Development of Low-Cost Ozone Measurement Instruments Suitable for Use in an Air Quality Monitoring Network

David E Williams,[a] Geoff Henshaw,[b] Brett Wells,[b] George Ding,[b] John Wagner,[a] Bryon Wright,[a] Yu Fai Yung,[a] Jennifer Salmond.[c]

[a]Department of Chemistry, University of Auckland, Private Bag 92109, Auckland, [b]Aeroqual Ltd, 109 Valley Rd, Mt Eden, Auckland, [c]School of Geology, Geography and Environmental Science, University of Auckland (e-mail: *david.williams@auckland.ac.nz*)

Introduction

Air quality concerns every individual and impacts directly on health and productivity. Air quality is inherently variable in time and space. Concentrations of air pollutants are primarily determined by the balance between emissions rates, chemical formation and the ability of the atmosphere to transport and disperse pollutants. In the troposphere, ozone (O_3) is formed as a secondary pollutant within urban and industrial plumes that may extend many hundreds of kilometres downwind of the source area. As the world population becomes increasingly industrialized and urbanised there is a need to improve our understanding of the processes influencing air quality in order to minimise population exposure.

Attempts to measure O_3 distribution have been limited by the instrumentation available. Conventional instruments are based on chemiluminescence methodologies which are bulky, expensive, and require AC power and temperature-controlled enclosures. This limits their deployment in the field. Monitoring sites are chosen typically to be representative of *average* or background concentrations in the region and not influenced by local sources of pollution. At this scale, sparsely distributed instruments are used to provide information about pollutant gas accumulation and transportation on a regional or district scale, and data are used to inform local authorities if pollutant levels in their areas are within or are exceeding acceptable levels. However, there remains considerable debate about the intra-region and particularly intra-urban homogeneity of pollutant concentrations due to variations in source strength, meteorology, topography, and location of monitoring sites.[1]

At urban to local scales the temporal and spatial heterogeneity of emission patterns, local wind flow patterns, and the complexity of the urban surface results in complex dispersion pathways at local scales within urban areas. This can lead to strong gradients in vertical and horizontal pollutant concentration.[2] In urban areas, people spend a substantial component of their outdoor time near busy roadways and intersections while commuting to work (on bicycles or foot), employed at local shops or cafes, or using the pavement space for retail or recreational activities.[3] Although individuals may not remain in this environment for more than a few hours each day, the prevalence of local pollutant hot spots often results in significant exposure. Even in densely populated areas of economically advanced countries, instrument spatial densities are at most 1 or 2 per square kilometer, as is the case with the London Air Quality Network (LAQN).[4] A limited number of fixed monitoring stations may not provide a good indication of personal exposure to pollutants, so hindering the establishment of strong relations between pollutant concentrations and meteorology[5] or health outcomes,[6] Such limitations have led to attempts to deduce the pollutant burden from measurement of traffic density, emission inventories and dispersion modeling.[7]

There is, therefore, a great need for the introduction of portable, low-cost ozone monitors that can easily be deployed in a high density network. The results from such a network will help inform the understanding of pollutant dispersion pathways and human exposure. Such data are essential to the formation of coherent air pollution abatement strategies. The work described in this article is part of an effort directed at enabling high spatial density air quality monitoring through the development of suitable low-cost instrumentation.

Gas sensors based on conductivity changes of heated semiconducting oxides[8] are widely used for industrial safety monitoring. While there are reports in the literature of gas-sensitive resistors being used for ambient atmospheric monitoring, there is a perception that the devices suffer from effects such as drifts of zero and calibration slope, and cross-sensitivities to other gases making them unsuitable for quantitative, long-term atmosphere measurement. However, we have shown that with careful attention to detail, based on a thorough understanding of the mechanisms underpinning device operation, these perceived deficiencies can be overcome. This article presents the design principles for low-cost instruments based upon heated metal oxide sensors for the reliable measurement of part-per-billion (ppb) levels of ozone in the atmosphere. Long-term performance data are presented, and common failure modes and their diagnosis are described.

## Semiconducting Oxides and Ozone Measurement

The very large conductance response at temperatures in the range 300–550 °C of highly porous layers of WO_3 to the introduction of ppb concentrations of ozone in air (Fig. 1) has been described and discussed in detail,[9,10] and there are preliminary reports in the literature describing the use of such sensors in ozone measurement instruments.[11,12] The response mechanism deduced[9,10] is given as Scheme 1. It has been shown that the conductance of the porous sensor assembly can adequately be described as a parallel equivalent circuit, with one element (the *interface*

element, representing the surface zone of the individual grains of the material) being dependent on the ozone concentration, and the other (the *bulk* element, representing the interior of the individual grains) being independent of the ozone concentration but dependent on oxygen partial pressure. Long-term drifts in baseline, which have been significant issues dogging the first attempts to develop monitoring instruments based on WO_3 sensor elements,[12] could be understood as resulting from the slow exchange of oxygen vacancies between interface and bulk elements. The predicted variation of conductivity with ozone concentration (Eq. 1) fitted the data well. The conductance difference in the presence and absence of ozone (Eq. 1) did not vary over several months of operation, consistent with the prediction of the assumed mechanism and equivalent circuit.

$$\sigma_{(o_{3=0})} - \sigma = \frac{aP_{o_3}}{bP_{o_3}+1} \qquad \text{(Eq. 1)}$$

Response Model basics

- Conductivity controlled by oxygen vacancies.

$$X \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} V + \frac{1}{2}O_2 \qquad V + O_3 \overset{k_2}{\longrightarrow} X$$
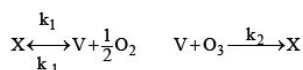
X = unperturbed lattice
V = neutral species (ion pair of oxygen vacancy + reduced lattice tungsten ion)

- Charge carriers produced by thermal excitation of electrons from reduced tungsten ions into the conduction band.

Charge carrier and therefore conductivity changes in response to changes in oxygen vacancy concentration at the interface (determined by [O3]).
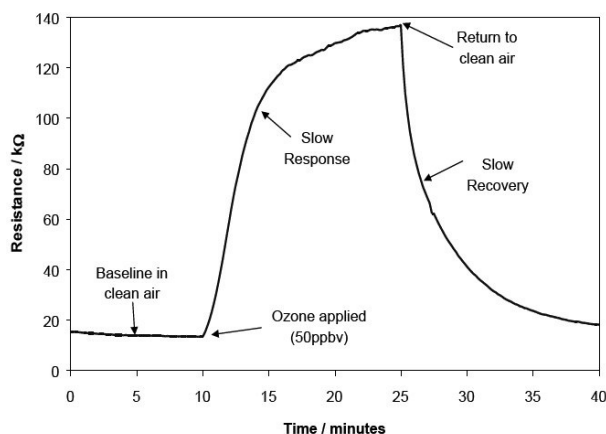
Scheme 1

Fig. 1. Resistance transient of a tungstic oxide sensor element in response to the application and removal ozone in air

Instrument Design and Operation

The atmosphere monitoring instrument has been developed from a successful commercial implementation of the design principles in a hand-held device (Fig. 2). Several thousand of these instruments have been sold and have operated successfully over several years. The atmosphere monitoring instrument design reflects the accrued operational experience. Because O_3 is such a reactive gas readily decomposed on surfaces (particularly if traces of organic matter are present), it is well-known to take care in the choice of materials for housings and pipework, and also in calibration.
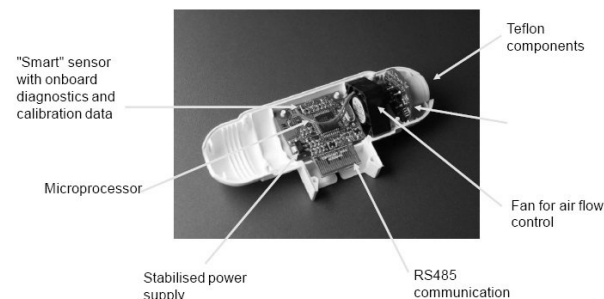

Fig. 2. Commercial implementation of a hand-held ozone meter utilizing a WO_3 sensor element (copyright Aeroqual Ltd., reproduced with permission)

Sensor Fabrication

The sensor substrate is a 2 x 2 x 0.250 mm alumina tile with a meandering platinum heater track printed on one side, and inter-digitated gold electrodes printed on the other. A thin (*ca*. 90 µm) layer of WO_3 is screen printed over the gold electrodes, creating the sensing element (Fig. 3). The sensor is held inside a sealed plastic housing with an inlet and outlet nozzle to allow sample gas to be drawn over the sensor at a controlled rate. Precise control of the operating temperature is essential to instrument precision and stability, simply because the oxide conductivity varies strongly with temperature: the activation energy is about 0.5 eV. The method employed for temperature control incorporates the platinum heater track (which has a well defined resistance-temperature relationship) into a Wheatstone bridge circuit whereby the out-of-balance signal across the two arms of the bridge is used to regulate the current through the sensor heater, thus controlling the heater temperature by keeping its resistance constant.[11] The sensor resistance is determined with a simple DC measurement, with the potential difference across the sensor controlled at 0.1 V. Higher potential differences across the sensor were found to cause an excessive resistance drift. The sensor housing is a cylindrical plastic enclosure
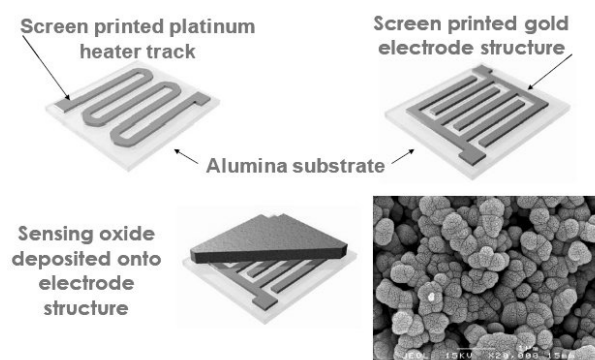

Fig. 3. Construction of the sensing element and micrograph showing grain structure; scale bar 1 μm

with four bonding posts in the base from which the sensor is suspended freely in the air by fine platinum connecting wires.

Instrument Operation

The two key problems to resolve were to overcome the limitations imposed by the very slow ozone response that is evident in Fig. 1 and to find a way to determine the zero ozone signal, so that the Eq. 1 could be applied and the zero drift compensated. The means adopted to resolve these issues have been crucial to the development of a successful operating procedure. The first problem, that of the slow response, was solved by the use of a temperature stepping regime.[9] At sufficiently high temperature, the ozone signal becomes essentially zero. The idea is that the surface comes rapidly to equilibrium with O_2 in the air, establishing a surface oxygen vacancy concentration that is repeatable, being dependent only on the temperature and the oxygen partial pressure. Thus, a step to a sufficiently high temperature establishes a repeatable initial condition for a subsequent step back to a lower temperature for the measurement. The theory[9,10] shows a clear and simple relationship between the initial rate of change of conductance and the ozone concentration, provided that the initial surface oxygen vacancy concentration is repeatably defined. Since the temperature control is accurate, the rate of change of conductance can be inferred from the conductance measured a fixed (short) time after the step. The choice of temperature and time is a trade-off between signal and cycle time. The upper temperature is also limited by the stability of WO_3, which will sublime at a significant rate at high temperature, especially in the presence of a high vapour pressure of water. This sublimation changes the microstructure of the sensing layer and hence the sensitivity. Loss of WO_3 from the sensor would ultimately lead to a loss of electrical continuity in the sensing layer and hence failure of the device.

The solution to the second problem, namely that of continually determining the zero ozone conductances, came from measurement of the dependence of the signal on the air flow rate over the sensor. The signal was independent of the air flow rate if this was sufficiently large but fell to zero if the air flow rate was decreased.[8] The explanation is that O_3 is rapidly decomposed on plastic surfaces, especially if these are warm; it is also rapidly decomposed in air if the temperature is sufficiently high. There is a thermal boundary layer just outside the sensing layer, and the power dissipated by the sensor warms the plastic housing. Both effects mean that the sensor signal is strongly dependent on the air flow rate over the sensor. Thus, a periodic zero measurement can be obtained by dropping the flow rate across the sensor to zero. Implementing a periodic zero flow condition, during which the sensor temperature is cycled between the high and low temperature states, provides a continuous measurement of the sensor baseline resistance. In the final implementation in the instrument, the high and low sensor temperatures are 600 ℃ and 520 ℃, respectively, which gives a good compromise of stability of microstructure of the sensing layer, sensitivity, and required cycle time. An entire measurement cycle lasts one minute and comprises a zero flow condition at

high and low temperatures and a high- flow condition at high and low temperatures. The low temperature conductance difference between high and low air flow states, measured a fixed time after the temperature step, follows Eq. 1.

Cycling of the air flow rate is obtained by drawing air across the sensor using an electrically-modulated fan or pump sealed against the base of the sensor housing, which has a hole drilled through it, centred on the sensor and with diameter just greater than the sensor diagonal. The entry face of the sensor housing is fitted with a tapered nozzle that directs the air flow onto the sensor. The sensor is protected from dust by a fine stainless steel mesh and a porous PTFE filter. All other components in contact with the gas before the sensor element are made from PTFE.

Air Quality Monitoring Instrument Construction

The instrument design for long-term air quality monitoring is essentially the same as that of the hand-held commercial instrument. The main differences are in the provision of a more reliable and accurate air pump, in the data handling and communication, in the housing, and in the provision of diagnostics for confirming reliability of the data. The instrument has been designed in two blocks: a sensor management block and a data management block. The sensor management block holds the calibration information and sensor identity. It manages the heater and air flow, makes the resistance measurement, and converts the result to concentration using the calibration information. The data management block controls the acquisition rate, acquires the concentration data, and stores and presents the output. These components are shown in (Fig. 4). The device is housed in an enclosure appropriate for its intended application.
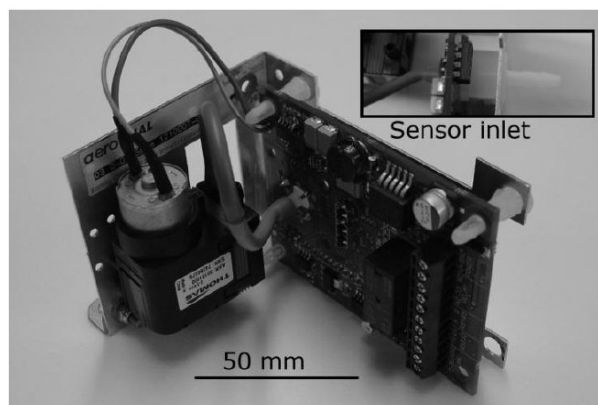

Fig. 4. Ozone instrument module for air quality monitoring (copyright Aeroqual Ltd., reproduced with permission)

Calibration

A significant part of the cost of any instrument is that incurred in calibration. As the capital cost of the instrument decreases so the calibration cost becomes more significant. Thus, a *low cost* instrument necessarily requires a *low cost* calibration procedure. We have split the calibration task into two parts: *linearization* and *calibration refinement*. The linearization part is a laboratory calibration using a restricted number of different O_3 concentrations, that can be performed reliably on a large number of instruments at any

one time, and whose purpose is to derive the parameters for the fitted curve of conductance vs concentration such that the imposed concentrations are reproduced with a precision of ±5% at worst. The derived calibration function linearises the output from the sensor, delivering a result measured in gas concentration units. The calibration refinement step comprises measurement in the atmosphere alongside a reference analyser for 24-48 hours. The idea is to use the natural variability of the atmosphere to sample the full range of concentration required, and to take advantage of the fact that the semiconductor-based instruments are small, rugged and portable. As we will demonstrate, sensor-indicated concentration is a linear function of analyser-indicated concentration, so that a simple linear correction factor can be applied to the laboratory calibration in order to derive an accurate result for the atmosphere measurement. After calibration refinement, the instruments would be moved to the desired location.

Linearization

Previous work described a burn-in phenomenon for WO_3 sensors for ozone[9] that was attributed to effects of a reaction of O_3 with traces of organic matter remaining from the sensor fabrication. The complete sensor modules (sensors inside their housing with air flow control and the control electronics) were run at the sensor operating temperature for 2 weeks in ambient air, prior to linearization. The use of an adequate burn-in time before calibration has been important to the success of the instruments described in this paper. Ambient air was scrubbed of hydrocarbons and NO_2 by passage through a packed bed of activated charcoal, then introduced to a 1.5 m^3 measurement chamber constructed of Perspex; there was no humidity control. The complete sensor modules were mounted on a stainless steel rack in the centre of this chamber. The air inside the chamber was circulated by a small fan and continuously sampled from the centre of the chamber, close to the sensor modules being linearized, to a spectrophotometric ozone analyser. An ozone generator inside the chamber was controlled from the ozone analyser output, to maintain a fixed concentration of O_3 inside the chamber around the sensor modules. This concentration was held in sequence at 0, 50, 100 and 150 ppb, for 20 min at each concentration before the measurement sequence was initiated on each module. As noted in the above, the sequence was a step from high to low sensor temperature at high and low air flow rate over the sensing element. Sensor resistances at the end of the low-temperature step were recorded at low and high air pump rate. Rather than an exact inversion of equation 1 to derive O_3 concentration from conductance difference, a quadratic fit to the conductance difference between high and low sensor fan speed was found adequate empirically to linearize the sensor output. Fig. 5 shows the distribution of deviations between set concentration and concentration inferred from the fit, for a typical set of 60 sensor heads. The variability stems from the sensor microstructure varying from one device to another, the underlying model is a greatly simplified one for the effect of microstructure on the response, and the use of a quadratic fitting function to derive concentration from measured conductance is itself an approximation. Sensor modules that showed average deviations greater than ±5% were rejected for this application.
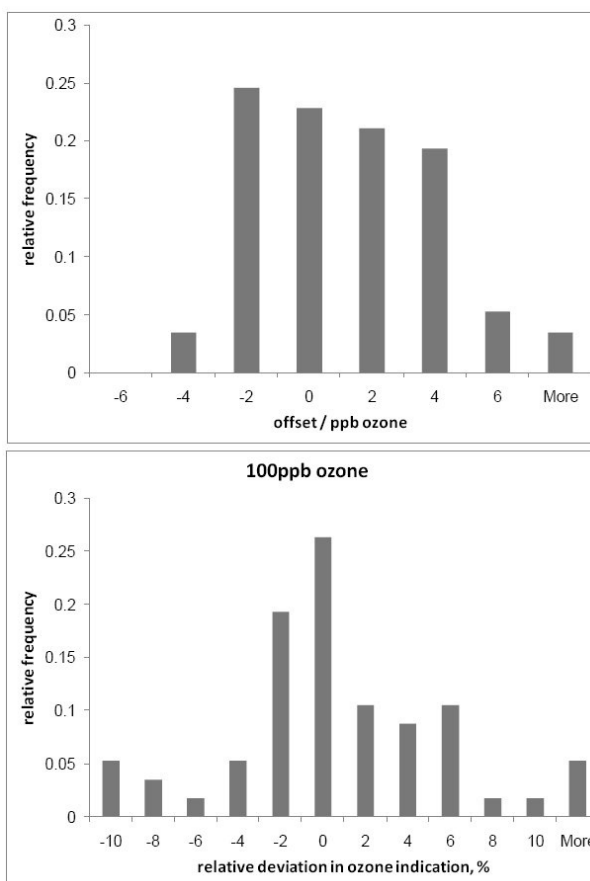

Fig. 5. Distribution of deviations in instrument indication following initial linearization

Field Calibration Refinement

An air monitoring station was established in a pod protruding some 6 m above the 7th floor of the physics building on the Auckland campus. This site is at a high point of the Auckland central business district near heavy traffic and is exposed to wind from all sides. A sample manifold comprising 15 m of 150 mm diameter PVC pipe and an in-line fan draws air from outside on one side of the building and exhausts to the other side at a rate of *ca.* 90 L/sec (see Fig. 6). A reference analyzer (Thermo 49 C) and the semiconductor-based ozone instruments sampled outside air from this manifold, *via* PTFE tubing, each making a measurement every minute. The data, logged on a networked computer, were recorded as a tab delimited text file with a line of data being written every minute. A new file was automatically created at the start of each day. Sample air temperature and humidity, rainfall, wind speed and direction, and room temperature and humidity were monitored during the sampling period. The sensor baseline resistance, derived from the low-flow, low-temperature measurement, and the heater current and potential difference for each semiconductor instrument were also recorded.

As the levels of ozone were fairly low in the Auckland region at the time, O_3 was introduced into the sample manifold, using the generator connected to a timer, for two hours between 2 and 4 a.m. every morning. This provided elevated O_3 levels to extend the calibration and test range. The calibration refinement phase was the first
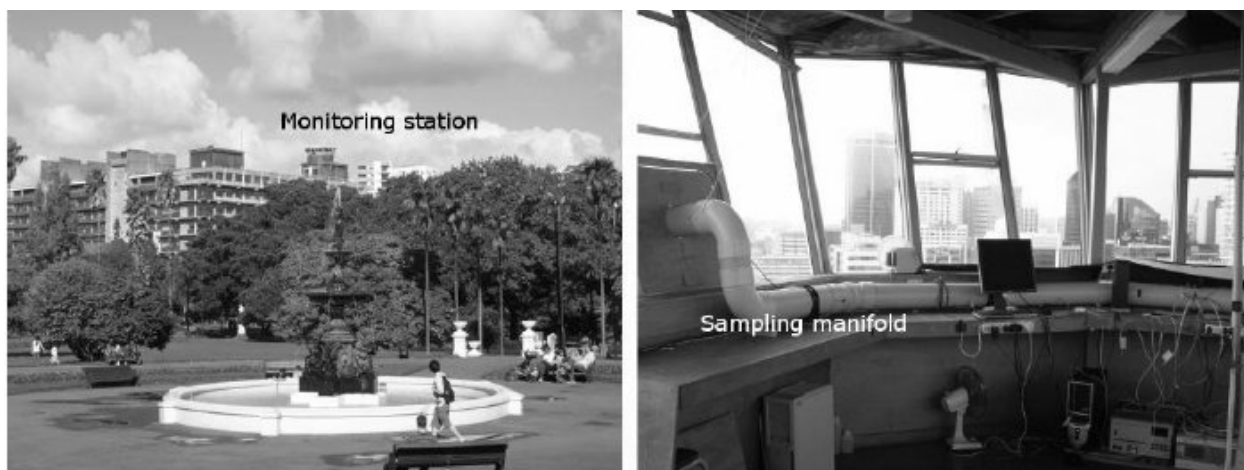
Fig. 6. Left; Image of monitoring station from ground level; right: image from inside monitoring station showing sampling manifold and exit port

period of 72 h of operation, while data from the final 48 h was used. A linear correlation function was calculated for each sensor against the reference analyzer. The example of Fig. 7 illustrates that the initial sensor output linearization procedure was adequately accurate. The standard error of estimate of the analyser indication derived from the semiconductor instrument indication using linear correlation, for all 5 instruments, was 2 ppb (n=3000). Fig. 8 shows the superposition of the time series of the analyser indication and the semiconductor instrument indication corrected by the linear correlation function.
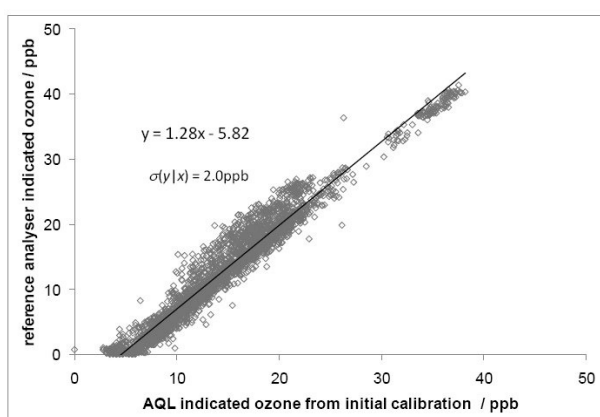

Fig. 7. Calibration refinement: linearized module output predicting the reference analyser indication, over 48 h
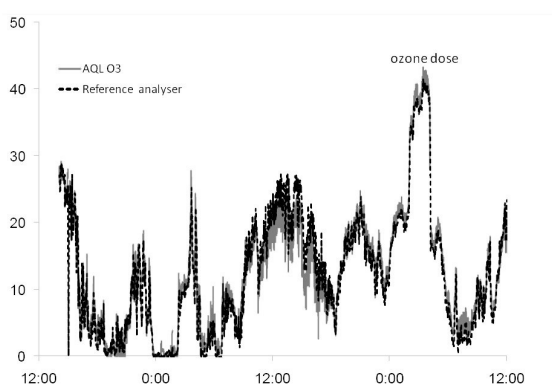

Fig. 8. Calibration refinement: linearized and *in-situ* calibrated module output tracking the reference analyser over a 48 h period

Field Measurements

Following the field calibration, the semiconductor-based instruments were left running continuously for a period of approximately 6 weeks with no intervention. The evolution of the slope and intercept of the linear correlation of analyser indication with semiconductor instrument indication is shown in Fig. 9. The evolution with time of the mean over each day of the difference between semiconductor instrument reading and analyser reading, each measured every minute, is shown in Fig. 10. A small and slow variation in the indication of the spectrophotometric reference analyser cannot be ruled out, giving an apparently correlated small drift of all of the semiconductor instruments. In addition
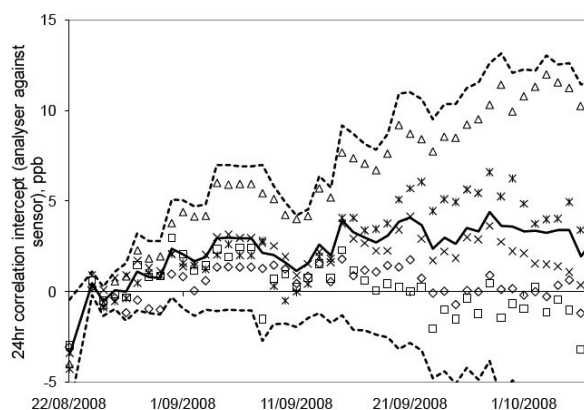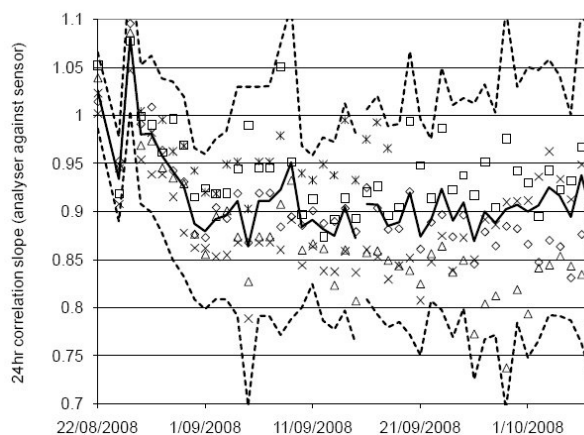

Fig. 9. Evolution over time of the 24 h correlation slope and intercept, between sensor module and reference analyser. Solid line is the mean of the 5 sensor modules; dashed lines are ±2 standard deviations
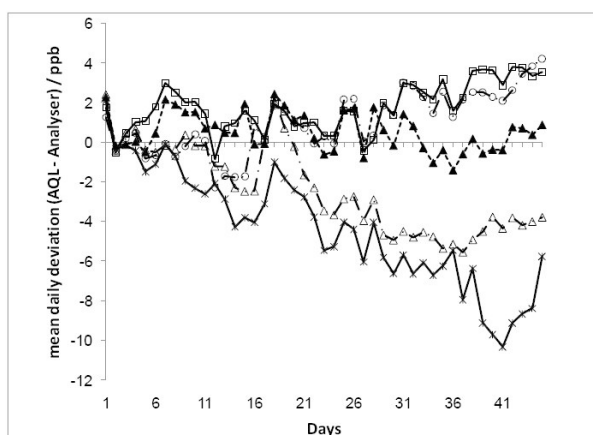
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Fig. 10. Evolution over time of the mean over each 24 h of the difference between the measurements made each minute by the sensor module and reference analyser, for 5 sensor modules

to this effect, there is some evidence that the result from one of the semiconductor instruments had drifted to a small additional extent over the 6 week period. It is clear however, that the small, simple low-cost semiconductor-based instruments reproduced the measurement of the spectrophotometer to within 10 ppb O_3 over this extended period of unattended operation. They meet the requirement for deployment in an air quality measurement network.

Failure Modes and Diagnostics

For confidence in the reliability of the data, a necessary condition for deployment of instruments into a monitoring network is that common failure modes are identified and means for recognizing failures are delineated. Three main cases of failures of the semiconductor-based instrument have been identified in the present work.

Pump Degradation: Diminution of Air Flow Rate over the Sensor

Control of the air flow over the sensor is critical to the correct operation of the instrument. Fig. 11 shows the variation in indicated O_3 concentration with alteration of the volume flow rate of air under the high-flow condition. If the flow rate is too high, then the convective heat loss from the device exceeds the power available from the heater driver circuit, and the sensor temperature falls. This results in a higher ozone signal. If the flow rate is too low, then the signal falls. There is a range of flow rates where the indicated signal is independent of flow: this is the desirable control condition for the instrument; Fig. 11 illustrates the effects. An O_3 concentration of approximately 100 ppb was maintained in an enclosed chamber. The concentration was monitored with a reference O_3 analyzer and a semiconductor ozone instrument with adjustable flow control. This instrument had been calibrated previously at a flow rate of 200 mL/min. The ratio of the reported O_3 concentration from the semiconductor instrument to that of the analyzer was determined for flow rate into the semiconductor instrument ranging between 20 and 1600 mL/min.

The air flow can change as a result of degradation of the air pump during continuous operation; the result would be an under-reading of the instrument. A simple diagnostic is to measure the current supplied to the heater and the potential

difference across it. The derived heater resistance confirms that the sensor is operating at the correct temperature and that this temperature is stable. The derived heater power dissipation indicates variations in the air flow rate, since the heater functions as a simple hot-wire anemometer. Fig. 12 shows an example where this simple diagnostic has uncovered a pump failure, with the associated under-reading of the O_3 concentration.
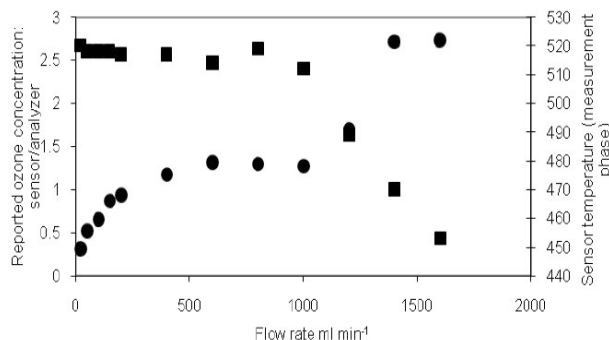

Fig. 11. Effect of gas flow rate on module indication and sensor temperature;. (●) ratio of the module-reported ozone concentration to that of an optical reference analyzer; (■) Sensor temperature in °C
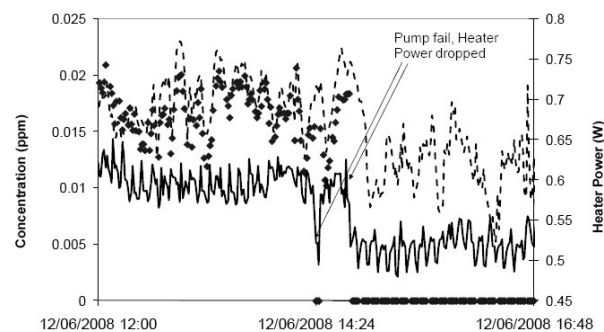

Fig. 12. Effect of pump failure on the ozone module signal, and its detection by heater power measurement. (♦) module indication; (—) heater power; (- - -) reference analyser indication

Dirt Accumulation: Ozone Decomposition on Dirt Deposited in the Inlet Filter

With long-term operation, particulates from the atmosphere accumulate on the PTFE and stainless steel filters protecting the sensor. Such material is catalytically active for O_3 decomposition and it also clogs the filter and reduces the air flow rate. The result is that the sensor underreads. Fig. 13 illustrates the effects for instruments where the filters were visibly dirty.
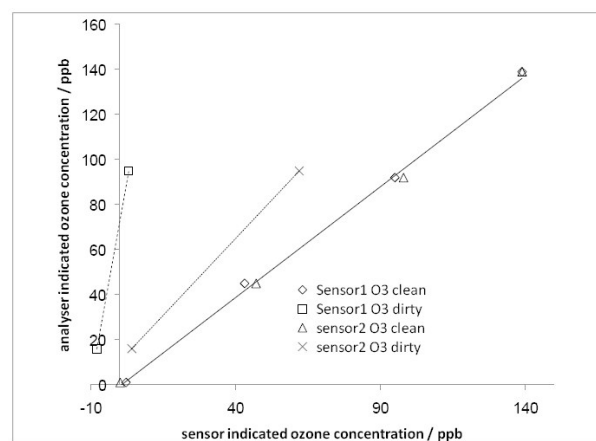

Fig. 13. Effect of dirt on the sensor filter on the module-indicated ozone concentration

Sensor Failure in High-Humidity Environments

WO_3 sublimes at elevated temperatures. We have observed that the effect is enhanced if the water vapour pressure is high, and it can become significant at the upper operating temperature of the sensor. The result is that the sensor grows whiskers of WO_3 thus allowing the microstructure of the sensor element to change slowly over time. The assumption behind the application of Eq. 1 is that the microstructure remains unchanged over time. Thus, a slow variation in microstructure over time would give rise to a drift in the indicated O_3 concentration. As the sublimation proceeds, then over a period of months to years (dependent upon the atmospheric humidity) the baseline resistance can rise to such an extent that the measurement moves beyond the range of the sensor electronics.

A variation in microstructure should be detectable by a variation in the zero-ozone resistance of the sensor. This number is available from the low-flow resistance measurement. Indeed, Fig. 14 shows that the variation in baseline resistance can be correlated with a slow drift of the signal that is most sensitively detected by a small drift in the intercept of the 24 h correlation between reference analyser and sensor-based instrument.
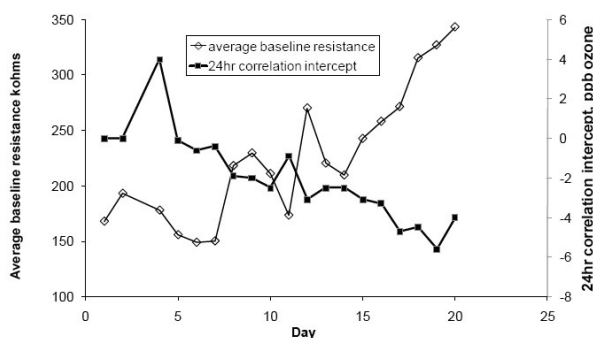

Fig. 14. Variation of sensor baseline resistance over time when resistance rose and module ozone signal began to change significantly: baseline resistance and intercept of the linear correlation between reference analyser and module against time

Conclusion

A low-cost instrument for monitoring ozone in the atmosphere, with estimation error (2σ) ±4 ppb compared to a spectrophotometric reference analyser over the range 0-100 ppb O_3 has been demonstrated. The instrument has a measurement cycle time of 1 min and is based on the resistance changes of a heated semiconducting oxide. Common failure mechanisms and means for diagnosing these have been described. The device has performance suitable for use in long-term atmosphere measurement, with remote diagnostics and minimal maintenance requirement.

Acknowledgement

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Melamine and similar substances like cyanuric acid can be detected by a number of methods including ELISA, gas chromatography, mass spectrometry, and high pressure liquid chromatography. But the real issue surrounding this food contamination scare is not about just these substances but the ease in a globalised economy, with which many countries can be affected by one country's mistake – whether it has been done deliberately or in ignorance. How will testing of products evolve to overcome what appears to be ongoing problems? How can effective and affordable testing regimes be put in place for the plethora of products from toys to food ingredients and finished food products when the possible contaminants could be anything? Is this a risk we just have to live with in our modern world or is it something humans have always lived with and today it just catches us by surprise as we put our trust in quality control? In November the US Food and Drug Administration opened their first office outside of the United States in China.

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