross section computations.

$$t_s = t_i \times S \quad (1)$$

$$f_s = \frac{1}{t_s} \quad (2)$$

t_s = sampling time
t_i = integration time
S = scan to average
f_s = sampling frequency

2. Ozone measurements using absorption spectroscopy

Requirement for accurate and fast ozone gas measurement cannot be compromised in the light of potential health risk and harmful tendency associated with undue exposure to ozone gas. There is also rise in both utilization and application of ozone [12-16]. Ozone measurements using absorption spectroscopy has often been in UV spectrum (200 - 300 nm) because of inherent advantages of strong absorption, feasibility and high sensitivity [17, 18]. Absorption of ozone in the visible spectrum (450 - 850 nm) [19] with a peak wavelength at 603 nm exists. This has not been fully explored [4, 18]. In this paper, we experimentally investigate effect of sampling frequency on ozone absorption cross section in the visible spectrum.

The measurement of ozone gas using absorption spectroscopy is regulated by the Beer-Lambert law. Relation among transmittance T of monochromatic light, path length of light l (m), gas sample concentration c (mole m^{-3}) and molar absorption coefficient ε (m^2 $mole^{-1}$) can be expressed mathematically as follows:

$$\varepsilon cl = -\ln T = -\ln \frac{I_t}{I_0} \quad (3)$$

From equation 3, concentration c is computed as:

$$c = -\frac{1}{\varepsilon l} \times \ln \frac{I_t}{I_0} \quad (4)$$

In our recent publication [20], concentration in parts per million (ppm) by volume has been expressed as:

$$c_{(ppm)} = -\frac{10^6 \times R \times T_p}{\sigma \times N_A \times P \times l} \times \ln \frac{I_t}{I_0} \quad (5)$$

Where:
R = Ideal gas constant
$= 8.205746 \times 10^{-5}$ (atm m^3 mol^{-1} K^{-1})
T_p = temperature (K)
σ = Absorption cross section
$= 5.18 \times 10^{-25}$ m^2molecules^{-1}
N_A = Avogadro's constant
$= 6.02214199 \times 10^{23}$ (molecule mol^{-1})
P = pressure in atmosphere (atm)
l = optical path length (m)
I_t = light intensity with sample (count)
I_0 = light intensity without sample (count)

Thus, I_0 and I_t are experimentally determined to measure concentration c.

3. Experimental set-up and procedure

Fig. 1 shows experimental set-up for measurement of ozone gas at wavelength of 603 nm. Items are as described according to the numbering in Fig.1.

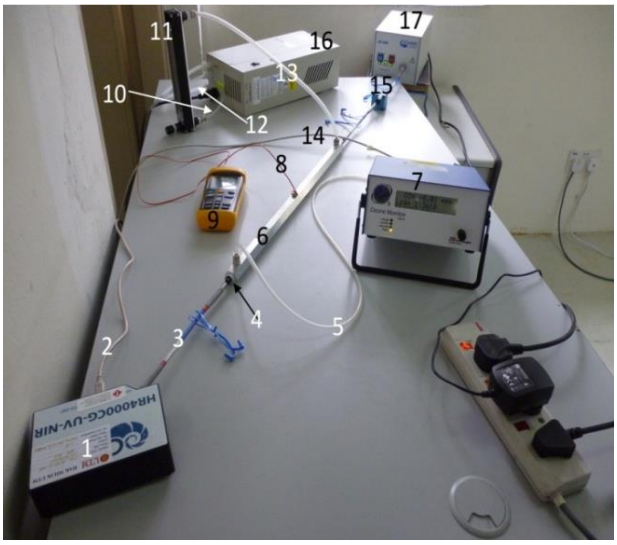

Fig. 1: Experimental set-up

(1) Ocean Optics HR4000CG-UV-NIR Spectrometer. (2) Spectrometer connection to a computer. (3) Ocean Optics solarisation resistant optical glass fibre with mono coil jacketing. It is 0.25 m in length and 400 µm in diameter. (4) 74-UV, 74 Vis collimating lens. The lens is 5 mm diameter and 10 mm focal length. (5) Silicone tube for the connecting ozone flow from gas cell to ozone monitor. (6) Aluminium gas cell of 0.5 m length. (7) 2B Technologies 106-M model ozone monitor which can measure ozone concentration between 0 and 1000 ppm. (8) Probe for digital thermometer. (9) 54 II B digital thermometer made by Fluke Corporation Everett, WA. (10) Silicone tube for connecting ozone flow from generator to flow meter. (11) Zero to ten litres per minute (LPM) ozone compatible flow meter by Ozone Solutions United States. (12) Vinyl tube for connecting flow of oxygen from oxygen tank to ozone generator. (13) Silicone tube for connecting ozone flow from flow meter to gas cell. (14) USB cable connecting ozone monitor to computer. (15) Attenuator for controlling intensity of light from going into saturation. (16) EXT50 Ozone generator made in United States by Longevity Resources Inc and (17) DH 2000 Ocean Optics light source, wavelength 200 nm to 1100 nm.

Oxygen gas of 99.999% purity was transported through a vinyl tubing to EXT50 Ozone generator. Ozone is generated for approximately two minutes for each scan to average values selected:1, 10, 20 ,30, 40 50, 60 , 70 , 80, 90 and 100 at integration time of 100 ms. Corresponding sampling frequencies in Hz are: 10, 1, 0.5 0.33, 0.25, 0.200, 0.17, 0.14, 0.125, 0.11 and 0.1 respectively. Ozone gas from the generator was regulated and fed to 0.5 m gas cell. Ozone from gas cell outlet is fed to ozone monitor. Gas cell temperature is monitored using digital thermometer. Values of transmittance (i.e. I_t / I_0) were obtained directly from spectrometer via laptop and Ocean View software. Value of concentration c (ppm), is obtained using ozone monitor. The monitor has minimum default frequency of 0.1Hz or sampling time of 10 s.

4. Results and discussions

Results presented are outcomes of several repeated experimentations. Fig. 2 (a - d) shows the effect of different values of sampling on ozone concentration output waveform. Ozone concentrations obtained were within 965.00 ppm to 991.8 ppm for 2 LPM ozone flow rate and 898.80 ppm to 915.00 ppm for ozone flow rate 2.75 LPM and at a pressure of 0.97 atm. The variation is due to fluctuations in oxygen flow. Flow meter design is analogue.

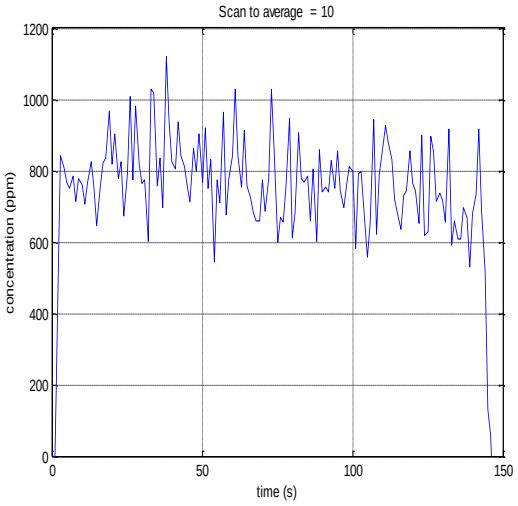

Fig. 2a:Ozone output at 10 points scan to average

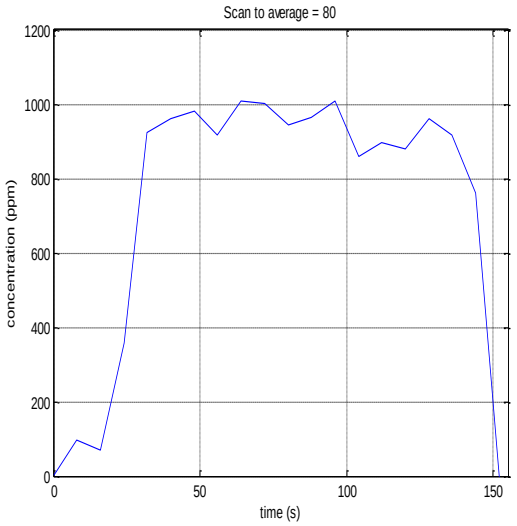

Fig. 2c:Ozone output at 80 points scan to average

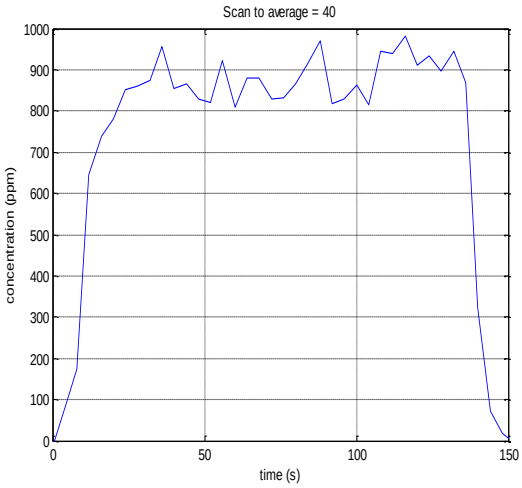

Fig. 2b:Ozone output at 40 points scan to average

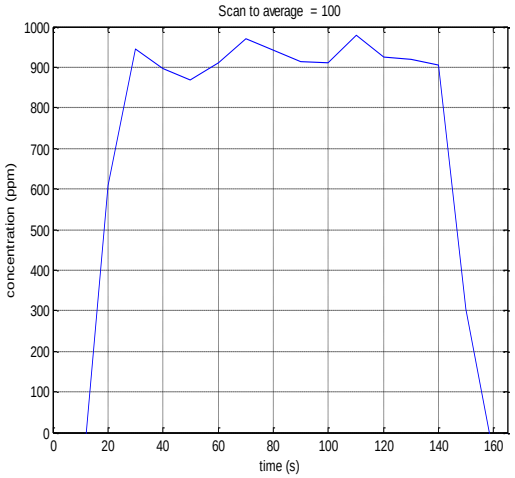

Fig. 2d:Ozone output at 100 points scan to average

From the ozone concentration output waveforms, it can be seen that the higher the scan to average value the smoother the ozone concentration output waveform. A Similar effect is also seen in Fig. 3, the effect of different sampling frequency values on the transmittance T of the light in gas cell. The range of transmittance for 2 and 2.75 LPM ozone flow rate are 0.99354 to 0.99460 and 0.99416 to 0.99485 respectively at wavelength of 603 nm. Transmittance output waveform, increasingly becomes smoother with increase in the value of sampling frequency.

Ozone absorption in the visible spectrum is between 550 nm and 650 nm. It has a peak at wavelength of 603 nm with absorption cross section of 5.18×10^{-25} m^2 $molecule^{-1}$ [4].

Absorption cross section at each scan to average was calculated using equation 6. Concentration values in ppm were obtained directly from ozone monitor while the transmittance values was obtained from spectrometer readings.

$$\sigma_{(603\ nm)} = -\frac{10^6 \times R \times Temp}{c_{(ppm)} \times N_A \times P \times l} \times \ln \frac{I_t}{I_0} \qquad (6)$$

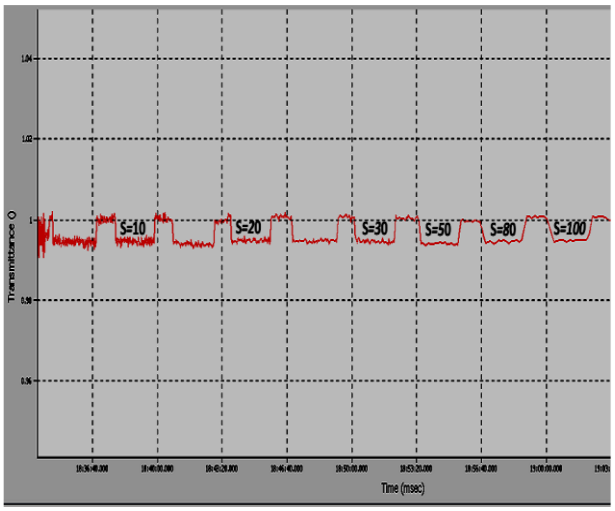

Fig. 3: Light transmittance T at different scan to average (Where S = Number of scan to average)

The experiment ran for an average of 2 minutes for each scan to average. Nine to ten readings where the ozone concentration were relatively stable were used for the computations of the absorption cross section. Deviations from 5.18×10^{-25} m^2 $molecule^{-1}$ [4] were computed with equations 7.

$$\frac{\sigma - \sigma_w}{\sigma_w} \times 100\% \qquad (7)$$

Where:

$\sigma = 5.18 \times 10^{-25}\ m^2\ molecules^{-1}$

σ_w = absorption cross section obtained in this work

Fig.4 shows deviation at each scan to average between 1 and 100 for ozone flow rate 2.75 LPM. Deviation in magnitude is between 0.19% and 7.30%. In between 1 and 10 points scan to average, the difference in deviation is 0.42%. Corresponding temperature and concentration differences are 1.40 K and 6.10 ppm respectively. For other points scan to average, the corresponding differences in deviation of absorption cross section, temperature and concentration are summarized in Table 1.

A common trend observed at sampling points where temperature is same such as scan to average of 10 (904.60 ppm, 303.90K, 5.42%) compared with 50 (906.30 ppm, 303.90K, 5.61%) and 20 (915.00 ppm, 303.80 K, 7.30%) compared with 30 (913.44 ppm, 303.80 K, 5.69%).

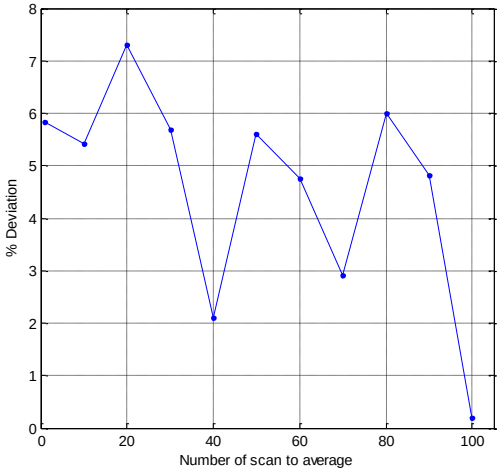

Fig 4: Comparison of deviation in absorption cross section at 2.75 LPM

Table 1: Difference in deviation, concentration and temperature at 2.75LPM

Sampling points intervals	Difference in deviations (%)	Difference in temperature (K)	Difference in concentration (ppm)
1and 10	0.42	1.40	6.10
10 and 20	1.88	0.10	10.40
20 and 30	1.61	0.00	1.56
30 and 40	3.58	0.60	11.04
40 and 50	3.51	0.70	3.90
50 and 60	0.86	0.40	5.50
60 and 70	1.83	0.30	5.10
70 and 80	3.07	0.10	0.50
80 and 90	1.17	0.20	7.60
90 and 100	4.62	0.10	1.00

Sampling points with lower concentration (i.e. lower absorption or higher transmission) has the lowest deviation of absorption cross section. In general, there was convergence towards 0% deviation from 1 to 100 scan to average.

Fig. 5 shows deviation between 1 and 100 scan to average for ozone flow rate 2 LPM. The deviation in magnitude is between 0.17% and 11.93%. In between 1 and 10 points scan to average, the difference in deviation is 5.37%. Corresponding temperature and concentration differences are 0.30 K and 7.60 ppm.

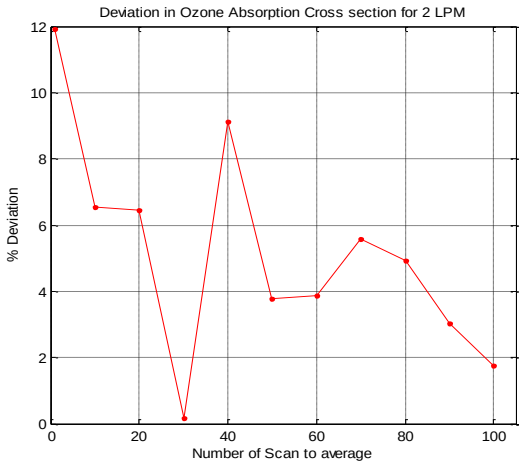

Fig 5: Comparison of deviation in absorption cross section at 2 LPM

Similarly, for other points scan to average, the corresponding differences in deviation of absorption cross section, temperature and concentration are summarized in Table 2. Similar trend was observed at sampling points where temperature is the same such as scan to average 80 (990.80 ppm, 297.40 K, 4.94%) compared with 100 (965.00 ppm, 297.40 K, 1.77%). Sampling point with lower concentration (i.e. lower absorption or higher transmission) has the lowest deviation. There was similar convergence towards 0% deviation from 1 to 100 scan to average.

Absorption cross section obtained is affected by temperature [21, 22] as well as by sampling frequency. At electronic ground state, vibrational and rotational distribution states change with temperature [23]. Sampling frequency effect is more pronounced at high transmittance values.

Published ozone absorption cross sections for the visible spectrum in literature are in the range of 4.71×10^{-25} to 5.43×10^{-25} m^2 $molecule^{-1}$ [18]. Deviation of these from 5.18×10^{-25} m^2 $molecule^{-1}$ (ozone absorption cross section determined by Vigroux [4, 24] which is considered as most accurate) is between 4.60 - 9.98% in magnitude.

Deviations obtained in this work between scan to average 10 and 100 are within range of accepted published work for both ozone flow of 2 and 2.75 LPM and that at S=1 for ozone flow rate 2.75 LPM is acceptable. However, deviations of 11.95% obtained at S=1 for ozone flow rate 2 LPM is unacceptable. It was further discovered that transmittance values much higher or lower than 0.99354 to 0.99460 and 0.99416 to 0.99485 for 2 LPM and 2.75 LPM ozone flow rate considered in this study give rise to deviations much higher than 9.98%.

Table 2: Difference in deviation, concentration and temperature at 2 LPM

Sampling point Intervals	Differences in deviation (%)	Difference in temperature (K)	Difference in concentration (ppm)
1and 10	5.37	0.30	7.60
10 and 20	0.09	0.30	7.30
20 and 30	6.30	0.10	6.90
30 and 40	8.96	0.50	5.50
40 and 50	5.34	0.20	4.90
50 and 60	0.08	0.10	2.30
60 and 70	1.71	0.10	16.80
70 and 80	0.63	0.40	21.90
80 and 90	1.90	0.30	0.70
90 and 100	1.27	0.30	25.10

5. Conclusion

Sampling frequency or number of points scan to average determines the extent to which noise are eliminated from signals and enhances signal smoothing. The results presented are obtained after repeated experimentations. Deviation from ozone absorption cross section of 5.18×10^{-25} m^2 $molecule^{-1}$ at wavelength 603nm was calculated to be between 0.17% and 11.93% for 1 to 0.1 Hz sampling frequencies at 2 LPM ozone flow rate. Similarly, deviation of 0.19% to 7.30% was observed for 1 to 0.1 Hz sampling frequencies for 2.75 LPM ozone flow rate. There was convergence towards 0% deviation from 1 to 100 scan to average. Sampling points where temperature is same for two or more points, sampling point with lower concentration (i.e. lower absorption or higher transmission) has the lowest deviation from absorption cross section. Transmittance values much higher or lower than the range (0.99354 to 0.99460 and 0.99416 to 0.99485 for 2 and 2.75 LPM ozone flow respectively) give rise to deviations much higher than 9.98%. Hence, it can be concluded that there is deviation in ozone absorption cross section due to sampling frequency effect. Deviations obtained in this study are within acceptable range of deviations obtained in previous work, except deviations 11.93% obtained at sampling frequency 1 Hz for ozone flow rate 2 LPM.

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