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Electrochemical ozone sensors: A miniaturised alternative for ozone measurements in laboratory experiments and air-quality monitoring

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ABSTRACT

Ozone (O_3) measurements are a critical component of air quality management and many atmospheric chemistry laboratory experiments. Conventional ozone monitoring devices based on UV absorption are relatively cumbersome and expensive, and have a relative high power consumption that limits their use to fixed sites. In this study electrochemical O_3 sensors (OXB421, Alphasense) were used in a miniaturised O_3 measurement device combined with LabJack and Labview data acquisition (DAQ). The device required a power supply of 5 V direct current (VDC) with a total power consumption of approximately 5 W. Total weight was less than 0.5 kg, low enough for portable *in situ* field deployment. The electrochemical O_3 sensors produced a voltage signal positively proportional to O_3 concentrations over the range of 5 ppb–10 ppm. There was excellent agreement between the performances of two O_3 sensors with a good linear coefficient (R^2 = 0.9995). The influences of relative humidity (RH) and gas sample flow rate on sensor calibrations and sensitivities have been investigated separately. Coincident calibration curves indicate that sensor performances were almost identical even at different RHs and flow rates after a re-zeroing process to offset the sensor baseline drifts. Rapid RH changes (~20%/min) generate significant and instant changes in sensor signal, and the sensors consistently take up to 40 min to recover their original values after such a rapid RH change. In contrast, slow RH changes (~0.1%/min) had little effect on sensor response. To test the performance of the miniaturised O_3 device for real-world applications, the O_3 sensors were employed for (i) laboratory experiments to measure O_3 loss by seawater uptake and (ii) air quality monitoring over an 18-day period. It was found that ozone uptake by seawater was linear to the volume of linoleic acid on a sea surface microlayer and the calculated uptake coefficients based on sensor measurements were close to those from previous studies. For the 18-day period of air quality monitoring the corrected data from the O_3 sensor was in a good agreement with those obtained by reference UV O_3 analyser with an r^2 of 0.83 (n = 8502). The novelty of this study is that the electrochemical O_3 sensor was comprehensively investigated in O_3 measurements in both laboratory and ambient air quality monitoring and it can to be a miniaturised alternative for conventional O_3 monitoring devices due to its low cost, low power-consumption, portable and simple-conduction properties.

1. Introduction

Ozone sensors are a technology for O_3 detection that are characterised as being compact in size, low cost, low power and fast response. Most commercially available O_3 sensors use either electrochemical sensing principles or are based on semiconductor O_3 sensors. Such O_3 sensors have in principle sufficient sensitivity to be used in the ppb-range as air quality monitors for outdoor air. The low cost nature of O_3 sensors allows them to be potentially deployed in denser networks of measurement, giving improved insight into human exposure. The low cost of sensors, as compared to traditional instruments, can enable a democratization of air quality observations to the general public and raise environmental awareness of air pollution. O_3 measurement is a critical component of not only air quality management but is also a key

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part of laboratory experiments in atmospheric chemistry, for example for the study of the interaction of O_3 with various chemicals including on surfaces. To date, the most commonly employed ozone monitoring devices are photometric ozone instruments based on UV absorbance, which require high sampling gas flow (>1 L/min), are high power-consuming, cumbersome and expensive. On some occasions the measurement of gaseous ozone using conventional instrumentation is impossible, for example during smog chamber simulation experiments where gas volumes are limited or cannot be supplied at flow rates high enough for UV instruments. Under such situations several optical methods including cavity ring-down spectroscopy (CRDS) and differential optical absorption spectroscopy (DOAS) can be employed for *in situ* ozone detection [1,2]. However, these optical methods are highly specialized making them unavailable for many laboratories. Air quality monitoring networks also typically use expensive measurement apparatus, usually in a fixed location, and equipped with a permanent ac power supply and other secure facilities. However, the densities of monitoring networks are relatively sparse for specific research such as personal exposure studies or mapping the fine scale spatial distribution of O_3 concentrations across large and complex cities [3,4].

The recent development of miniaturised gas sensor technologies has created the opportunity to develop cheap and simple techniques for the rapid and sensitive *in situ* O_3 measurement without requirement for high gaseous sample flows in laboratory experiments. Compared with above three conventional O_3 monitoring devices O_3 sensors are much lower in cost (<$200), have lower power consumption (<5 W), are lighter in weight (<10 g), whilst maintaining high time-resolution (1 s) of measurement. For air quality monitoring, gas sensor techniques can potentially realise low cost flexible networks at high spatial resolution, reducing air pollution monitoring costs and increasing coverage especially in remote areas [5,6]. Cost-efficient ozone sensors based on gas-sensitive semiconducting oxide technology were previously deployed for accurate surface O_3 monitoring in a high spatial density in a valley of New Zealand [3]. Several portable gas sensors was employed to capture the spatial variability of traffic-related air pollution such as O_3 and NO_2[4]. Due to their portability and low power consumption, other atmospheric gas sensors have been utilised on several specific occasions such as during aircraft measurements and for personal exposure determinations. A custom, compact, laser-based methane sensor was developed and coupled to an unmanned aerial vehicle, which was flown around a compressor station to quantify fugitive methane emissions [7]. A black carbon sensor combined with a smartphone was employed to continuously measure black carbon levels to estimate personal exposures related to residential air pollution and commuting based on personal location and physical activity level [8]. Electrochemical sensors have been employed for monitoring ambient air quality on several occasions [9–14]. However, there are a wide range of sensor types and brands and the sensor performances are still not well understood or comprehensively tested [12,15].

In this paper miniaturised electrochemical O_3 sensors were used in a portable O_3 measurement device combined with an "in house" data acquisition system. The O_3 sensor device was evaluated at low gaseous sample flow rates (0.3 L/min) to study O_3 uptake coefficients of the seawater surface microlayer with polyunsaturated fatty acids, which react with ozone. The performances of the O_3 sensor for ambient air quality monitoring was also investigated during an 18-day summer field campaign, where the sensor response was compared with a reference UV O_3 monitor (Thermo 49C UV absorption ozone analyser). The influences of relative humidity (RH) and gas flow rate on sensor performances were investigated independently.

2. Experimental

2.1. Commercial O_3 sensors

Two commercial O_3 sensors (Model OX-B421), their support circuit boards and their gas hoods for individual sensor were purchased from Alphasense, UK. The O_3 sensor was integrated with the support circuit board and gas hood, where the circuit board, which is pre-configured for each sensor and provides a low noise and high resolution signal output, through its electrodes. The gas hood is sealed on the cap of sensor to assist sample gas contact with the diffusion barrier allowing ozone diffusion into the electrolyte. In laboratory experiment two sensors were used to measure the O_3 mixing ratios at inlet and outlet of a flow reactor, respectively (Fig. 1(b)). During air quality monitoring two sensors were compared with each other to evaluate differences between devices (Fig. 1(c)). The O_3 sensors are based on electrochemical reactions that take place within the sensor between O_3 and a certain electrolyte. The specifications of the electrochemical sensor are listed in Table 1. The O_3 sensor has a working electrode (WE), a reference electrode (RE) and a counter electrode [10]. The RE response is used to compensate for drifting of the offset zero voltage. The resulting voltage between WE and RE are the signal current from the target gas measurement. The circuit board is preconfigured for each individual sensor with fixed zero and electronic gain (sensitivity, unit: voltage/ppb) and also provides a buffered voltage output from both the WE and RE with lowest noise. The gas concentrations measured by such electrochemical sensors can be calculated according to the following equation.

$$\text{gas concentration (ppb)} = \frac{(WE_i - WE_0) - (RE_i - RE_0)}{\text{Sensitivity}} \quad \text{(E1)}$$

In the above equation WE_0 and RE_0 are the offset voltages of the WE and RE, respectively, which are used to compensate for the sensor specific offset voltage of each sensor. These values were determined against dry zero air. WE_i and RE_i are the output voltages of the WE and RE during the measurement of the gaseous sample.

The sample gas temperature, pressure and humidity were measured in line using a LM35 temperature sensor (Texas Instruments), MPX4200A absolute pressure sensor (Freescale Ltd.) and an HIH-4000-001 humidity probe (Honeywell), respectively. During the analysis periods, in line gas temperature and pressure were consistent, $20.2 \pm 0.7\,^{\circ}C$, 1.0003 ± 0.0009 bar respectively, minimising their effects upon the sensors.

2.2. Data acquisition

All sensors were connected through LabJack data-acquisition (DAQ) device (U6 Series, LabJack Corporation, USA) to our LabVIEW in-house designed DAQ software. Through this software we monitor the output voltage of the sensor and convert the voltage signals into gas concentrations. The data acquisition rate was 1 Hz (averaged to 1 min intervals for laboratory measurement and 5 min intervals for ambient O_3 monitoring, respectively).

The control software for the DAQ system was written using LabVIEW software (LabVIEW 2012, National Instrument, USA). The host PC displays the user interface including four tabs such as sensor control, sensor data, diagnostic data etc., by which the user can specify the data acquisition rate, the file-path of data saving, auto-zeroing the voltage of WE and RE, and the sensitivity setting (Voltage/ppb). Once deployed, the control software runs autonomously and the O_3 concentrations are displayed continuously on the tab of sensor data. All data are saved automatically during the sensor working period including O_3 concentration (ppb), voltages of WE and RE, RH, temperature, air pressure, respectively.