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Progress in Ozone Sensors Performance: A Review

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Graphical abstract

Sensor type
Issues Addressed
Application
Measured Concentration
Methodology
Limitations and Research directions

Abstract

There has been a surge in ozone gas relevance in agriculture, environment and in the industry. This has resulted in increased research activities in areas involving ozone gas generation, application, safety and sensing. In this manuscript we present reviews of selected recent works (2011–2015) on ozone gas sensors based on absorption spectroscopy. Issues addressed include sensors applications versus requirements; sensors performance versus limitations and cost of sensors. Outstanding research issues are also outlined. While the review is mainly biased towards sensing of ozone using conventional absorption spectroscopy, other methods such as photo acoustic, photo reductive, photo stimulated, metal oxides, electrochemical, chemical, solid state and resistive ozone sensors were also considered in light of their performance criteria. Generally, it was observed that new applications of ozone gas lead to new sensing research challenges. Several sensing parameters were repeatedly investigated and improved upon over the years. Some of these parameters include: selectivity, sensitivity, speed of response, cost of sensor, lower detection limit and portability.

Keywords: Application; ozone; limitations; methodology; research directions; review

1.0 INTRODUCTION

There has been a surge of ozone gas relevance in agriculture, environment and in the industry [1-5]. This naturally has resulted in increased research activities on ozone generation, application, safety and sensing [6-10]. In the industry, ozone is employed for degrading of contaminants that emerge from water in pilot plants [11-13]. Ozone measurement is used as a means of understanding low doses of radiation chemical yields [1]. Ozone combined with UV is applied to modify carbon nanotubes thereby expanding the scope of the utilization of nanotubes [14]. A similar combination of ozone and UV has also been proposed as potential disinfectants for seawater [15]. Ozone gas is used as a benchmark for the evaluation of urban air pollution [16, 17]. Ozone has also been found to be very useful in the aerobic process for stable and reduced quantity of sludge produced during biological treatment and removal of endocrine disrupting compounds [18]. Varying dosage of ozone is in fact employed in the removal of active pharmaceutical ingredients from biologically treated wastewater [19].

In agriculture, ozone is considered in the application as a possible fumigant for the control of insects in stored-grain [20]. It's ability to inactivate microorganism has resulted in it becoming a very efficient agent for the treatment of vegetables and fresh fruits after harvesting [21-24]. For grape storage at a temperature of 273 k, it is recommended that, 1.0 mg/L of ozone- water concentration be used, as it offers the best condition for storage [25]. Ozone gas trapped in ice is characterized with the potential for deodorization and sterilization, hence becoming a useful method for cold food storage [26].

However, ozone may also be detrimental as in the form of a pollutant, ozone has been identified as damaging to crops and hence a threat to food security [27, 28]. For instance, an average of 30% decrease in seed yield occurred when soybean plants were exposed to high ozone concentrations resulting in a reduction in productivity. In addition nitrogen and chlorophyll

content of leaves were also reported to have decreased [29]. In fact a laboratory test indicated that ozone concentrations exceeding 80 parts per million by volume (ppm) has the potential to tamper with necessary interactions that normally exist between plants and animals during pollination [30].

Between 2008 and 2010, ozone concentration in excess of 0.1 ppm were discovered to be trapped in cabins of commercial aircraft that were without ozone scrubbers [31]. Ozone measurements due to increase in road traffic in the Pyrenees Mountains which is the border between Spain and France, showed the mean value of ozone concentrations increasing with height; with 23 ppm and 52 ppm of ozone concentrations measured at a height of 335 m and 2877 m above sea level respectively [32]. Ozone has also been identified as a secondary pollutant contributing to atmospheric oxidizing ability variation and composite pollution in the region of Beijing [33].

Ozone concentration in air as stated by the international health and safety standards should not exceed 0.05–0.10 ppm [34] as the human body can experience irritations [35]. Exposure to high concentrations for a long period can result in abnormality in the lungs [36] and other health hazards [37-40]. Hence, while ozone applications continue to grow, the need to accurately and timely detect ozone also abound. A close study of various approaches employed for ozone detection can be classified as: chemiluminescence [41, 42], electrochemical concentration cells [43], cavity ring down spectroscopy [44, 45], cavity enhanced absorption spectroscopy (CEAS) [46, 47], UV absorption [48], solid state sensors[39], photo reductive [49] and photo-acoustic sensors[50, 51]. These various methods have attempted to address several issues that are associated with the sensing of ozone. This paper discusses possible enhancements of these parameters.

Table 1 Ozone sensors based on optical absorption spectroscopy

Sensor Type	Issues Addressed	Application	Measured Concentration	Methodology	Limitations and Research Directions	Reference
Cavity ring down spectroscopy (CRDS)	Limitation of cavity ring down spectroscopy method when applied directly for ozone gas detection.	Recommended for ozone measurements in aircraft and periodic measurements of ozone.	Ozone concentrations in the range of 0.026 parts per billion per volume (ppbv) to 200 ppbv.	Indirect measurement of ozone by converting it to an oxide of nitrogen which was then measured with CRDS as a by-product.	Method is associated with background signals that are unavoidable.	[44]
Optical absorption spectroscopy	Sensor cost and resolution.	Ozone detection in harsh environment.	75 ppm of ozone.	Use of new LEDs as light sources in combination with optical fibres and photo detectors.	Strong dependence on temperature of LEDs when used as light sources and difficulty of precision and stability in their optical outputs	[52]
Cavity enhance spectroscopy	Cost of light source, sensitivity and higher ozone absorption.	Ozone monitoring.	8.4 ppbv of ozone was reported as limit of detection.	Application of low cost and rugged atomic line sources for ozone measurements at 253.7 nm.	Sensitivity improvements	[46]
UV absorption spectroscopy	Sensor portability and speed of response.	Ozone measurements in the atmosphere.		Portability achieved with the aid of polarization optical-isolator configuration, while speed of response improved by configuring both the inlet and exhaust.	Accuracy enhancements	[48]
UV absorption spectroscopy	Sensitivity, stability and sensor lifespan, avoiding harmful mercury as light source and compactness.	Depletion of ozone in nature.	0.1 ppm of ozone with an accuracy of 0.5%.	DUV LED at 280nm NB: the detect limit of the sensor can be improved by obtaining an LED with a higher power rating.	Life time of DUV LED btw 5000hrs to 10 000hrs while that of LED operating in the blue region is 70 000hrs.	[53]
UV absorption spectroscopy	Cross sensitivity, linearity, precision and portability.	Monitoring of ozone in a printing press to prevent its adverse effect as a carcinogen gas.	Sensing resolution of 0.005 ppm of ozone gas.	Reflection as a means of increasing optical path length and thus achieving a compact design. Use of two photo detectors to compensate drift of light source.	Application of LED as a light source in a compact design will minimize drift and reduce cost of using an additional photo detector.	[54]
UV absorption spectroscopy	Ozone discharged in Medium Voltage switch board which is an efficient diagnostic indicator of initial failure of electrical components.	Medium Voltage (MV) Switchboard.	0.05 to 0.3 ppm changes in ozone concentrations.	Retro reflector was employed to increase path length of light and thus increasing sensor sensitivity.	Sensing response time of 60 seconds as compared to the requirement of 0.2 to 1 seconds [41].	[55]

Sensor Type	Issues Addressed	Application	Measured Concentration	Methodology	Limitations and Research Directions	Reference
Visible absorption spectroscopy	Measured transmittance consistency, absorption cross section, cross sensitivity and application of LED.	Recommended for laboratory experiments and ozone photometers in visible spectrum.	3, 311.57 to 31,902.99 ppm of ozone.	Use of yellow orange LED in visible spectrum with fibreless connections.	Larger errors due to weak absorption of ozone; and slow sensing speed attributed to length of gas cell and cross sensitivity of ozone with NO_X.	[56]
UV absorption spectroscopy	Sensitivity and sensor speed.	Not specified	Not stated	Configuring two retro reflectors by taking advantage of their ability to reflect back incident light at right angle.	Cost not taken into consideration, hence the possibility of using light reflectors which are much lower in cost is an area to be further explored.	[57]
UV absorption spectroscopy	Optical path length, cost and dynamic range.	Wide range of ozone concentration.	16.50 ppm to 214.49 ppm and 31.82 ppm to 413.67 ppm.	Expansion through sensor reconfiguration.	Expandable configurations for part per billion by volume (ppb) concentration range and for visible spectrum which is associated with cost reduction [58].	[59]

2.0 OZONE SENSORS BASED OPTICAL ABSORPTION SPECTROSCOPY

In Table 1, a succinct overview of selected works on ozone sensors using optical absorption spectroscopy in the period between 2011 and 2014 is presented. A wide range of issues were addressed including direct application of cavity ring down spectroscopy for ozone gas detection, sensor cost and resolution, cost of light source, sensitivity and higher ozone absorption, sensor portability and speed of response, stability, sensor lifespan and harmful light sources, compactness, cross sensitivity, linearity, precision and portability, ozone detection in MV switch board which is an efficient diagnostic indicator of initial failure of electrical components, measured transmittance consistency, absorption cross section, application of LED as light source, optical path length, and dynamic range.

The following issues are deduced as limitations and suggested as possible future research directions: unavoidable background signals, LED dependence on temperature, precision and stability difficulties, sensitivity improvements accuracy enhancements, short life span of DUV LED, compact design, drift and cost reduction, sensing response time, errors due to weak absorption of ozone in visible spectrum and selectivity, use of less expensive reflectors and expandable configurations for ppb concentration range.

Table 2 Photo acoustic, photo reductive, photo simulated and metal oxide ozone sensors

Sensor Type	Issues Addressed	Application	Measured Concentration	Methodology	Limitations and Research Directions	Reference
Photo simulated gas sensor	Limited sensor detection range (sensor dynamic range), cross sensitivity.	Industrial and safety applications.	0.01 ppm to 200 ppm of ozone.	Photo stimulating metal oxides instead of heating.	Use of micro hot plates to reduce energy consumption of electro-chemical sensors.	[37]
Photo simulated gas sensor	Humidity effects on photo simulated sensors.	On site measurement of ozone in water.	Ten to hundreds ppb.	Integration of photo stimulated sensor with a water repellent membrane that is gas transparent.		[60]
Photo-acoustic	Designing an ozone sensor with the sensor head totally coupled via fibre only.	Measure ozone in the one-digit ppm or four digit ppb range.	Lowest ozone concentration measured was 2130 ppb ± 20 ppb.	Modification of Quartz-enhanced photo acoustic spectroscopy.	Improve detection limit to satisfy the 0.05–0.10 ppm international health and safety standards requirements [34].	[61]
Photo acoustic	Cost, LED as light source, and sensor robustness.	Wind power plants generator housing.	1.27 ± 0.08 ppmv detection limit of ozone.	A UV-LED at a wave length of 285nm was use as a light source in off-beam quartz enhanced photo-acoustic spectroscopy.	With a detection limit of 1.27 ± 0.08 ppmv obtained in this study as compared to 0.075ppm [62, 63] safe exposure limit for ozone, there may be a further need to improve upon detection limit for safety applications.	[64]
Photo-acoustic	Detection of ethylene as an ozone gas (green house gas) precursor.	Exhaust of vehicles that uses ethanol as fuel.	16 ppbv of ethylene a precursor of ozone gas.	Photo acoustic spectroscopy.	Continuous evaluation of emitted pollutants associated with the chemical process involving ethanol.	[65]

Sensor Type	Issues Addressed	Application	Measured Concentration	Methodology	Limitations and Research Directions	Reference
Photo reductive	Sensitivity, sensor response, sensor recovery time and high operation energy requirements of semi conductor metal oxides.	Commercial ozone monitoring.	2.5 ppm of ozone.	Use of impregnation method to co-doped WO_3 with platinum a noble gas and TiO_2 which yields high sensor response.	Response time requirement for ozone sensors is in the range of 0.2 to 1.0 seconds [41]; hence there is need to improve upon the response time of 890 seconds obtain in this work.	[66]
Photo reductive	Inexpensive ozone sensor with high response and simple to fabricate.	Industrial application.	1000 ppb to 7500 parts per billion (ppb) ozone concentration.	Enhancement of TiO_2-WO_3 sensing response by impregnating with Au in combination with a visible blue light as light source.	Response time range of 105s to 580s reported is very high in comparison to 0.2s to 1s requirements for safety applications.	[67]
Metal Oxide gas micro sensors	Cross sensitivity	Origin of noise and spectrum behaviour.		Adsorption-desorption noise theory.	Development of noise spectroscopy to improve sensor selectivity.	[68]
Metal Oxide gas micro sensors	Limitations of UV method in terms of size and cost. High temperature requirements of metal oxide sensors.	Ozone measurements at ambient temperature.	58 ppb to 217 ppb of ozone concentration.	Metal oxide modification using synthesis of sol-gel in alcohol at ambient temperature.	Extended sensor exposure to ozone yields a good response. However, this produces a long sensing recovery time.	[63]
Metal Oxide	Limitations in sensor fabrication, size and cost which is attributed to high temperature requirements of metal oxides.	Room temperature applications.	0 - 20 ppm	Alloys of ZnCdO were grown by method of cosputtering RF. Photo reduction and photo oxidation investigated with a violet LED and a UV lamp.	28.61s to 58.32s response time reported is not suitable for ozone sensors used for safety applications.	[69]
Metal semiconductor oxides gas sensor	Evaluation of gas sensing characteristics of silver tungstate (α-Ag_2WO_4) for ozone measurements.	Various applications	80 ppb of ozone concentration.	Microwave-assisted hydrothermal method was used to obtain nano structures of α-Ag_2WO_4.	Improving upon the response time of 7s and 6s reported to within the range of 0.2s to 1s.	[38]
Metal Oxide	Disadvantages associated with the use of heat to enhance sensing parameters and the non practicability of modulating irradiation in real life application.	Room temperature applications.	5 - 14 ppm	Radio frequency sputtering method along with UV continuous irradiation.	Response time of 250s reported requires improvements.	[70]
Metal semiconductor oxides gas sensor	Slow response of SnO_2 in sensing oxidizing gases.	Industrial environments was mentioned.	Range of ozone concentration is 400 ppb to 24 000 ppb.	Resistance rate of change method.	Improvement on detection limit below 400 ppb and sensing time below 30s.	[71]

3.0 PHOTO ACOUSTIC, PHOTO REDUCTIVE, PHOTO STIMULATED AND METAL OXIDE OZONE SENSORS

The classification in Table 2 focuses on the application of light for ozone measurements between the period of 2011 and 2015, as compared to light application in optical absorption spectroscopy which was discussed in section two (2) of this article. In some of the literatures reviewed, metal oxide sensor was referred to as photo reductive and hence its inclusion in Table 2. Sensing issues addressed include: limited sensor detection range (sensor dynamic range), cross sensitivity, weather effects (e.g. humidity) on photo simulated sensors, design of ozone sensor with the sensor head totally coupled via fibre, cost, LED as a light source, and sensor robustness. Detection of ethylene as an ozone gas precursor, sensitivity, sensor response, sensor recovery time and high operation energy requirements of semi conductor metal oxides were also looked into. Additionally, cost and simplicity of sensor fabrication, limitations in sensor fabrication, size and cost which is attributed to high temperature requirements of metal oxides, evaluation of gas sensing characteristics of silver tungstate (α-Ag_2WO_4) for ozone measurements and slow SnO_2 response in sensing oxidizing gases and limitations of UV method in terms of size and cost were also addressed.

Suggested research directions include but are not limited to: use of micro hot plates to reduce energy consumption of electro-chemical sensors, improvement of detection limit to satisfy 0.05–0.10 ppm international health and safety standards requirements and continuous evaluation of emitted pollutants associated with chemical process involving ethanol. Recommended response time requirement for ozone sensors is in the range of 0.2 to 1.0s. This suggest that there is a urgent need to improve the response time of 6s, 7s, 30s, 28.61s to 58.32s, 105s to 580s and 890s reported in several current literature. Development of noise spectroscopy to improve sensor selectivity. Extended sensor exposure to ozone has been shown

to yield a good response. However, this produces a long sensing recovery time. Thus, the detection limit needs to be improved to be below 400 ppb level.

■4.0 ELECTROCHEMICAL AND OTHER TYPES OF OZONE SENSORS

Electrochemical sensors, solid state sensors, chemical sensors, SAW RFID sensors and resistive sensors are presented in Table 3. The sensing issues addressed within the period of 2013 to 2014 include the use of thin film nano structures sensitivity to ozone, trace levels of ozone detection at room temperature, high temperature requirements of detectors which translate into high energy consumption, disadvantages associated with use of membranes and the requirement of electrolytes, interference, sensitivity and stability, cost, size and sensor ability to be query-able and effect of humidity on sensing.

Table 3 Electrochemical and other types of ozone sensors

Sensor Type	Issues Addressed	Application	Measured Concentration	Methodology	Limitations and Research directions	Reference
Solid State	Thin film nano structures sensitivity to ozone.	Recommended for use as ozone gas sensor.	0.075 ppm to 0.6 ppm	Authors took advantage of ozone sensitivity to thin films of p-type $SrTi_{1-x}Fe_xO_3$. They applied method of polymeric precursor to obtained samples of crystals.	With reference to reported response time of 60 and 120 seconds for two samples, there is a need to improve on the response time to satisfy the response time requirement for ozone sensors in the range of 0.2 to 1.0 seconds.	[39]
Chemical sensor	Trace levels of ozone at room temperature.	Detection of trace quantity of ozone at room temperature.	0.0215 ppm of ozone	Hybridization of nanotubes and Metal oxide.		[72]
Electro-chemical	High temperature requirements of detectors which translate into high energy consumption.	Ozone concentration measurement at room temperature.	1.4 ppm of ozone	Zinc oxide based on film bulk acoustic resonator (FBAR).	Sensor integration with wireless sensor network.	[73]
Electrochemical	Disadvantages associated with the use of membranes and the requirement of electrolytes. Interference, sensitivity and stability.	Recommended for ozone detection in mediums termed as electrolyte - free.	0.49µM to 740µM of dissolved ozone with a limit of detection of 0.185 µM.	Use of doped electrodes of boron and without the requirements for electrolytes.	Ozone sensing in other solvents other than water is a possible area to explore in future research activities.	[74]
Chemiluminescence	Sensitivity, sensor response time and signals stability.	Field measurements of ozone gas.		Sensor disc optimization through parameters variation and dyes combination with reagents.	Authors recommended improvements on TLC silica disc surface properties for adsorption matric.	[41]
SAW RFID sensors	Cost, size and sensor ability to be query-able.	Ozone detection in air.	63 ppb-min of ozone was the detection limit.	Detection at Ultra high frequency range (UHF) by means of X-ray photoelectron spectroscopy.	Mention was made of the suitability of the sensor for indoor applications, hence outdoor sensor performance could be a possible aspect of improvements.	[75]
Resistive	Effect of humidity on sensing.	Low concentration of O_3 at room temperature.	0.02 - 2.4 ppm of ozone.	Use of nano-casting procedure in synthesizing Mesoporous indium oxide and illumination with blue light.	Investigation of effects of other weather or climate conditions could be a research possibility for exploration.	[76]

Suggested research directions include: improvement on response time of 60 and 120 s that were reported in comparison to 0.2 to 1.0 s required for ozone monitors used for safety applications, and sensor integration with wireless sensor network. Ozone sensing in other solvents other than water is also a possible area to explore for research activities. Current designs tend to focus on the suitability of sensors for indoor applications, creating a gap in sensor design for outdoor applications thus providing research opportunities in areas such as improving the outdoor sensor capability. Investigating effects of other weather or climate conditions could also be a possible research area to be explored.

■5.0 FUTURE WORK

It is important to note that while new applications generate new research challenges, several sensing parameters display a high

tendency of reoccurrence, such as: selectivity [77], sensitivity [77], speed of response[38], and sensor cost. This suggest that there is indeed a need to investigate these parameters further with the aim of enhancing the performance of ozone sensors.

6.0 CONCLUSION

In view of the rise in ozone utilization in several applications there is a need to design sensors for specific applications which is tailored towards satisfying specific sensing parameters requirements such as accuracy, cost, cross sensitivity (with respect to specified interfering gases in specified environment), dynamic range, sensitivity, sensor response and speed. Chemical processes that yield ozone either as a by-product or end product also need to be studied closely with a view of designing ozone sensors that matches the process, application and other specific requirements that may arise.

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