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Pang, Xiaobing, Shaw, Marvin D. orcid.org/0000-0001-9954-243X, Lewis, Alastair C. orcid.org/0000-0002-4075-3651 et al. (2 more authors) (2017) Electrochemical ozone sensors:A miniaturised alternative for ozone measurements in laboratory experiments and air-quality monitoring. SENSORS AND ACTUATORS B-CHEMICAL. pp. 829-837. ISSN: 0925-4005

<https://doi.org/10.1016/j.snb.2016.09.020>

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

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ARTICLE INFO

Article history:

Received 9 May 2016

Received in revised form 28 July 2016

Accepted 6 September 2016

Keywords:

Ozone sensor

LabVIEW

Relative humidity

Ozone uptake

Air quality monitoring

ABSTRACT

Ozone (O₃) 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 O₃ sensors (OXB421, Alphasense) were used in a miniaturised O₃ 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 O₃ sensors produced a voltage signal positively proportional to O₃ concentrations over the range of 5 ppb–10 ppm. There was excellent agreement between the performances of two O₃ 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 ($\sim 20\%/min$) 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 ($\sim 0.1\%/min$) had little effect on sensor response. To test the performance of the miniaturised O₃ device for real-world applications, the O₃ sensors were employed for (i) laboratory experiments to measure O₃ 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 O₃ sensor was in a good agreement with those obtained by reference UV O₃ analyser with an r^2 of 0.83 ($n = 8502$). The novelty of this study is that the electrochemical O₃ sensor was comprehensively investigated in O₃ measurements in both laboratory and ambient air quality monitoring and it can be a miniaturised alternative for conventional O₃ monitoring devices due to its low cost, low power-consumption, portable and simple-conduction properties.

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1. Introduction

Ozone sensors are a technology for O₃ detection that are characterised as being compact in size, low cost, low power and fast response. Most commercially available O₃ sensors use either elec-

trochemical sensing principles or are based on semiconductor O₃ sensors. Such O₃ 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 O₃ 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. O₃ 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 were 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.

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

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 ± 0.7 °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.

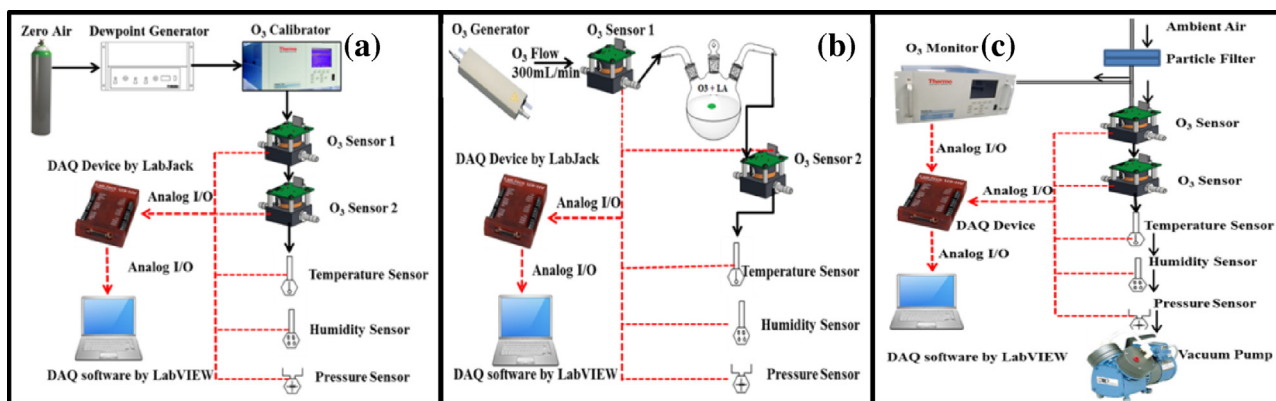


Fig. 1. Schematic diagrams of the experimental setup for O₃ sensor performance tests. (a) calibration setup for O₃ sensors, (b) O₃ uptake by seawater with linoleic acid (LA) on its surface, (c) ambient O₃ measurement by two O₃ sensors.

Data files are saved in a LabVIEW format which can be easily converted to .txt or .csv data for future use.

2.3. Calibration

All O₃ sensors were initially zeroed using zero grade air. All O₃ sensors were initially zeroed using zero grade air, which is produced by mixing pure oxygen (20%) and pure nitrogen (80%) and provided by BOC, UK and then calibrated under a series of O₃ standard gases to ensure their accurate sensitivities. The experimental setup for the calibration is schematically shown in Fig. 1(a). A certified multi-gas calibrator (S6100, Environics, US) with an internal O₃ generator was used for O₃ sensor calibration. 10 ppb–1000 ppb O₃ standard gases were generated for the calibration since this range of O₃ mixing ratios cover O₃ concentration in ambient air and laboratory experiment in this study. For O₃, the reference instrument was a Thermo Environmental Instruments (TEI) 49C UV absorption ozone analyser which is a United States Environmental Protection Agency (USEPA) equivalent method. Calibration of the instrument was carried out using a TEI Primary Ozone standard, which itself is certified yearly by the UK National Physical Laboratory (NPL). The instrument provided minute averaged data.

During calibration the observed raw concentrations on exposure to the O₃ standard gas (defined as C_{raw}) are based on the initial sensitivities (defined as S_{initial}), which is provided by the manufacturer according to Eq. (E1). The C_{raw} is a little different from the true concentration (defined as C_{true}), which was directly read from the O₃ calibrator. Through the (E1) equation the calibrated sensitivity of sensor (defined as $S_{\text{calibrated}}$) can be calculated and obtained based on Eq. (E2).

$$S_{\text{calibrated}} = \left(\frac{C_{\text{raw}}}{C_{\text{true}}} \right) * S_{\text{initial}} \quad (\text{E2})$$

The $S_{\text{calibrated}}$ was then input into the LabVIEW DAQ software to replace the S_{initial} and the O₃ sensor then reports data calibrated to the reference gas. All O₃ sensors were subsequently zeroed at the flow of zero grade air, which is produced by mixing pure oxygen (20%) and pure nitrogen (80%) and provided by BOC, UK, and calibrated weekly. To investigate the effect of RH on sensor performance a dew-point generator (DG3, Michell Instruments, UK)

was employed to produce various RH sample gases in the range of 15%–85% RH, which covers the main RHs in ambient air.

2.4. Effect of RH and flow rate on sensor calibrations and sensitivities

Relative humidity (RH) and flow rate are two of essential factors for sensor performance that can cause variations in sensor sensitivity, sensor gain and sensor baseline [16]. In this study the sensor calibrations were conducted on various RHs (15%, 45%, 60%, 75% and 85%, respectively) and the flow rates of gas sample (300, 500, 700, and 1000 mL/min, respectively) and the variations of sensor sensitivity were investigated simultaneously. The O₃ sensors were firstly calibrated with O₃ standard gases at eight mixing ratios including 0, 60, 120, 180, 240, 320, 480, and 960 ppb, respectively, which were produced by the O₃ generator.

2.5. Sensor applications: O₃ uptake and air quality monitoring

To evaluate the sensor performance, the O₃ sensors were applied to quantitatively determine O₃ in both laboratory experiments and air quality monitoring separately. In the laboratory, O₃ sensors were applied to measure ozone uptake by seawater through the determination of O₃ at the inlet and outlet of a reaction vessel, where O₃ (210 ppb at 300 mL/min) reacted heterogeneously with linoleic acid at the surface microlayer of seawater (200 mL). The O₃ concentration difference between two positions in the reaction vessel was assumed to be exclusively due to O₃ loss through surface reaction with linoleic acid, which can be utilised to calculate the O₃ uptake coefficient. The detailed experimental setup is schematically shown in Fig. 1(b) and the experimental conditions for O₃ uptake experiment are listed in Table 2.

For air quality monitoring an O₃ sensor was employed to monitor ambient O₃ over an 18-day period (from 7th to 25th August 2015) alongside reference measurements. The sampling site is located in the campus of University of York, UK and the air sample was drawn from a building roof (10 m above ground level). Ambient air was introduced to the gas hood of the O₃ sensor from the main sample inlet using a stainless steel diaphragm metal bellows pump (Senior Aerospace, MB302) at a flow rate of 1 L/min. The air sample flow passed simultaneously into a UV photometric O₃ anal-

Table 1
Specifications of O₃ sensor employed in this study.

Sensor model	Size (L × W × H) ^a	Weight (g) ^a	Power supply (VDC)	Linear Range (ppm)	Noise (ppb)
O ₃ , OX-B421	4.5 × 4.0 × 4.0 cm	100	5	0–20	15

^a The size and the weight are measured based on the sensor, individual sensor board, gas hood, and mounting kits in a whole.

Table 2
Experimental conditions for experiments measuring O₃ uptake by seawater and for air quality monitoring.

Experiment	Flow Rate (L/min)	RH (average) (%)	Temp. (average) (°C)	Time Resolution (min)
O ₃ uptake	0.3	70–80 (76.2)	20–22 (21.2)	1
air O ₃ monitoring	1.0	40–90 (59.6)	12–26 (17.1)	5

yser (Model 49C, Thermo Electron Corporation, USA) for reference measurement. Sensor and reference measurement data were averaged to 5 min intervals and evaluated over the 18-day period. The detailed experimental setup is schematically shown in Fig. 1(c) and the experimental conditions are listed in Table 2.

The selectivity of this electrochemical O₃ sensor can be affected by cross interferences from other gases including NO₂, NO, and RH in ambient air when the O₃ sensor was employed in air quality monitoring [15]. The interferences have observable effects on the WE voltage but no influences in AE voltage of the sensor during the experiments. The corrected WE voltage of O₃ sensor during air quality monitoring can be calculated by the following Eq. (E3).

$$WE_{correct} = WE_{initial} - [NO_2] \times NO_{2response} - [NO] \times NO_{response} - RH \times RH_{response} \quad (E3)$$

In the above equation $WE_{correct}$ and $WE_{initial}$ are the corrected WE voltage and initial WE voltage of O₃ sensor. $NO_{2response}$, $NO_{response}$, and $RH_{response}$, are the WE responses (mV ppb⁻¹) due to the presence of NO₂, NO, and RH in ambient air, respectively, which were calculated and listed in our previous study [15]. During the 18-day period of air quality monitoring the ambient concentrations of NO₂ and NO were monitored by a single channel chemiluminescence instrument (Air Quality Design Inc., USA) [17]. The corrected WE voltages obtained from E3 were employed to calculate actual O₃ concentrations through Eq. (E2).

3. Results and discussions

3.1. Relationship between output voltage of O₃ sensor and O₃ concentration

The operational theory of electrochemical gas sensors is that the target gas diffuses into the sensor through a capillary diffusion barrier to the working electrode where it is oxidized or reduced [16]. This electrochemical reaction results in an electric current that passes through the external circuit. The output voltage from the sensor is linearly proportional to the gas concentration in a certain range. In this study the output voltages of the O₃ sensor were

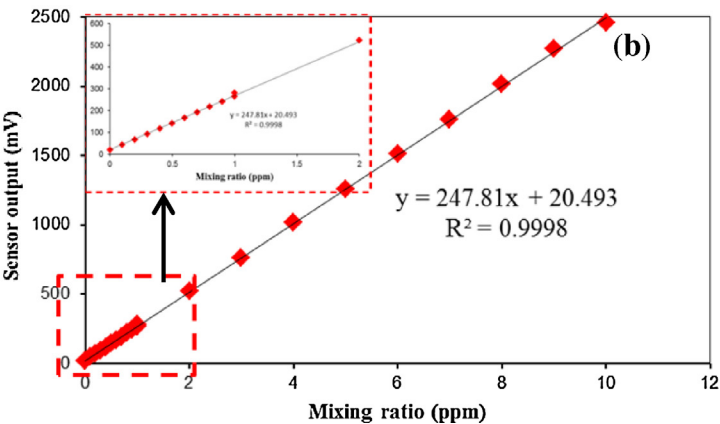
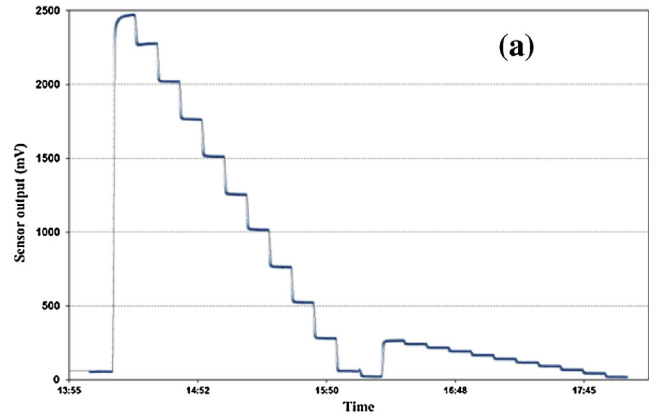


Fig. 2. (a): Relationship of O₃ sensor output voltage and O₃ concentration varying from 100 ppb to 10 ppm; (b): A good linear relationship can be observed between sensor output voltage and O₃ concentrations with a linear coefficient (R^2) of 0.9998. Experimental conditions: RH: 60 ± 5%, flow rate of sample gas: 300 mL/min, temperature: 20 °C.

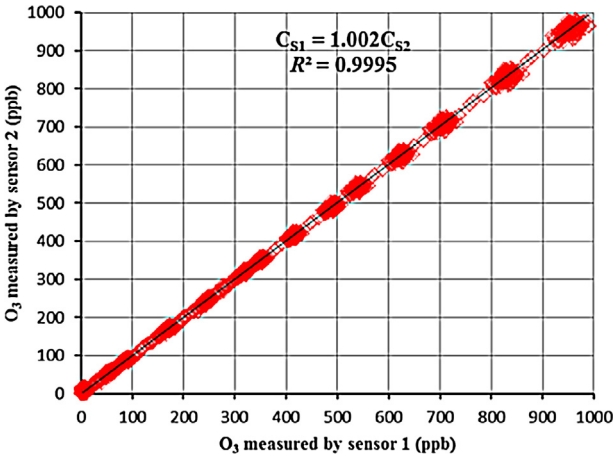


Fig. 3. Comparison between sensor 1 and sensor 2 for O₃ measurements from 0 to 998 ppb. A good agreement is found between two O₃ sensors with a linear coefficient ($R^2 = 0.9995$, $n = 6257$). Experimental conditions: RH: 60 ± 5%, flow rate of sample gas: 300 mL/min, temperature: 20 °C.

observed to linearly increase from 43 mV to 2500 mV as O₃ concentration increased from 100 ppb to 10 ppm (Fig. 2a). A significant linear relationship with a coefficient (R^2) of 0.9998 can be observed between the sensor output voltage and O₃ concentration (Fig. 2b).

3.2. Inter-comparison of sensor performance

In this study two O₃ sensors were used to measure O₃ concentrations at the inlet and outlet of a reaction vessel to measure the ozone loss. It is crucial that, once calibrated, the two sensors can perform consistently with respect to one another. Two O₃ sensors were utilised to simultaneously detect a series of O₃ standard gases from 4.0 ppb to 975 ppb. The performances of two sensors to O₃ standard gases were compared and shown in Fig. 3. It can be seen that the performances of two sensors correlate well with a linear coefficient (R^2) of 0.9995 ($n = 3040$) when O₃ mixing ratios varied in the range of 10 ppb–1000 ppb. It should be noted that the limit of detection of the sensor is 5 ppb, which can explain why the perfor-

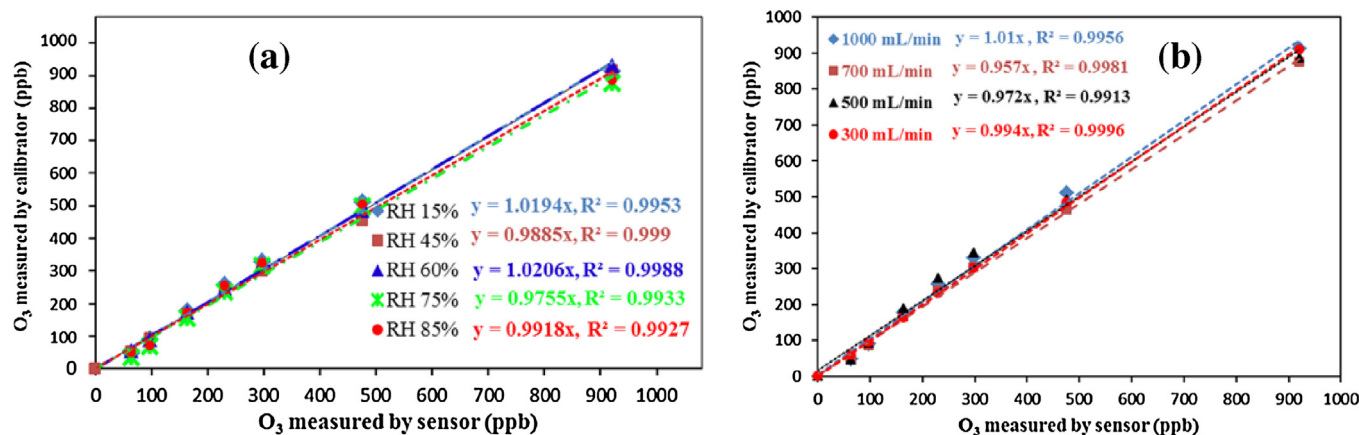


Fig. 4. (a) Sensor calibrations under different relative humidity (RH). Experimental conditions: flow rate of sample gas: 500 mL/min, temperature: 20 °C; (b) Sensor calibrations under various gas flow rates. Experimental conditions: RH: 60 ± 5%, temperature: 20 °C.

manances of two sensors were inconsistent to the gas samples with O₃ mixing ratios below to 5 ppb.

3.3. Effects of relative humidity and flow rate on calibrations

The O₃ sensors had been calibrated under five different RHs including 15%, 45%, 60%, 75% and 85%, respectively. The sensor baseline drifted after each RH change and the sensor was zeroed to offset the drift of baseline before the calibration at each RH. The sensor was then calibrated under eight different O₃ mixing ratios. A calibration curve at each RH was set up between the values of O₃ concentration obtained by the sensor and the reference values provided by the O₃ generator. Those calibration curves under various RHs are almost coincident each other (Fig. 4a), which indicates the sensor performances were almost identical at different RHs. The maximum derivation (4.6%) of the slopes of calibration curves, which was found between those of RH 60% and RH 75%, may be due to the random variability of measurements. This result demonstrates that the performances of the O₃ sensor can be consistent at different RHs after a zeroing process to offset the baseline drifts due to RH change. Accuracies and precisions of sensor performances were listed in Table 3 at various RHs to different O₃ mixing ratios. The accuracies at most measurements are below to 15% and the precisions are lower than 5%, which indicates the performances of O₃ sensor are satisfactory in deployment.

However, the sensor performance is slightly different if the sensor was not zeroed to offset the baseline drift due to each rapid RH change. As Fig. 5(a) shows the sensor reading dramatically decreases to approximately 0 ppb from 70 ppb at the beginning of each rapid RH decrease at a rate of −20%/min and then gradually recovers to their initial value (70 ppb) after 40–60 min. In contrast if the RH rapidly increases at 20%/min, the sensor signal rapidly jumps to 300 ppb from 70 ppb and then gradually drops down to the 80–100 ppb after a balance period of 15–40 min. If the RH changes slowly, the situation of sensor response is quite different. As Fig. 5(b) shows, the sensor signals remain stable in the range of 65–75 ppb when the RH slowly decreased from 60% to 30% over six hours at a rate of 0.1%/min. As the RH further rapidly decreased from 30% to 5% in 15 min, the sensor reading significantly reduced to 0 ppb from 75 ppb and then gradually recovered to 70 ppb in 15 min at the stable RH (5%). These experiments imply that sensor performance is relatively consistent if the environmental RH varies slowly. So the influence of RH on sensor performance can be ignored if the sensor was employed for experimental gaseous samples at stable RH or for air quality monitoring under a stable weather con-

dition with slower RH ambient changes [18]. The relation between RH variation and sensor recovery time is unclear based on above experimental phenomenon.

The voltage outputs of both WE and RE were investigated during a process of RH increases in a gas sample containing the consistent O₃ mixing ratios (Fig. 6). The voltage outputs of WE and RE showed the same varying tendency, i.e. both initially increased with the increased RH and then gradually stabilised at higher values (Fig. 6). The WE voltages increased dramatically during the initial minutes of the RH change, which can explain why the O₃ sensor reading sharply rose at the beginning of the RH change. The final stabilised voltages from WE and RE can explain why the sensor reading recovered to a stable level after a 40 min period (Fig. 5a). The RH was observed to have a positive linear relationship with the voltages from WE and RE (Fig. 6c) but the slope of the calibration curve between WE and RE was a little higher than that between RE and RH. As the increase of WE voltage is higher than that of the RE voltage (Fig. 6c) the O₃ concentrations calculated by the Eq. (E1) will be higher. This result can explain why the O₃ sensor data were sometimes greater than the initial data after a RH increase in Fig. 5a.

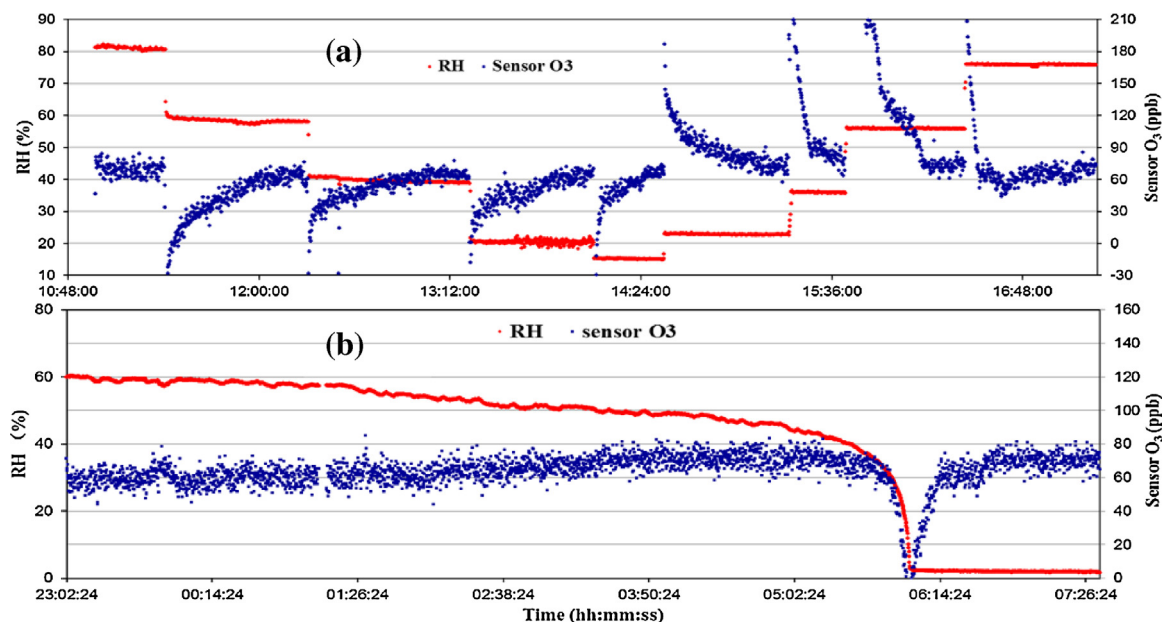
The effect of gas flow rate on O₃ sensor performance was investigated under four flow rates including 300 mL/min, 500 mL/min, 700 mL/min and 1000 mL/min, respectively. Calibrations were conducted under the four flow rates and a series of calibration curves were obtained and shown in Fig. 4b. The calibration curves indicate that the sensor data are nearly equal to those data from O₃ calibrator under the four flow rates with their slopes approaching unity varying between 0.972 to 1.01. Therefore, it can be concluded that the flow rate of sample gas has little influence on the O₃ sensor performances within this range.

3.4. Effects of relative humidity and flow rate on sensitivity

According to Eq. (E1), sensor measurements are controlled by both the sensitivity and output voltage. The effects of RH, flow rate and O₃ concentration on sensor sensitivity were separately studied. As Fig. 7(a) shows that sensor sensitivities are constant in the RH range of 15%–60% and decrease gradually as the RH further increases to 85%, at which point sensor sensitivity is equal to the 80% of those at the RH of 15%. As shown in Fig. 7(b), the sensor sensitivities were nearly stable over the whole concentration range at RHs of 85% and 75% whilst at RHs of 30% and 45% the sensitivities were stable in the range of 60–300 ppb but decreased by about 8% with the further increase of O₃ to 990 ppb. As Fig. 7(c) implies, gas flow rate has a clear negative correlation on the sensor sen-

Table 3Accuracy and precision of O₃ sensor at various RHs to different O₃ mixing ratios.

Refer. Value(ppb) ^a	15% (RH)		45%		60%		75%		85%	
	Accuracy (%) ^b	Precision(%) ^c	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision
64	−14	5	9	4	7	5	−23	5	15	4
97	−7	4	1	3	1	4	−15	6	2	4
164	7	2	5	4	3	4	−11	5	11	3
230	11	2	7	2	5	3	−5	4	6	1
298	10	1	9	1	8	2	−2	2	3	2
476	7	1	11	1	7	1	2	1	1	2
921	−1	1	0	0	2	1	−6	1	1	1

^a Reference values are the O₃ mixing ratios provided by the O₃ generator.^b Accuracy is calculated by the equation of (Sensor value – Refer. value)/Refer. value * 100%. Sensor value are the average of over 100 data.^c Precision is calculated by the equation of (Standard derivation/Sensor value * 100%).**Fig. 5.** Humidity effects on O₃ measurement by the sensors. (a): O₃ sensor responses to rapid RH changes where RH decreased from 80% to 15% and then increased from 15% to 75%. (b) O₃ sensor responses to slow RH changes where RH gradually decreased from 60% to 30% in 7 h and further decreased from 30% to 4% in 5 min. Experimental conditions: O₃ concentration in gaseous flow is 70 ppb and the gaseous flow rate is 300 mL/min.

sitivity, which decreases from 8.8×10^{-4} V/ppb at 300 mL/min to 5.2×10^{-4} V/ppb at 1000 mL/min with a pronounced decrease up to 40%.

As mentioned above, the voltages of both the WE and the RE increase with increasing RH for the gas samples in the presence of same O₃ mixing ratio (Fig. 6). The elevated output voltage due to the RH increases is actually the offset voltage rather than signal voltage from O₃ measurement. So lower signal voltage will be output after the O₃ sensor is zeroed to balance the higher offset voltages due to a RH increase. As a result, to reach the same and accurate values the sensitivity of the sensor accordingly decreases due to the lower signal output from the sensor based on Eq. (E1). The same mechanism can be used to explain why flow rate has a negative effect on the sensor sensitivity in this study.

3.5. O₃ sensors in laboratory experiments and air quality monitoring

To validate and evaluate the performance of O₃ sensors in both laboratory and field employments, we evaluated the O₃ sensors through the sensor application to study the ozone uptake by unsaturated organic acid on seawater in laboratory and to monitor ambient O₃ in a field campaign. The schematics of the two experimental setups are shown in Fig. 1(b) and (c).

Uptake of ozone by unsaturated fatty acids on microlayer in seawater is a crucial process affecting the global ozone budget and has recently drawn extensive research attention [1,19,20]. In the ozone uptake experiment two ozone sensors were used to measure the initial ozone concentration at the inlet location of reaction vessel and the final O₃ concentration at the vessel outlet. The difference between two sensor measurements is the O₃ loss by the seawater uptake. Ozone sensor performance was compared with the reference instrument and both data are consistent, which is shown in Fig. 8(a). We successively measured O₃ concentrations in the gas flows prior to the inlet of reaction vessel and from the outlet of the reaction vessel containing five artificial seawater samples (200 mL), which were prepared by dissolving sea salt into purified water to 3.5% salt mass concentration, with the additions of with 0.00, 1.25, 2.50, 3.75, and 5.0 μ L of added linoleic acid, respectively. The evolution of O₃ concentration with respect to time are displayed in Fig. 8(b). The O₃ concentration prior to the inlet of reaction vessel immediately (1 min) reached and kept at a stable level of 210 ppb after the ozone generator was turned on. In contrast, the outlet O₃ concentrations took longer to reach a stable level since O₃ was absorbed by the seawater and reacted with LA in the reaction vessel reaching equilibrium in approximately 20 min. It was observed that the ozone loss was positively proportional to the LA volume on the surface microlayer of seawater from the above experimental

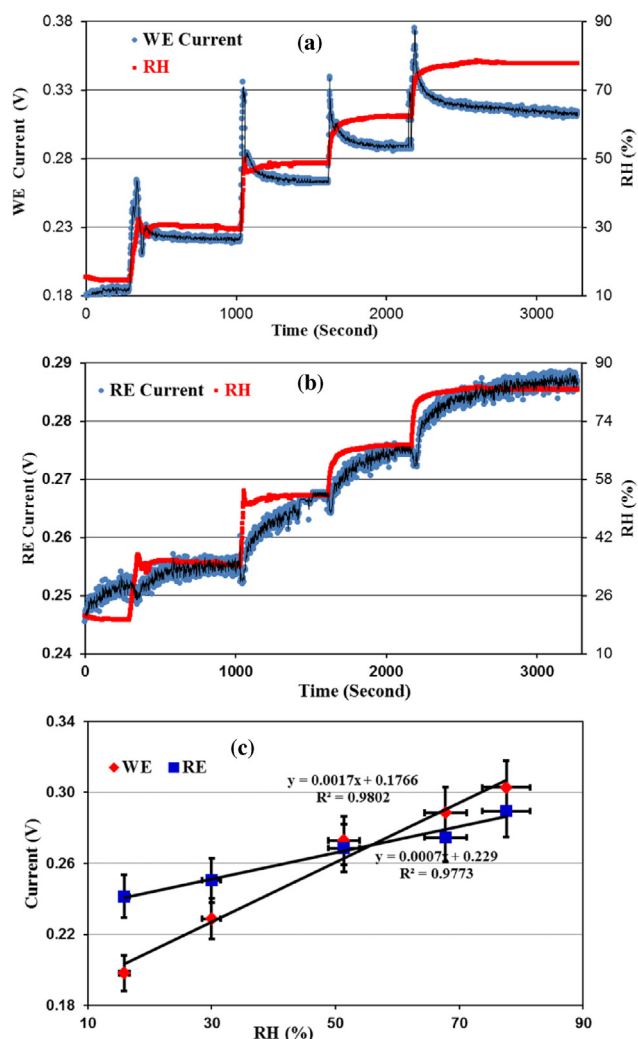


Fig. 6. RH effects of gas sample on WE (panel (a)) and RE (panel (b)) voltage outputs of O_3 sensor and the linear relationships among WE voltage, RE voltage and RH of O_3 gas sample (panel (c)).

result (Fig. 8(c)) since the contact surface of heterogeneous reaction between O_3 and LA on seawater surface increases with the LA concentration.

An O_3 sensor was employed in air quality monitoring and compared with a reference UV photometric O_3 analyser on ambient O_3 measurements over an 18-day period (7/8/2015–25/8/2015). The corrected sensor data are averaged to 5 min intervals and shown in Fig. 9(a) combined with the data of reference measurement. The corrected sensor data are in good agreement with reference data over the whole campaign period with an R^2 of 0.84 ($n=4768$) (Fig. 9(b)), however, the O_3 sensor measurements overestimated the O_3 concentrations by 20–40% compared with the reference method during peak periods. Average O_3 mixing ratios determined from the sensor and the reference measurements were 24.8 ± 14.5 and 23.6 ± 12.3 ppb, respectively. Average ambient humidity was $59.1 \pm 12.1\%$ ($n=4768$) during the field campaign, which is within the optimal RH range for the O_3 sensor performance. Based on the consistent measurements between the O_3 sensor and UV photometric O_3 analyser in the field campaign an unambiguous conclusion was that the O_3 sensor can be employed in air quality monitoring and its performance is in good agreement with conventional UV photometric O_3 analyser.

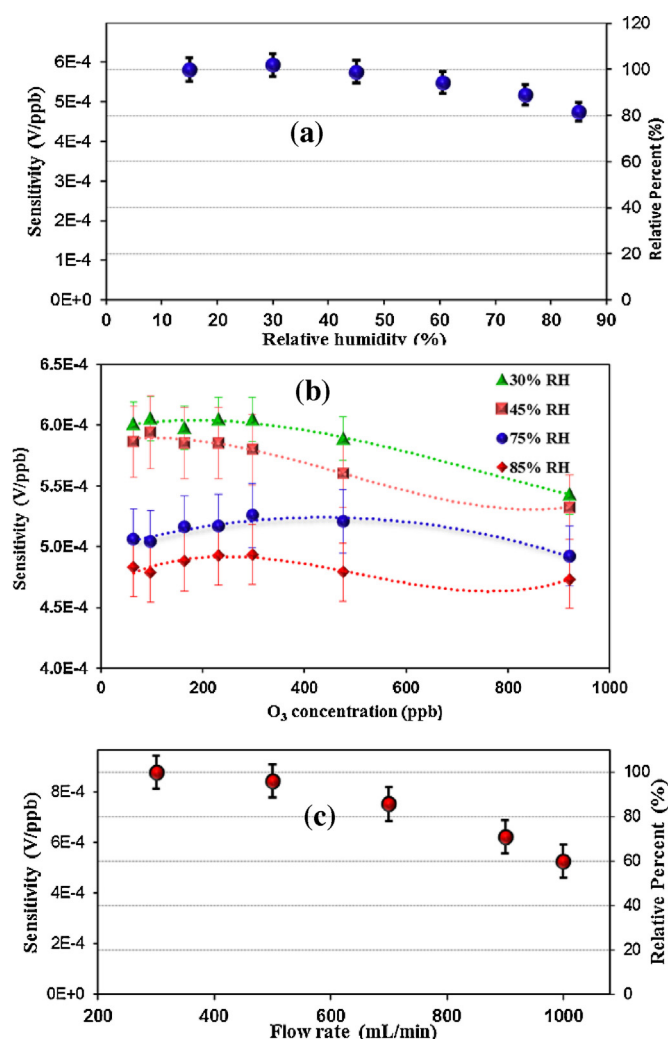


Fig. 7. Effects of relative humidity and flow rate of sample gas on O_3 sensor sensitivity. (a) RH effect on O_3 sensor sensitivity with RH varying from 15% to 85%. Experimental conditions: O_3 concentration is 320 ppb and the gas flow rate is 500 mL/min. (b) O_3 sensor sensitivity varies with O_3 mixing ratio at different RHs. Experimental conditions: gas flow rate is 500 mL/min. (c) Effect of flow rate on O_3 sensor sensitivity. Experimental conditions: O_3 mixing ratio is 320 ppb and RH in gas sample is 45%.

4. Conclusions

In this study the performance of electrochemical O_3 sensors were investigated in both laboratory and ambient air quality monitoring. We show that O_3 sensors can be deployed as a miniaturised alternative for conventional O_3 monitoring devices at lower cost and with low power consumption. The performance of low cost ozone sensors has been characterised under various RHs and sample gas flow rates and then further evaluated in both laboratory experiments and field campaign measurements. All results indicated that the miniaturised O_3 sensor were a suitable alternative for O_3 measurements in both laboratory experiment and air-quality monitoring. The O_3 sensor output voltage was found to have a significant positive linear relationship with O_3 concentration from 5 ppb up to 10 ppm. The performance of two different sensors were strongly correlated to each other after calibration. The sensors performed well only if the sensor was zeroed to the higher offset voltage. The consistent calibration curves for the O_3 sensors working under various RH and flow rates confirm the consistent performance of sensor. However, the voltages of both the WE and RE increase with rapidly increasing RH and flow rates; this causes a

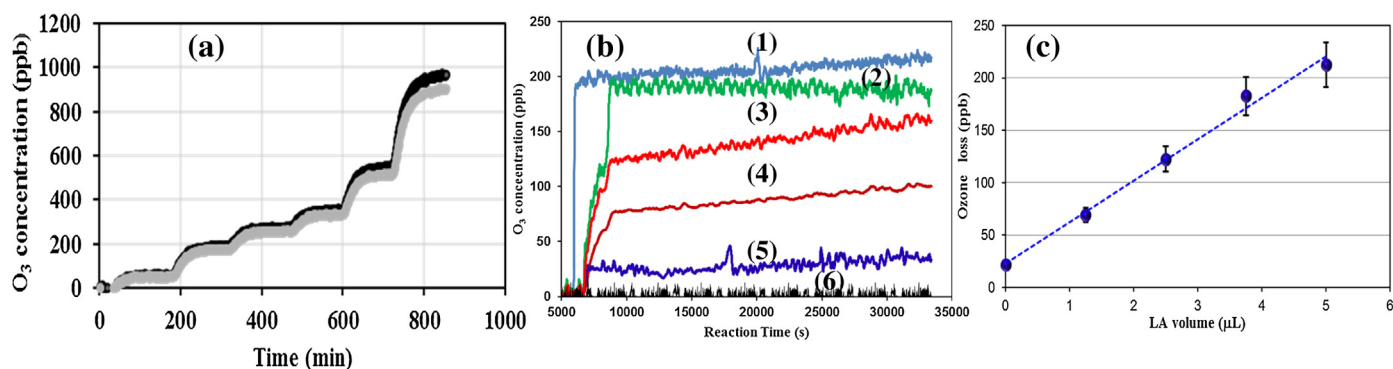


Fig. 8. Evolution of O_3 during an experiment to measure the O_3 uptake by seawater with different volumes of linoleic acid (panel (b)) on its surface. Consistency between ozone sensor (grey line) and reference instrument (black line) (panel (a)). The O_3 evolutions in panel (b) from top to bottom are the O_3 from the outflow of the empty glass vessel reactor (light blue line (1)) and four seawater samples in vessel reactor with 0.00 (green line (2)), 1.25 (red line (3)), 2.50 (brown line (4)), 3.75 (blue line (5)), and 5.0 μ L (black line (6)) linoleic acid (LA) on the seawater surface, respectively. Panel (c): the linear relationship between O_3 loss and LA volume on the seawater surface. Experimental conditions: O_3 concentration is 200 ppb and flow rate passing through glass vessel is 300 mL/min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

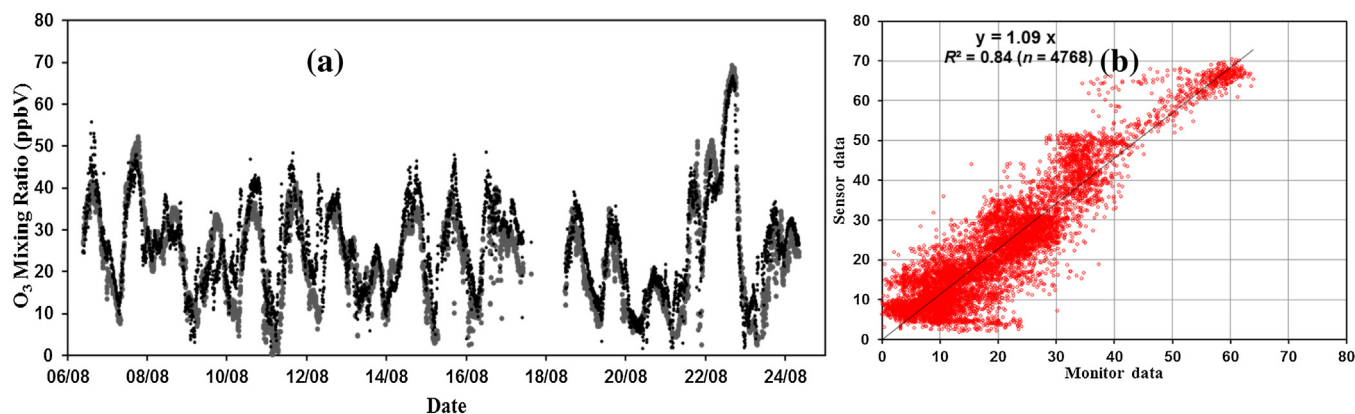


Fig. 9. A time-series comparison between O_3 sensor (black dots) and reference photometric O_3 instrument (grey dots) in air quality monitoring of ambient O_3 (5-min average) during an 18-day (from 7 August 2015 to 25 August 2015) field campaign (panel (a)) and the linear relationship between sensor data and reference instrumental data (panel (b)).

higher offset voltage of the sensor. RH and flow rate have negative influences on the sensor sensitivity since they increase the offset voltage of the sensors thus reducing the sensor output voltage. A caveat, however, has is that the O_3 sensor has a LOD of 5 ppb but that the performance is easily interfered by environmental RH and co-existing compounds. Sensor performance is significantly degraded by any rapid RH variations and the sensor usually takes around 40 min to recover to the initial working status after each rapid RH change. To overcome the RH effects, sensors should be zeroed after each rapid RH variation, or data during the recovering period should be ignored. In a field campaign over an 18-day period, during which RH changed only slowly in ambient air, the O_3 sensor was observed to perform consistently when compared against a reference O_3 analyser. In the foreseeable future the functions of wireless communication and remote control will be added on the sensor DAQ program by LabVIEW software, which will facilitate wider usage of the gas sensors in both research and air quality monitoring. The relation between RH variation and sensor recovery time is unclear and need to be studied further.

Acknowledgements

XP thank National Natural Science Foundation of China (41322035) for financial support. This study is supported by the AIRPRO-Beijing NERC consortium project.

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