



A low-cost in-line ozone gas monitor via ultraviolet absorption spectroscopy

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Abstract

A low-cost in-line ozone monitor based on the principle of ultraviolet absorption was built and tested for different ozone for concentrations up to 300 mg h⁻¹ and flow rates up to 5 lpm using air as a feed source. A widely available T5 ultraviolet (UV) tube was used as a UV source and two UV light absorption cells were made to act as reference and measuring cells. The output of the two cells was used to calculate the ozone concentration using Beer-Lambert's law. To correlate the output readings of the ozone monitor with those obtained using the iodometric titration method, a correction factor of 1.5117 was determined and applied. The results demonstrate a strong linear correlation ≥ 0.99 between estimated and measured ozone concentration values. Relative errors less than 10% were observed for ozone concentrations ranging from 400 to 5000 ppb, while a relative error up to 16% was reported for concentrations below 400 ppb. The developed monitor offers a cost-effective alternative to expensive ozone monitoring systems for standard applications, with a total construction cost under \$100.

Keywords: ozone monitor; UV-absorption; Beer-Lambert law.

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1- Introduction

Ozone (O₃) is a highly oxidative chemical compound, with a broad range of applications such as in air and water disinfection, agricultural, food, and medicine [1]. It supports United Nations Sustainable Development Goals (UNSDG), primary through its roles in water and air purification, public health, and environmental protection (e.g. goals 3, 6, and 9). Ozone is formed naturally in the atmosphere either with the aid of the sun's ultraviolet light (i.e. UV light) or by electrical discharge during thunderstorm lightning [2, 3] according to the net reaction:



Ozone can also be generated in the lab or produced commercially by many means such as ultraviolet [4, 5], electrical discharge [6, 7], or by electrolytic ozone generators [8]. However, due to its short lifetime; it is necessary that generation equipment be close enough to where it is applied or required [9-11].

The growing demand on ozone across different sectors and its future potential applications increases the quality requirement of generated ozone in terms of its concentration measurement. For gas or liquid phase, iodometry is the most common and widely acceptable method for ozone concentration measurements since it is

easy to accomplish, carried out at affordable price, and give highly accurate results [12, 13].

However, the method is not well suited for in-line direct real time monitoring of ozone concentration since it requires manual activities to be carried out by the operator (e.g. titration). Electrochemical sensors are also available providing a low-price and convenient solution for ozone gas basic monitoring or detection [14].

Unfortunately, the sensors have many complicated challenges such as short shelf-life, base-line drift, sensitivity and selectivity issues, highly affected by water vapor and other contaminants (e.g. volatile organic compounds), and require very careful condition and periodic calibration to provide barely accurate results [15, 16].

Here, UV absorption-based method comes to solve these issues and providing in-line, fast, and accurate monitoring of ozone in real time [17, 18]. However, UV absorption-based ozone branded monitors/analyzers are expensive devices with a price ranging up to \$5000 for general industrial applications and higher than that figure for laboratory or specialized purposes.

It is possible to build an ozone monitor in the visible range of the light spectrum since ozone absorbs visible light as well [19, 20]. However, measuring ozone concentrations in the visible band requires a long



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measuring cell due to the weak absorbency in this region of the spectrum [21].

- Background of UV-absorption by ozone

At room temperature, ozone absorbs UV light in the range between 195-350 nm, showing a maximum absorbency at 253.65 nm with an absorption cross section value of $1147 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ [22, 23]. According to Beer-Lambert law, the amount of light being absorbed by ozone is linearly proportional with material concentration to some degree of extent according to the relation [24-26]:

$$A = \ln\left(\frac{I_0}{I}\right) = \sigma lc \quad (2)$$

Where A is the absorbency, I and I_0 represents the light intensity in the presence and absence of the target component respectively. σ represents the absorption cross section ($\text{cm}^2 \text{ molecule}^{-1}$), l is the length of the path being traveled through the measured medium (cm), and c is the concentration (molecule cm^{-3}). So, the measuring principle requires: (1) a UV light source, (2) a measuring cell in which ozone gas is going to flow through, and (3) a photocell to measure the intensity of the incident light. Of course, there should be a processing algorithm to deal with the received signals and turn them into a significant equivalent meaning. Fig. 1 shows a schematic diagram for the basics of the measuring principle.

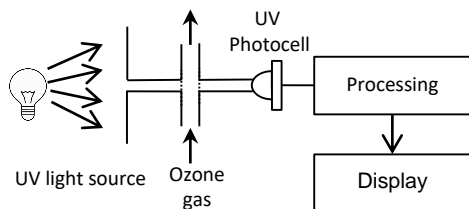


Fig. 1. Measuring principle of in-line ozone monitoring

To count for the concentration (e.g. in mg/l), Eq. 2 should be re-arranged to:

$$c = \frac{10^6}{\sigma l} \left(\frac{M_w}{N_A} \right) \ln\left(\frac{I_0}{I}\right) \quad (3)$$

Where M_w is the molecular weight of ozone and N_A is Avogadro's number. Taking the effect of temperature and pressure changes and measuring deviations into accounts, Eq. 3 can be written as:

$$c = \frac{10^6}{\sigma l} \left(\frac{M_w}{N_A} \right) \ln\left(\frac{I_0}{I}\right) \left(\frac{P_o}{P} \right) \left(\frac{T}{T_o} \right) k_c \quad (4)$$

In which, P and P_o are the measured pressure and standard reference pressure respectively, T and T_o are the measured temperature and the standard reference temperature respectively, and k_c is a correction factor to compensate for the results coming out from the iodometry method. Assuming negligible pressure effects, the

pressure correction term can be canceled out from Eq. 4 in the calculation process.

In this study, the rate of UV absorption by ozone method is employed to monitor ozone concentration at the outlet of an ozone generator or that leaving a reaction vessel enabling real-time detection of unreacted ozone. This approach significantly facilitates kinetic studies involving ozone by providing continuous and accurate concentration measurements. The novelty of the work lies in the unique configuration adapted to construct the monitor, which achieves good measurements accuracy using readily available components at a budget price. This is among the first implementations of such a low-cost yet reliable UV-based ozone monitoring system for kinetic and process applications.

2- Experimental work

2.1. Chemicals

Potassium iodide (Hopkin & Williams, UK), anhydrous sodium thiosulphate (Loba Chemie PVT Ltd., India), starch (BDH Chemicals Ltd., UK), and glacial acetic acid (Thomas Baker, India), Activated carbon (Qinyuan Group Ltd., China), silica gel (Impark Corp., USA), and distilled water was used in all experiments. All Chemicals are used according to the manufacturer specifications without further treatment or tests.

2.2. Ozone generator output calibration

Enaly 1KNT-24 ozone generator (China) was used to generate a maximum ozone rate of 300 mg h^{-1} when dry air was used. The ozone generation rate can be adjusted from 0~100% via a panel regulating dial. However, the produced ozone by the device must be precisely measured for calibration purposes and to count for k_c value. So, the iodometry method was adapted at first as follows [27]: ozone was bubbled through a bottle containing 50 ml of acidified 1.4% KI solution which was prepared by dissolving 14g KI in 1 liter solution of distilled water acidified with 40 ml acetic acid. Acetic acid enhances the dissolution of ozone and acts as hydroxyl ions scavenger. Ozone generation rates of 10%, 30%, 50%, 70%, and 100% were selected for ozone production measurement. At each setting, ozone was bubbled in the KI solution for 30, 60, 90, 120, 150, and 180 seconds respectively at a flow rate of 0.4 lpm. Ozone will oxidize the iodide ion to produce iodine turning the solution into a brownish color according to the reaction:



Fig. 2 shows a schematic diagram for conducting the ozone generator measurements. Air was fed from a compressor and passes through a column filled with activated carbon to remove any unwanted odors and then to a second column filled with silica gel to remove the moisture. The moisture content in all experiments was about $5 \pm 2\% \text{ RH}$ and the temperature was 27°C . The air

flowrate was monitored via a Winpower OCS-3F3.0 ultrasonic oxygen concentration/flow monitor respectively. Ozone was bubbled through a microporous diffuser. It is assumed that all ozone was consumed by KI inside the contactor since no ozone was detected at the vent gas stream.

By titrating with 0.64% sodium thiosulphate solution, each sample color should turn from amber to colorless indicating the consumption of iodine by thiosulphate according to Eq. 6. 1% starch indicator was used to justify the titration reaction endpoint. Calculations show that each 1 mg of ozone will consume about 0.97 ml of thiosulphate. Fig. 3 shows the titration setup and typical photos taken at different ozone generation powers.

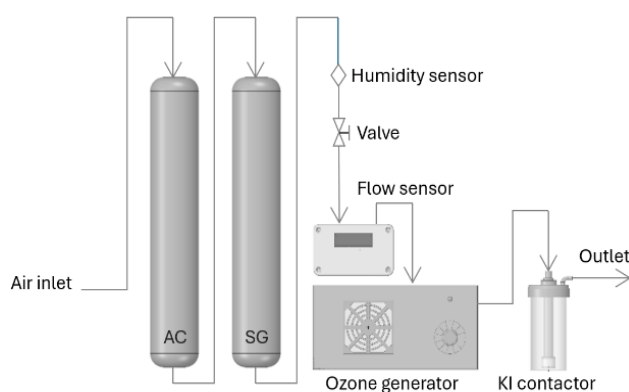


Fig. 2. Schematic diagram for calibration of ozone generator

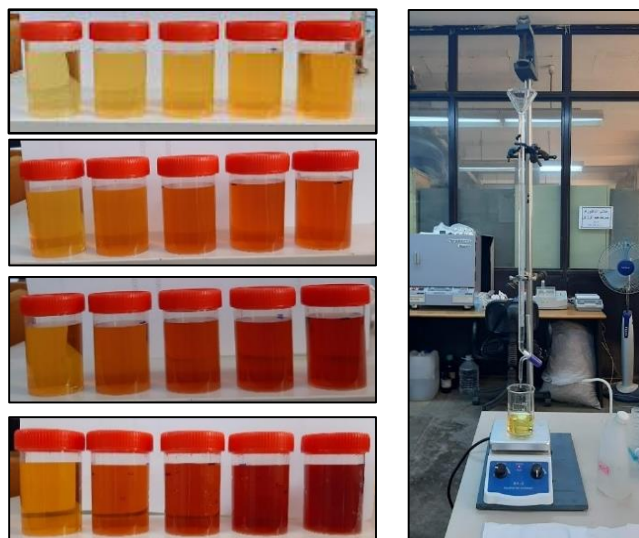


Fig. 3. Titration setup and typical photos of KI solution ozonation taken at different times and power levels from 10% (top), 30%, 50%, and 90%

2.3. UV Absorption measuring unit

The designed measuring unit was composed mainly of two identical cells attached to one single 8W 253.7nm T5 UV tube (China) working as a source for UV light as seen in Fig. 4. Each cell consisted of a single 20mm ID of 100

mm long quartz tube. Each end of the tube was connected to a 3d printed reducer so that the outlet diameter was 4mm. This makes the tubing and connections easier to deal with. The quartz tubes pass through a 3D printed block of two sides: the first side was attached to the UV tube, and the other side was attached to the UV photocell. The block has a small rectangular opening allowing the UV light to pass through the quartz tubes and to reach the photo sensor on the other side. The unused parts of the uv tube were covered by a PVC tape so that no light would be exposed to the surrounding. Once the unit is turned on the photo sensors start to measure the intensity of the incident UV light immediately. As the intensity of the incident light increases the sensors show more responsive and vice versa. The first cell will record the intensity of the UV light for ozone free stream (i.e. air only) and act as a reference cell output (I_0). The air is then passed to the ozone generator in which the ozone-rich stream will pass through the second cell. The intensity of the UV light in the second cell depends mainly on the concentration of the generated ozone being passed through (I) due to the absorption of UV light by ozone. The output of the two cells were adjusted so that they both have 0.0 V output if only air was passed.

The main control board that reads the signals, processes, and displays the results is the Arduino Uno board. DHT22 temperature and humidity sensors were used to measure the inlet air temperature and relative humidity. The UV photocell sensor being used is the S12SD which provides analog output proportional to the amount of the received UV light in the range of 240-370nm wavelength. The photocell sensor signal was adjusted and amplified in two stages using an LM385 operational amplifier so that the output would produce a significantly measurable voltage value. An ADS1115 I2C 16-bit analog-to-digital converter was used to convert the cell analog signals and pass the equivalent digital values to the Arduino. A 2x16 character LCD screen was also attached to the Arduino board to display the measurement results on the front panel of the device.

3- Result and discussion

The exact wavelength of the tube was measured and confirmed using a CCD Thorlabs spectrometer as shown in Fig. 5. The figure also shows a second peak above 270nm, but its effect would be negligible since it is far from the absorption wavelength of ozone. Fig. 6 shows the titration results for the ozone generator output (i.e. Enaly 1KNT-24) at different times. These results show a high linearity with R-squared values of more than 0.99 for all tested ozone generation rate settings which indicate a high output stability. These slopes represent the rate of ozone production and converting their values to $mg\ h^{-1}$ would show the output relation between the dial rate setting and the actual output of the ozone generator.

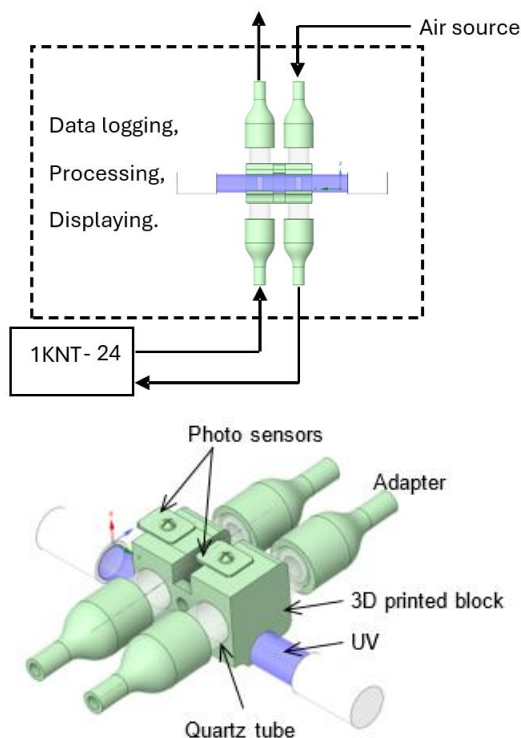


Fig. 4. Reference and ozone measuring cells

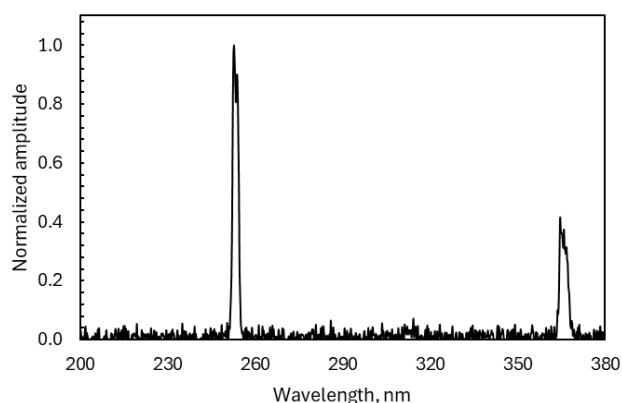


Fig. 5. UV spectrum verified by CCD USB spectrometer

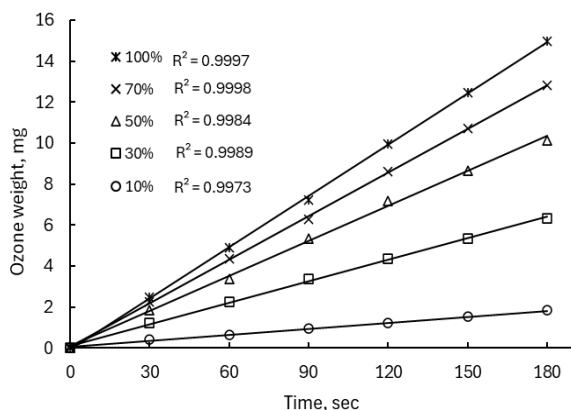


Fig. 6. Iodometric measurement for calibrating ozone generator output

Fig. 7 shows the relationship between the ozone generation rate setting and the actual generated ozone in mg h^{-1} . However, the device output doesn't follow a linear relationship! This non-linearity might be due to the ozone generator circuitry characteristics itself. The output is better represented by a sigmoid model with R-squared value of 0.992 as:

$$\text{output (mg h}^{-1}\text{)} = \frac{458.9}{1 + e^{-0.039(x-22.37)}} - 136.13 \quad (7)$$

After measuring the temperature, I , and I_0 , the calculation proceeds to get the concentration according to Eq. 4. The results were adjusted to that given by idiomatical methods showing an averaged value of k_c to be 1.5117.

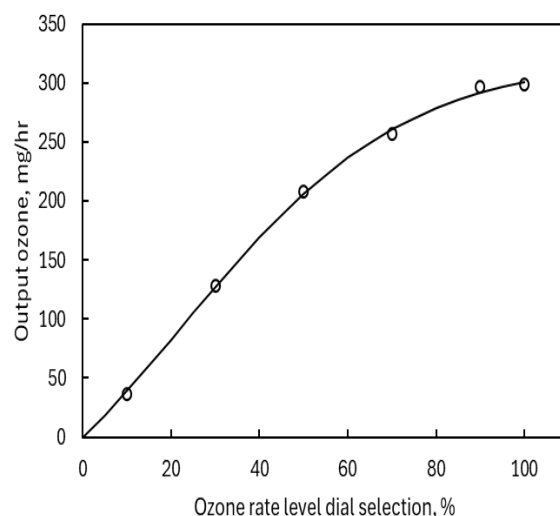


Fig. 7. Ozone generator output as a function of ozone generation rate settings

Fig. 8 shows the measured ozone concentrations carried out at different air flow rates from 1 up to 5 lpm showing a high degree of linearity with R-squared value of 0.99. Each measurement was repeated many times to ensure consistency during the device operation, and the results show a high repeatability - typically within the instrument resolution (± 7.63 ppb) which is equivalent to a standard deviation of 2.2 ppb based on the quantization noise of the signal conversion - indicating excellent precision within the full range.

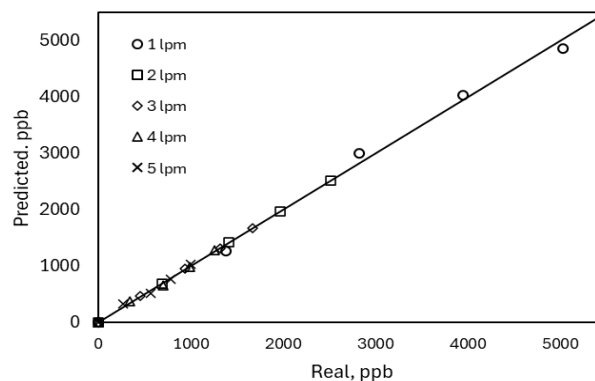


Fig. 8. Real vs predicted ozone concentrations at different flow rates

Fig. 9 Shows the reported relative errors for each measurement. All relative errors were found to fall within the 10% for all measurements above 400 ppb which is a very good estimate if taking the whole range up to 5000 ppb. However, below 400 ppb, relative errors increased a bit up to 16% due to deviation caused by the fitting itself from the real measured value (see Fig. 6).

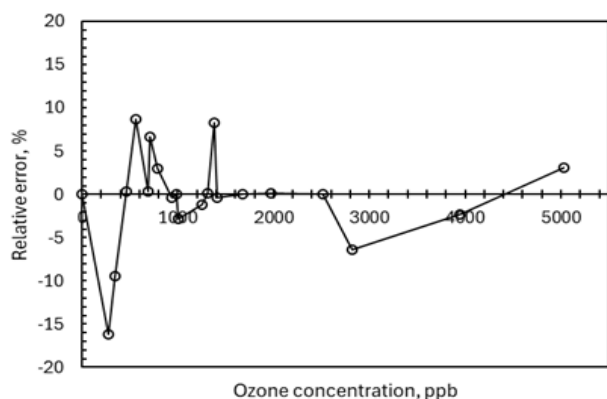


Fig. 9. Measurement of relative errors

4- Conclusion

A UV-based ozone monitor using simple T5 UV tubes and a few available electronic components can be built at an affordable budget of less than \$100. The device can be used for ozone measurements instead of the highly expensive commercial ozone monitors, especially if relative errors within 10% are acceptable. The monitor can produce fast, reliable, and acceptable measurements compared to the iodometry method. However, a comparison of the results with that obtained by the iodometry method suggests a correction factor of 1.5117 to be inserted in the calculation equation to match the measurements. High-linearity was observed at different ozone flow rates / concentrations with r-squared values of more than 0.99.

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جهاز مراقبة غاز الاوزون واطئ الكلفة عبر الامتصاص الطيفي للأشعة فوق البنفسجية

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الخلاصة

تم بناء واختبار جهاز واطئ الكلفة لمراقبة غاز الاوزون باستعمال مبدأ الامتصاص الطيفي للأشعة فوق البنفسجية ولغاية ٣٠٠ ملغ/اسا ومعدل جريان لغاية ٥ لتر/دقيقة باستعمال الهواء كمصدر لتوليد الاوزون. استعملت شمعة نوع T5 كمصدر لتوليد الأشعة فوق البنفسجية مع خليتين تعمل احدهما للقياس والاخرى كخلية مرجعية. تم استعمال خرج الخليتين لقياس تركيز الاوزون باستعمال قانون بير-لامبرت. لمعايرة القياسات تم استعمال طريقة التحليل الكيميائي بالتسحيح باستعمال اليود ووجد ان ثابت تناسب مقداره ١,٥١١٧ يكفي لتطابق القرائنين. بينت النتائج تطابق بين القراءات المقاسة عبر الجهاز وتلك التي تمت بالتحليل الكيميائي علاقة خطية بتطابق يصل ال اكبر من ٠,٩٩. اخطاء نسبية بواقع ١٠% وجدت في التراكيز بين ٤٠٠ و ٥٠٠٠ جزء ملياري ونسبة خطأ ١٦% للتراكيز الاقل من ٤٠٠ جزء ملياري. جهاز المراقبة يوفر حل رخيص وبديل مناسب عن الاجهزة الغالية بكلفة تصل الى اقل من ١٠٠ دولار.

الكلمات الدالة: مراقب اوزون، امتصاص الأشعة البنفسجية، قانون بير-لامبرت.