Experimental Structures for Ozone Gas Detection Using Absorption Spectroscopy: An Overview

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Abstract-Experimental structures for ozone gas sensing using the absorption spectroscopy method are reviewed in this article. Basically, the structures of interest are the direct method of sensing and the cavity ring down spectroscopy because of its pronounced sensitivity. Basic experimental structures components are outlined. The article emphasizes taking advantage of recent and modern developmental inventions in the field of optics and electronics to maximise performance and efficiency and at the same time minimizing cost.

Keywords: ozone, spectroscopy, absorption, spectrum, experimental setup.

I. INTRODUCTION

Optical methods are known to play major roles in various fields of analytical sciences [1]; they are means of monitoring the optical absorption/emission/scattering of a gas analyte at specific wavelengths [2]. Light can interact with matter in any one of the following ways: dispersion, absorption, diffraction, interference, and reflectance [1]. Chemical compounds containing covalent bonds, absorb electromagnetic radiation; which is as a result of different mechanisms whose effects are seen throughout the electromagnetic spectrum [3]. Electron resonance at a given frequency is responsible for light absorption by a molecule at that frequency [4]; the excitation of valence electrons in the atoms of molecules is responsible for the absorption of light by ozone (the gas of interest in this study) in the UV region (200 to 400 nm, 6.2 to 3.0 eV) to the visible region (400 to 780 nm, 3.1 to 1.6eV) of the spectrum [3, 15].

Ozone, a word which originates from the Greek word smell; has a sweet clover – like smell at low concentration typical values of 0.0076ppm however, at higher concentration it is a toxic gas [5,6]. The interaction between short-wavelength radiation from the sun and nitrogen dioxide is said to results in ozone formation [7]. Ozone is the most important molecule in the terrestrial atmosphere [8], an allotrope of oxygen and an ideal sterilizer and deodorizer [9], is a toxic, light-blue gas with a pungent odour [10]; whereas as a liquid it is a blue indigo meta-stable liquid [8]. While atmospheric ozone gives a form of protections from cancer of the skin; that generated from mans activities adversely affects respiratory health, agricultural crops, and forests [11]. As an oxidizing gas, ozone can lead to irritations in the human body for concentrations above approximately 100 ppb [6]. Long time exposure of low concentrations, negatively affects the function of the lungs and the respiration system. Ozone concentration threshold as recommended by World Health Organization (WHO) is summarized in table 1.

Table 1: Ozone Concentration thresholds proposed by WHO [16]

Threshold	$\mu g/m^3$	PPB (Part Per Billion)	Max. Exposure Time
Protection of Health	150 – 200	64 - 85	1 Hour
Protection of Vegetation	200	85	1 Hour
Protection of Health	100 - 120	43 – 51	8Hour
Protection of Vegetation	65	28	8 Hour

Different compartment of the respiratory system absorbs ozone resulting in many health problems [12]. Increased hospital admissions for respiratory causes and worsening asthmatic conditions is link to ozone exposure [7]; Ozone reacts with the linings in the lungs causing inflammations, this result in weakening and premature aging of the lungs [13]. Ozone is also classified both as a dangerous pollutant and a secondary pollutant most frequently occurring in the

atmosphere [14]. The U.S. Clean Air Act of 1970 declares it as a criteria pollutant [15, 16].

The protection of the earth's life zone from the sun's UV rays is affected by Ozone concentration variations [17]. Ozone concentrations are much higher in mountain regions, where the UV-radiation is stronger; and at summertime, life can be inconvenient due to the increase in smog and ozone concentrations [6]; researchers in Anantapur, India, discovered ozone concentration to be a function of seasons [12]. Adequate and accurate measurement of ozone concentrations has been emphasized in literature as it was observed that considerable quantity of ozone is use for decontamination of water, industrial affluence etc; which exposes personnel's to the risk of action of high ozone concentrations [18]. On a general note hazards associated with gases generally makes it mandatory to monitor gases and thereby enhance safety; table 2 refers. They need therefore to continually sense and monitor ozone concentration accurately are of great analytical interest [19]. In this article, we present an overview of experimental structures for ozone gas detection using the absorption spectroscopy method.

Table 2: Gas Hazards [26]

Types of monitoring	Purpose	Hazard	Possible source of hazard
Personal protection	Worker safety	Toxic gas	Leaks, fugitive emissions, Industrial process defects
Explosive	Worker and facility safety	Explosions	Presence of combustible gases/Vapours due to leaks, industrial process defects

II. ABSORPTION THEORY:

According to Beer and Lambert, the concentration of an analyte can be determined by detecting the intensity of the output light. Lambert–Beer law describes the relationship of the input light and the output light that effects with the measuring gas. Beer lamberts law states that: if radiation of intensity I_0 is directed at a sample of path length l, radiation of intensity I_t leaves the sample [20]. The absorbance A can be defined as:

$$A = \log\frac{I_o}{I_t} = \varepsilon cl \quad (1)$$

Where:

ε = the decadic molar absorption coefficient of the species in question, having typical values of 104 to 105 M^{-1} cm^{-1} (with M being moles per litre) and

c = the concentration of the sample.

When ε is high and l is large, the absorption-sensor can be very sensitive. [1]

The ratio $\frac{I_t}{I_o}$ is defined as the transmittance T, given by:

$$T = 10^{-\varepsilon cl} = \frac{I_t}{I_o} \quad (2)$$

Equation (1) can also be expressed using natural logarithm as shown in the following:

From logarithm functions:

$$\ln x = 2.303 \log x \quad (3)$$

If $x = \frac{I_o}{I_t}$, Then

$$\ln\frac{I_o}{I_t} = 2.303\log\frac{I_o}{I_t}$$

Hence,

$$\frac{1}{2.303}\ln\frac{I_o}{I_t} = \log\frac{I_o}{I_t}$$

Therefore,

$$A = \frac{1}{2.303}\ln\frac{I_o}{I_t} = \varepsilon cl \quad (4)$$

And

$$T = e^{-\varepsilon cl} = \frac{I_t}{I_o} \quad (5)$$

III. REVIEW ON EXPERIMENTAL STRUCTURES

There has been several attempts made in the past and there has been recent increasing efforts in literature to enhance accuracy both in measurement and monitoring of ozone gas concentrations in diverse scenarios; a close observation of the experimental structures for these studies reveals that the structures goes from very simple form to structures that are a lot involving. What follows is a brief overview of different types of experimental structures in literature.

In the review paper by G Berden [21] on cavity ring down spectroscopy (CRD), while illustrating the simplicity of an experimental set up, they stated clearly that the use of CRD in any spectral region can not be restricted, once there is the availability of high reflective mirrors, detectors with a good and fast time response, and pulsed lasers that can be tuned [21]. They described a typical experimental CRD set-up which consists of a pulsed laser system, a ring-down cavity, a fast detector, a fast and deep analogue-to-digital converter, and a computer for data handling. It is as shown in Figure 1.

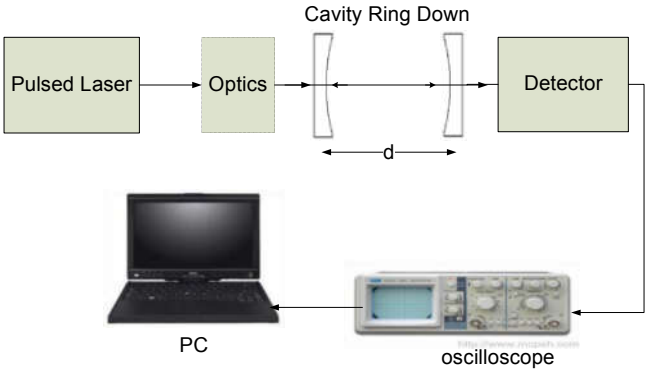

Figure 1: Scheme of the experimental set-up for CRD spectroscopy (Redrawn from [21])

They made the following additional clarifications: components to be used depends on the wavelength region in which the CRD spectrum needs to be recorded; according to them also, CRD spectroscopy is usually performed with pulsed dye lasers in the visible region; and photomultiplier tube can enhance time-dependent detection of the light leaking out of the ring-down cavity. [21].

J. Chen and D. S. Venables [22] in their paper describing a novel incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) instrument for measuring very weak absorption spectra from 335 to 375 nm; describes their IBBCEAS system comprising of a 75W arc Xe lamp as a source of light, cavity mirrors which also acted as band rejection filters [22].

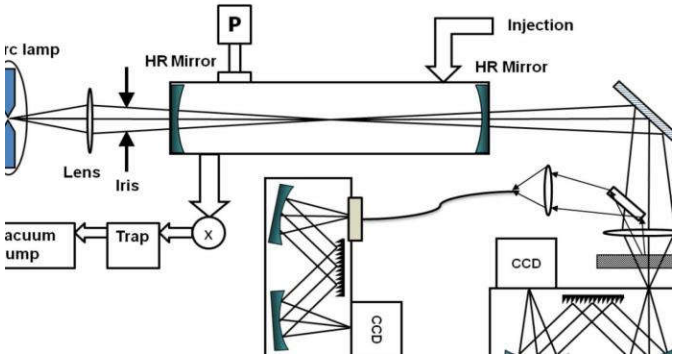

Figure 2: Schematic diagram of the IBBCEAS instrument (from [22]).

The mirrors reflectivity and radius of curvature are 99.8% at 365 nm and 5m respectively. Light exiting the cavity was focused into a Czerny-Turner spectrograph-Andor SR-163, while Andor 420A-BU was used for spectrum measurements [22]. They calibrated the wavelength scale of the spectrograph by fitting several emission lines of an Hg/Ne lamp to a second order polynomial function. Schott UG11 band pass filter was used to remove most visible and near-IR light in the system [22]. A heat-absorbing filter (Schott KG1) was used to screen wavelengths above 900 nm. A band-pass filter (Semrock FF01-357/44-25) was placed in front of the spectrograph to make provision for close match of the filter transmission to the high reflectivity range of the cavity mirrors and a usable spectral region [22]. Absorption values were obtained by measuring a small portion of the light reflected by the Semrock filter, transmitted through band-pass filter (Andover 320 nm), and recorded in another spectrograph (Andor SR-303) [6]. A sample cell and an optical cavity were enclosed in a vacuum tight system with the middle of the cell enclosed by a 100 cm glass tube. The outlet was connected to a fore line trap and rotary vane pump. Leybold CTR 90 capacitance manometer was used for monitoring the pressure of the system [22]. Samples of chemical compounds such as Acetone, 2-pentanone, 2-butanone, bromine and SO_2 were added into the chamber at well-defined flow rates via MKS mass flow controllers. Ozone was produced in a flow of oxygen by an ozone generator (OzoneLab OL80W) [22]. The challenge encountered by them was that of filtering the extremely broadband light - Xe arc lamps to the high reflectivity region of the cavity mirrors. Figure 2 is the schematic diagram of the IBBCEAS instrument.

The sensor design for Ozone gas detection in the ppm and ppb range by M. Degner *et al* [6] is a prototype setup of a potentially low cost sensor designed as a modular system; it is illustrated in Figure 3 below. The setup consist of: Fife fibre coupled LEDs with peak emission wavelength at 255 nm, 285 nm, 320 nm, 405 nm and 590 nm as spectral selective light sources; this light is guided by optical fibres through the reflection sensor cell which was received by broadband fibres coupled photodiodes as light detectors [6]. The system employed two reflection cells with different length, a small one with an absorption path length of two times 4 cm and a bigger one with a dimension of 40 cm. It is controlled by a DSP that communicates via USB with a laptop, where the online calculated data can be visualized and stored [6]. A developed digital signal processing program allowed a smooth signal acquisition with a variable measurement time and an independent parallel control and communication with the host PC [6].

K. Teranishi et al [23] measured ozone concentration using the visible photo absorption method by employing the experimental structure described as a block diagram in Figure 4. The absorption cell is made of stainless steel tube has an inner diameter and light path lengths of 0.8 cm and 50 cm respectively [23]. An orange LED and photo diodes at both ends of the cell functioned as a light source and photo detector

respectively. The LED was driven with a dc voltage of 15 V through a 560-Ω resistor

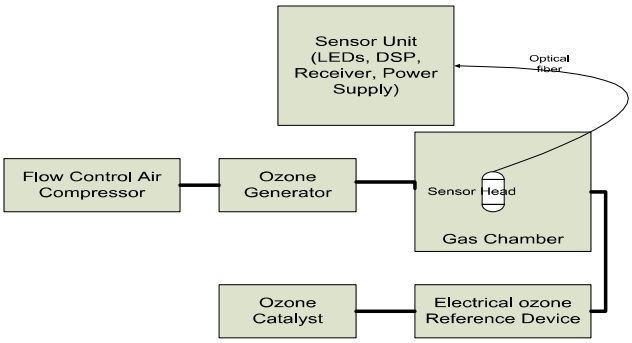

Figure 3: Schematic of the ozone measurement setup with ozone generator and ozone reference device (Redrawn [6]).

The photo current of the PD was amplified and detected using a current-to-voltage converter implemented by an operational amplifier [23]. The output voltage of the converter was measured by a 5.5-digits digital multi-meter. Ozone was produced using a piezoelectric transformer (PT)-based ozone generator by feeding 99.9%-grade oxygen [23].

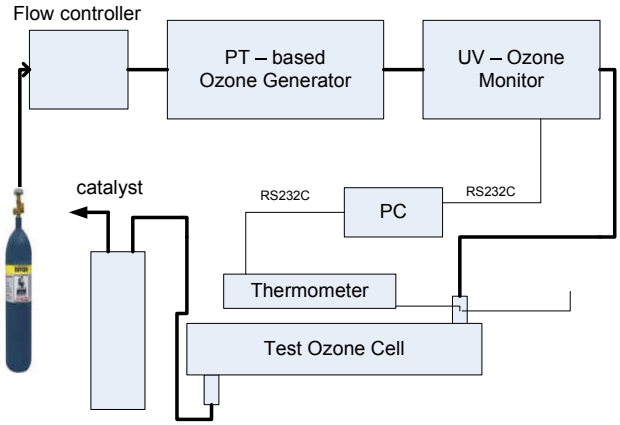

Figure 4: Experimental setup (Redrawn [23]).

The generated ozone enters the test absorption cell through an UV ozone monitor as a known standard to calibrate the ozone concentration. A thermistor was used for temperature measurements inside the absorption cell; while they controlled the ozone concentration by varying the applied voltage for the PT and the gas flow rate [23].

S. O'Keeffe *et al* [24] used an extrinsic sensor which is based on an open path sensing method. Since the set up was made to measure ozone concentrations both in the visible and UV region, the optical fibre sensor set-up consists of two fibres; premium grade optical fibre assemblies, from Ocean Optics for the UV region and PMMA based plastic optical fibres, supplied by Optoelectronic Manufacturing Corporation for visible region. Both fibres were terminated using SMA connectors, and connected to collimating lenses at each end of the aluminium gas cell [24]. These fibres were connected to a light source and a read fibre, which was also connected to a spectrometer. Ozone gas was generated from medical grade oxygen using the OzoneLab- OL80A/DLS ozone generator. The system used DH-2000 deuterium tungsten halogen as light source. A linear variable filter was used to obtain a balanced spectrum within the wavelength region required for the absorption measurements [24]. Other components for the experiment are the S2000-TR multi-channel fibre Optic spectrometer from Ocean Optics used to spectrally resolve and detect the fibre transmission; notebook PC with lab view installed for the display of the spectrum; IN USA - Mini-HiCon high concentration ozone monitor for measuring ozone flowing through the cell based on UV absorption at 254 nm [24]. The whole set up is illustrated pictorially in Figure 5.

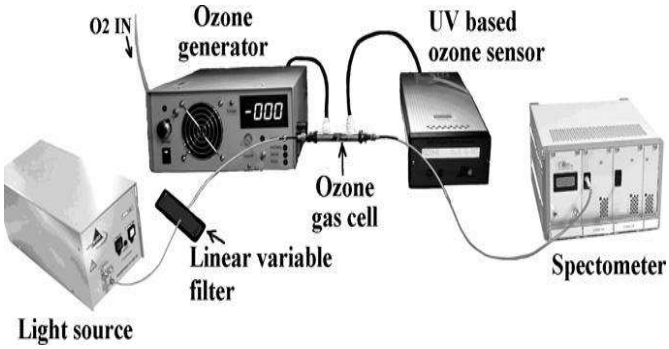

Figure 5: Experimental set-up to monitor ozone gas concentrations (from O'Keeffe, S. et al, 2007)

A fast response cavity enhanced ozone monitor based on Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBB-CEAS) system proposed A. L. Gomez and E. P. Rosen [25], consists of: a UV source/detection, measurement cells, a flow handler, and an ozone generation/ neutralization components [25]. A band pass filter (Semrock: 252–268 nm) was used in guiding the light from the UV and a 70T /30*R* thin plate dielectric beam splitter was used for light splitting. The system had 1.6mm^2 SiC as a light detector while an SRS-570 low noise current amplifiers were used in amplifying the detector signals [25]. A data acquisition program written in Lab view with the aid of a National Instruments DAQ was used to record the detector signal. The sample gases for the experiment were drawn through the system using a diaphragm pump. Monitoring and regulation of the gas flow was achieved with a Swagelok ball valve and a

Matheson flow gauge respectively [25]. While ozone gas was generated by flowing air through a home-built aluminium reaction cell, an inline canister of high surface area granular carbon was used by as ozone neutralizer [25].

Figure 6 shows a block diagram of a work by J. Malicet *et al* [20]. The scheme consists of Jobin-Yvon THR 1500 or HR 640 spectrometer as a source which gave light radiations that was channelled through an absorption cell on a photomultiplier-Hamamatsu R 925 [20].

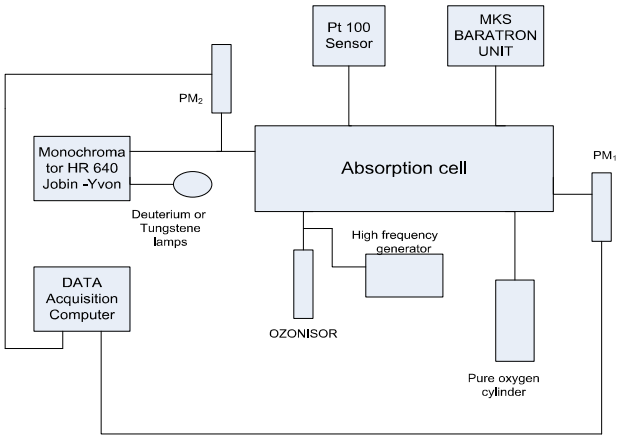

Figure 6: Experimental scheme (redrawn from [20])

Another photomultiplier located behind a semi-reflecting strip was used in achieving radiation stability at the exit of a monochromator. Light signals from detector were acquired and analysed with the aid of a PC. MKS baratron manometer was used in measuring the pressure of gaseous mixture in the cell while a two-stage cryostat (MATON) was used in regulating the temperature [20]. A cryostat was connected to a double-walled absorption cell by a methanol circulation for the purpose of heat exchange. Thermal losses were kept minimal while ambient vapour condensation prevented, by maintaining vacuum at each end of the absorption cell and the system by a 5-cm layer of closed cells foam. High-precision platinum sensors were also set along the cell for temperature control [20].

IV. PROPOSED EXPERIMENTAL STRUCTURES

Based on this review, we have considered few techniques and mechanisms that can be applied in ozone sensing. As we are concern with sensor's sensitivity, the cavity ringdown (CRD) technique which can increase the path length up to kilometers range have been selected. This is according to the work by Mulrooney, (Mulrooney, *et al.*, 2007) which showed that the resolution of gas sensor can be improved by extending the length of optical path. A proposed experimental structure for ozone sensing utilizing CRD technique in the visible region is illustrated in Figure 7. Ozone is generated and fed into the cavity cell via the ozone monitor and exited via the ozone neutralizer; the light source emits visible ray into the cavity which interacts with the ozone and is afterward received by a suitable detector which forwards the signal via a data acquisition card (DAQ) to a PC for analysis with the aid of LabVIEW soft ware.

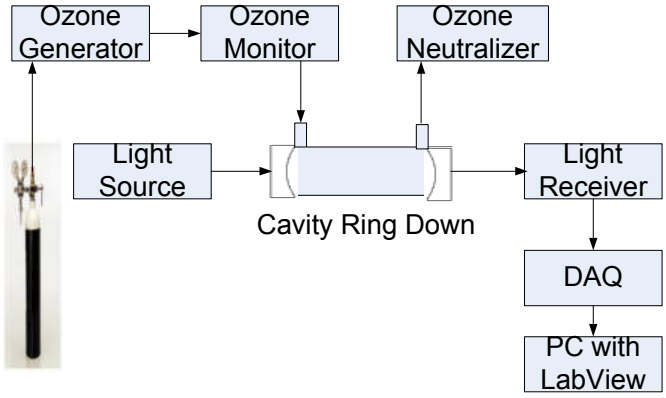

Figure 7: Proposed diagramme for ozone gas sensor

V. CONCLUSION

The basic components for an experimental structure for ozone gas detection include: ozone generation, monitoring and neutralization components; light sources detectors, and amplifiers; gas cell chamber and all its accessories, thermometers and barometers, data acquisition components, fibre cable and couplers, optical lenses and optical mirrors. The structures overviewed above utilized assorted components with some of them having their limitations. As such, we have come out with a proposed experimental setup which can be used for ozone detection using CRD technique. The proposed setup is to be based on visible light wave application, particularly at 603nm wavelength.

VI. ACKNOWLEDGMENT

The authors would like to thank Universiti Teknologi Malaysia (UTM) for supporting this research work under Research University Grant Scheme, grant no: 05J60 and Nigerian University Commission for the financial support giving inform of Tertiary Education Trust Fund (TET-Fund).

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