Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 125 (2007) 372–378
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

# An optical fibre based ultra violet and visible absorption spectroscopy system for ozone concentration monitoring

S. O'Keeffe*, C. Fitzpatrick, E. Lewis

*Department of Electronic & Computer Engineering, University of Limerick, Ireland*

Received 12 October 2006; received in revised form 13 February 2007; accepted 13 February 2007
Available online 17 February 2007

**Abstract**

The use of optical fibres for the measurement of ozone based on the optical absorption of UV light at 254 nm and visible light at 600 nm is investigated and tested. Sensing in the UV region allows for highly sensitive detectors due to its high absorption in that region. The visible region has a significantly lower absorption of ozone and so it is possible to monitor high ozone concentrations. Calculations based on the Beer–Lambert law are presented to demonstrate the high resolution of the UV based sensor in determining the concentration of ozone in the range of 0–1 mg/l and the ability of the visible based sensor to measure high concentrations over a wide range of 25–126 mg/l.


*Keywords:* Optical fibre sensing; Gas sensing; Ozone; Absorption spectroscopy

## 1. Introduction

The use of ozone within industry has increased significantly in the last number of years. It has been shown to be effective against bacteria and viruses, e.g. cryptosporidium, *Escherichia coli* and Legionella [1–3], and as such is used widely in the sterilisation of water supplies, the sterilisation of contaminants in controlled air supplies and also in the environmental packaging of food products. With this increase in the use of ozone, there is a greater demand for an accurate, low cost ozone monitoring system. Three generic types of ozone sensors exist on the market today namely electrochemical sensors [4], semiconductors [5] and optical sensors based on absorption in the UV region [6]. Current electrochemical sensors have very short lifetimes, typically 3–4 weeks, at high ozone concentrations and are often bulky and very expensive. One of the main problems associated with semiconductor sensors is that they are unsuitable for use in harsh environments. Ozone is often produced in electromagnetically harsh environments using electrical discharges or novel techniques such as high power microwave plasma ultra-violet lamps [7]. This can render conventional semiconductor detectors useless due to the intense electromagnetic fields in their proximity. Although they are low in cost, MOS ozone sensors are extremely sensitive to particulate interference such as smoke and are thus unreliable over long periods in industrial environments. Current commercially available optical sensors are based on monitoring the absorption due to ozone in the UV region. Although these ozone sensors offer good long-term stability and selectivity, they are very expensive due to the component costs when measuring in the UV region. Many also use mercury discharge tubes to generate the UV, which is extremely hazardous to human health if damaged or broken. This is obviously particularly undesirable in food and water treatment applications. Additionally, UV causes a breakdown in ozone to molecular oxygen and oxygen free radicals, which is undesirable in an electrical sensing system. However, due to the high absorption by ozone in the UV region, sensing in this region offers highly sensitive ozone measurement systems. There are also some reported optical fibre sensors. For example, silica core optical fibres have been demonstrated as ozone sensors, between 0.4 and 7 mg/l, based on evanescent wave absorption in the UV region [8].

The work presented here investigates the use of optical fibres for the measurement of ozone, based on its optical absorption in the UV and visible region. The most significant feature of an optical fibre sensor is that the information is transmitted using light signals as opposed to electrical signals. Consequently, optical fibres are immune to electrical and electromagnetic interferences. Their ability to remotely monitor ozone concentrations

* Corresponding author.
*E-mail address:* sinead.okeeffe@ul.ie (S. O'Keeffe).

0925-4005/$ – see front matter 
doi:10.1016/j.snb.2007.02.023

is also an advantage, as the sensor can be placed away from the control electronics. These features make optical fibres highly suitable for use in harsh environments. The oxygen free radicals present during the ozonation process have a more corrosive effect on metallic objects whilst being much more passive to dielectric materials, making optical fibres the ideal basis for an ozone sensor. Further advantages include its small size, durability and weight. By using solarisation-resistant silica-core optical fibres it is possible to monitor UV absorption due to ozone in the UV region, where the fundamental absorption of ozone occurs. This allows for the development of an ozone sensor with good sensitivity.

By sensing in the visible region, PMMA based plastic optical fibres can be used, resulting in the fabrication of low cost, manageable sensors can be realized. PMMA based optical fibres offer a number of advantages over standard silica fibres. Due to the large fibre cross-section of plastic optical fibres, 1 mm core, connecting to the light source and detector is non-problematic. This means that, in contrast to silica-core optical fibres, no expensive precision components are required for centring the fibres. The large fibre core diameter also means that minor contamination, e.g. dust on the fibre end face, does not result in the complete failure of the sensor system due to its large core diameter. Consequently, fibres can be connected on site in industrial environments with relative ease and without affecting the system. PMMA is also easy to cut, grind and melt and so an uncomplicated process, requiring relatively little time, for processing the end faces is necessary to achieve a clean and smooth surface. Plastic optical fibres are also considered easier to handle when compared to glass optical fibres. Glass fibres tend to break when bent around a small radius, which does not occur with plastic fibres. These fibres are extremely low in cost when compared with glass optical fibres. The properties of PMMA plastic optical fibres also results in relatively economical connectors for the system, which further contributes towards a low cost solution [9]. Sensing in the visible region of the spectrum also results in less breakdown of ozone when compared with monitoring in the UV region. The use of visible LEDs to monitor ozone has previously been demonstrated [10], however the use of polymer optical fibres will allow for remote real-time monitoring, which is important when monitoring high ozone concentrations. By sensing in the visible region, using PMMA plastic optical fibres, fabrication of low cost, easily applicable sensors, based on visible LEDs and photodiodes is possible. The sensitivity of the sensor based on absorption in the visible region is lower than UV based sensors, due to the lesser absorption in this region. However the sensitivity achieved is sufficient for many industrial processes where high ozone concentrations are generated.

## 2. Optical absorption by ozone

Much work has been done in the past to determine the absorption cross-section, given by the symbol $\sigma$, of ozone in the visible and UV regions of the spectrum [6,11–13]. Those determined in the ultra-violet region by Inn and Tanaka [12] and in the visible region by Vigroux [13] are considered to be the most accurate

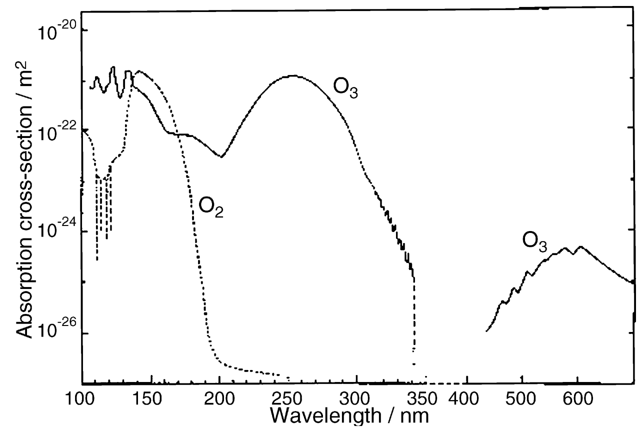


Fig. 1. The variations with wavelength of the absorption cross-sections of ozone. From Campbell, I. "Energy and the Atmosphere: A Physical–Chemical Approach" [15].

[6,14]. Ozone absorbs UV and visible light in four main regions known as the Hartley band (spectral region: 200–310 nm), the Huggins band (spectral region: 310–375 nm), the Chappius band (spectral region: 375–603 nm), and the Wulf system (spectral region: beyond 700 nm). From the graph of the absorption cross-section, shown in Fig. 1, a high absorption region for ozone can be seen between 230 and 320 nm, with peak absorption found at 253.7 nm ($\sigma_{254} = 114.7 \times 10^{-21}$ m$^2$). However, there is also a lesser absorbing region between 550 and 650 nm, which peaks at 603 nm ($\sigma_{603} = 5.18 \times 10^{-25}$ m$^2$). A negligible amount of absorption is observed in the 350–420 nm region, where the deep minimum is found at 377.5 nm ($\sigma_{377} = 4.4 \times 10^{-29}$ m$^2$) [14].

A variation of the Beer–Lambert law using the Decadic absorption coefficient, given by the symbol $\varepsilon$, is shown in Eq. (1):

$$\frac{I_L(\lambda)}{I_0(\lambda)} = 10^{-\varepsilon c L} \quad (1)$$

where $I_L(\lambda)$ is the intensity of light of wavelength $\lambda$ transmitted through path length $L$ of the medium containing concentration $c$ of the absorbing species expressed in moles per unit volume. $I_0(\lambda)$ is the incident intensity. The units of $\varepsilon$, expressing $c$ in mol dm$^{-3}$ and $L$ in dm, will be dm$^2$ mol$^{-1}$ [15]. From this we can develop an equation to calculate the ozone concentrations from the intensity values obtained from the spectrometer:

$$C_{O_3} = \frac{-48 \times 10^3}{\varepsilon L} \log\left(\frac{I_L(\lambda)}{I_0(\lambda)}\right) \quad (2)$$

$48 \times 10^3$ is the molar mass of ozone in mg/mol, which expresses the ozone concentrations in mg/l.

## 3. Experimental set-up

An extrinsic sensor is used during this work and is based on an open path sensing method. The optical fibre sensor set-up consists of two fibres. For measuring in the UV region Premium-grade optical fibre assemblies, from Ocean Optics [12], were used as these had better transmission in the UV region when compared with the PMMA based plastic optical fibres, supplied