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Transmittance optimization for high sensitivity ozone concentration measurement

Tay Ching En Marcus*, Mohd Haniff Ibrahim, Nor Hafizah Ngajikin, Asrul Izam Azmi

Department of Communication Engineering, Faculty of Electrical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

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ABSTRACT

In ultraviolet absorption spectroscopy, sensitivity of ozone concentration measurement is low when transmittance is too high or too low. This is because transmittance of light influences sensitivity of measurement. Here, we derive a new equation based on Beer–Lambert law to determine sensitivity of sensor. The proposed equation is applied to optimize transmittance for high sensitivity ozone concentration measurement. The proposed equation is validated by comparison to Twyman–Lothian equation, theoretical calculation, spectralcalc.com simulation and experiment. Simulation and experimental results show high sensitivity of measurement when ozone is sampled at optimum transmittance.

1. Introduction

Ultraviolet absorption spectroscopy is commonly applied for ozone concentration measurement because ultraviolet absorption based ozone sensor is reliable for long lasting operation. When ultraviolet light passes through ozone, part of the ultraviolet light is absorbed. Amount of ozone concentration measurement is determined based on amount of light that passes through ozone. Transmittance is zero when light is fully absorbed; whereas, transmittance is unity when no light is absorbed. Based on literature review, there is close relation between transmittance and quality of measurement data. Firstly, transmittance approaching unity is not optimum for measurement. This is because forward scattering occurs at very high transmittance (0.99) [1]. Scattering is considered negligible for absorption measurement based on Beer–Lambert law [2]. Therefore, scattering affects accuracy of absorption measurement. For example, measurement of ozone concentration at transmittance that is close to unity (up to 0.995) has high relative error of ozone concentration measurement (up to 9%) [3]. Relative error of ozone concentration is reduced when transmittance of measurement is reduced away from unity [3]. Similarly, transmittance values of previous work are reported to range from 0.516 to 0.995 only [4,5]. This is because ozone concentration measurement at transmittance 0.995 (0.10 mg L^{-1}) is noisier in comparison to transmittance at 0.516 (0.97 mg L^{-1}) [4,5]. Secondly, transmittance approaching zero is not optimum for measurement. This is because sensor is not sensitive when there is not enough light allocation for measurement [6,7]. For example, transmittance below 0.2165 exhibits non-linear measurement behavior, as measurements deviate from Beer–Lambert law [8]. Based on previous experimental findings, we infer that there is a need to determine optimum transmittance for high sensitivity ozone concentration measurement.

There is lack of systematic effort to optimize transmittance for high sensitivity ozone concentration measurement via ultraviolet absorption spectroscopy. There are attempts to optimize optical path length and absorption cross section for specific range of ozone concentration measurement at high sensitivity [6]. In this work, we optimize transmittance for specific ozone concentration measurement at high sensitivity. In previous work, Twyman–Lothian equation is often applied as a guide to justify optimum transmittance range for ozone concentration measurement [3]. For example, transmittance between 0.25 and 0.5 is recommended for low relative error of ozone concentration measurement [9]. Based on this motivation, we propose a new equation based on Beer–Lambert law to determine sensitivity of ozone concentration measurement. The equation is a breakthrough for optimization of transmittance for high sensitivity ozone concentration measurement.

* Corresponding author.
E-mail addresses: cemtay2@live.utm.my (T.C.E. Marcus), hanif@fke.utm.my (M.H. Ibrahim), nhafizah@fke.utm.my (N.H. Ngajikin), asrul@fke.utm.my (A.I. Azmi).

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2. Derivation of sensitivity equation for transmittance optimization

Beer–Lambert law for ozone concentration via ultraviolet spectroscopy is commonly expressed in Eq. (1) [6,8,10]. When light passes through ozone, portion of the light is absorbed by ozone. The transmittance of light is defined in Eq. (2). Sensitivity of measurement is defined to be the first derivative of sensor output (transmittance) with respect to sensor input (concentration) as shown in Eq. (3) [11–13]. Based on sensitivity definition in Eq. (3), Eq. (1) is differentiated once to yield Eq. (4). Based on relation in Eq. (1), parameters in Eq. (4) are simplified to yield Eq. (5). Eq. (5) shows expression of sensitivity that we propose based on derivation from Beer–Lambert law.

$$T_r = \exp\left(-\frac{\sigma N_A P l c}{10^6 RT}\right) \quad (1)$$

$$T_r = \frac{I_t}{I_o} \quad (2)$$

$$S = \frac{\mathrm{d}T_r}{\mathrm{d}c} \quad (3)$$

$$\frac{\mathrm{d}T_r}{\mathrm{d}c} = -\frac{\sigma N_A P l}{10^6 RT}\exp\left(-\frac{\sigma N_A P l c}{10^6 RT}\right) \quad (4)$$

$$\frac{\mathrm{d}T_r}{\mathrm{d}c} = \frac{T_r \ln T_r}{c} \quad (5)$$

Here, c is concentration of ozone in parts per million by volume (ppm); I_0 is intensity of specific ultraviolet wavelength that passes through oxygen in count; I_t is intensity of specific ultraviolet wavelength that passes through ozone in count; l is optical path length in m; N_A is Avogadro's constant, $6.02214199 \times 10^{23}$ molecule mol^{-1}; P is pressure in atm; R is the ideal gas constant, 8.205746×10^{-5} atm m^3 mol^{-1} K^{-1}; S is sensitivity of sensor in ppm^{-1}; T is the absolute temperature in K; T_r is transmittance of light; Δc is absolute error of ozone concentration; ΔT_r is absolute error of transmittance; $\Delta c/c$ is relative error of ozone concentration; σ is the absorption cross section of ozone in m^2 molecule^{-1}.

For comparison purpose, the sensitivity equation is derived through an alternative approach based on Twyman–Lothian equation. The Twyman–Lothian equation is typically used to relate transmittance and relative error of ozone concentration as shown in Eq. (6) [3,9]. For small changes of transmittance, ΔT_r and concentration, Δc, sensitivity could be written as Eq. (7). Hence, equation to express sensitivity in Eq. (8) is derived based on Twyman–Lothian equation in Eq. (6). There is high similarity between between Eq. (5) and (8). This shows sensitivity equation could be derived based on Twyman–Lothian equation or Beer–Lambert law. In previous work, sensitivity is defined for a range of ozone concentration measurement [6]. In this work, sensitivity is defined for any ozone concentration measurement. The sensitivity equation in Eq. (5) is further applied for transmittance optimization at specific ozone concentration.

$$\frac{\Delta c}{c} = \frac{\Delta T_r}{T_r \ln T_r} \quad (6)$$

$$\frac{\mathrm{d}T_r}{\mathrm{d}c} = \frac{\Delta T_r}{\Delta c} \quad (7)$$

$$\frac{\Delta T_r}{\Delta c} = \frac{T_r \ln T_r}{c} \quad (8)$$

Objective of optimization is to maximize sensitivity of ozone concentration measurement at optimum transmittance. Based on sensitivity equation in Eq. (5), first derivative of sensitivity with respect to transmittance is expressed in Eq. (9). At maximum sensitivity, first derivative of sensitivity with respect to transmittance equals to zero as shown in Eq. (10). Eq. (11) is a result of substitution of Eq. (9) to (10). Eq. (12) is the solution of solving Eq. (11). Eq. (12) shows optimum transmittance for maximum sensitivity ozone concentration measurement is e^{-1} or 0.3679. In previous work, minimum relative error of ozone concentration occurs at transmittance e^{-1} or 0.3679 [9]. This shows theoretical calculation result is in good agreement with previous work.

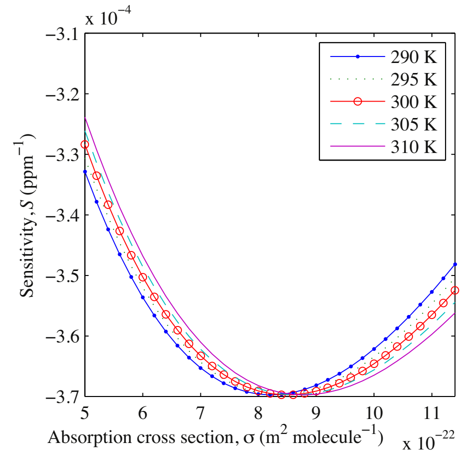

Fig. 1. Graph of sensitivity versus absorption cross section obtained from theoretical calculation at concentration 995 ppm, optical path length 5 cm, pressure 0.9671 atm and temperature from 290 K to 310 K.

$$\frac{\mathrm{d}S}{\mathrm{d}T_r} = \frac{1}{c} + \frac{\ln T_r}{c} \quad (9)$$

$$\frac{\mathrm{d}S}{\mathrm{d}T_r} = 0 \quad (10)$$

$$\frac{1}{c} + \frac{\ln T_r}{c} = 0 \quad (11)$$

$$T_r = \exp(-1) \quad (12)$$

3. Detailed analysis of parameter changes with respect to sensitivity

Sensitivity is expressed using Eq. (4). Hence, if any of the parameters (concentration, c, temperature, T, pressure, P, absorption cross section, σ and optical path length, l) change, sensitivity can be calculated using Eq. (4). For analysis purpose, transmittance of measurement is theoretically calculated using Beer–Lambert law in Eq. (1). The transmittance values are used to calculate sensitivity of measurement using Eq. (5). Fig. 1 shows graph of sensitivity versus absorption cross section obtained from theoretical calculation at concentration 995 ppm, optical path length 5 cm, pressure 0.9671 atm and temperature from 290 K to 310 K. This graph is chosen for analysis because absorption cross section of ozone can be easily changed by selecting suitable wavelength for ozone concentration measurement. Secondly, there is possibility of temperature change during continuous operation of ozone generator. Thirdly, optical path length of gas cell is usually fixed throughout experiment. Fourthly, practical values of absorption cross section up to 1.14×10^{-21} m^2 molecule^{-1} are chosen to predict sensitivity values. This is because strong ozone absorption cross section is known to occur at 1.147×10^{-21} m^2 molecule^{-1} at mercury wavelength 253.65 nm [14]. Based on Fig. 1, optimum sensitivity −0.0003697 ppm^{-1} is calculated when ozone is measured at moderate absorption cross section 8.4×10^{-22} m^2 molecule^{-1} and temperature 300 K. This is because ozone sensor approaches saturation when ozone is measured at strong absorption cross section [6,8]. When temperature is increased from 290 K to