The optimisation of a paired emitter-detector diode optical pH sensing device

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Abstract

With recent improvements in wireless sensor network hardware there has been a concurrent push to develop sensors that are suitable in terms of price and performance. In this paper a low cost gas sensor is detailed, and significant improvements in sensor characteristics have been achieved compared to previously published results. A chemical sensor is presented based on the use of low cost LEDs as both the light source and photodetector, coupled with a sensor slide coated with a pH sensitive colorimetric dye to create a simple gas sensor. Similar setups have been successfully used to detect both acetic acid and ammonia. The goal of this work was to optimise the system performance by integration of the sensing technique into a purposely deigned flowcell platform that holds the colorimetric slide and optical detector in position. The reproducibility of the sensor has been improved through this arrangement and careful control of deposited film thickness. The enhanced reproducibility between sensors opens the potential of calibration-free measurement, in that calibration of one sensor can be used to model the characteristics of all sensors in a particular batch.

Keywords Chemical sensing, Colorimetric sensing, LED based sensors, Calibration, Sensor Networks, PEDD

1. Introduction

Over the last two decades chemical sensing has consistently remained an important research topic owing to a diverse range of applications in various areas such as clinical assays [1,2,3], food quality monitoring [4,5], process monitoring [6], and environmental sensing [7,8].

In order for sensing devices to be practical, key parameters such as sensitivity, reliability, reproducibility, sensing range, automation, cost, size and ease of use must be carefully considered [9]. The use of paired LEDs, in which one LED serves as a light source (forward biased), while the other serves as a photodetector (reverse biased) is an approach that can be used to make very low cost, low power chemical sensors. In these so-called P.E.D.D. (paired emitter detector diode) devices, the light coupled between the emitter and the detector passes through a chemical coating wherein the color changes due to chemical effects resulting in a chemical sensor [10, 11]. PEDDs are low cost, small in size, consume a small amount of power and have a simple principle of operation. Most importantly, this LED sensing technique shows good sensitivity and excellent signal to noise ratios with target gas detection in the low ppm to ppb region being reported [10, 11, 12].

In search of sensitive, reproducible, reliable and low cost sensors ideal for sensor net applications [13], we present here the optimization of a colorimetric gas sensor which is coupled with a PEDD optical measurement device, with a significantly enhanced performance over previous sensor configurations [11, 14]. These improvements have been achieved through the alteration of the fabrication method for sensor film preparation, and the development of a flowcell housing to hold both the sensor film and the optical detection setup securely in position. The development of the flowcell with a mechanical flow control allows for a greater level of control over our samples, and as a result more effective experimentation.

2. Experimental

2.1 Film Preparation

The chemical formulation used is based on a pH indicator dye (bromophenol blue) a phase transfer salt (tetraoctylammonium bromide) and a polymer (ethyl cellulose) dissolved in 1-butanol as developed by Lau *et al* [17]. The formulation undergoes a colour change from blue in its alkaline state towards yellow in the presence of acidic species. Previously, films have been drop cast directly onto the LEDs surface [10, 11], but this results in uneven coatings and sensors that were not very reproducible. In this paper a novel flowcell housing has been designed to hold and secure the position of the sensor slide coated with the chemo-sensitive film. Designing the platform to accommodate a sensor slide allows the deposition of the coating onto a PET substrate, which can be done in a more reproducible fashion than direct coating of the LED surface. The films were prepared by casting a 50 mm x 40 mm film onto a 1.8 mm thick clear flat PET sheet. The films prepared were measured to be 5-6 µm thick using a Wyko NT1100 Optical Profiling system. 10mm x 10mm squares were cut from this film, from its most uniform midsection for experimentation.

2.2 Flowcell Fabrication

The flowcell was CNC milled from PTFE (Teflon), chosen for its high temperature stability and more importantly its high chemical resistance [16]. The housing accepted two LEDs, a rubber gas seal, four locking screws, the coating slide and two M5 pneumatic gas fittings (Figure 1) which acted as the gas inlet and outlet. Two LEDs were aligned on the same axis facing each other, on opposite sides of the coated slide and acted as the optical detection system. The emitter LED pulses light on one side of the slide and the light intensity reaching the detector LED is modulated by the colour change of the colorimetric film indicating the presence and concentration of our target species (acetic acid). As part of this study the paired emitter detector diode setup was redesigned in a flowcell configuration for a number of reasons.

- In many previously published paired emitter detector diode setups there have been a number of system or performance variables being very loosely controlled or often not being controlled at all. It was decided that a redesign of the sensor housing would be used to more effectively control these experimental variables, which were affecting system readings and inhibiting good repeatability. These variables included distance between LEDs (the distance was optimized to achieve maximum light coupling through use of an adjustable test rig), alignment of LEDs, position of coating slide etc.
- The flowcell design was also chosen to allow for more effective experimentation, where close control of the gases coming in contact with the colorimetric pH indicator slide could be guaranteed.

- The flowcell design also allows for the system to be easily coupled with a grab sampler. Running the device with the grab sampler insures that there will be a gas flow inside the device at all times, not like in older setups where the device relied on plumes of contaminant blowing in contact with the sensor of their own accord. (This also opened up the potential for the sensor to be developed within a standalone system).

- The flowcell design importantly accommodates the use of a coating slide, by immobilizing the coating on a transparent substrate it opens up the potential of using far more reproducible deposition techniques in creating the colorimetric coatings.

- Lastly, the flowcell design also serves to protect the slide from external light sources, and possible degradation of the chemically sensitive slide from photo bleaching and external influences.

2.3 Test Chamber

A purpose built test chamber was used for the gas sensing experiments in this study. The chamber was equipped with an injection port and septum, through which acetic acid was manually injected using a syringe (Figure 2). The base of the enclosure housed two purge points which could be opened or closed. With both open, one side was attached to a vacuum line and the other to ambient air to purge the test chamber. Inside the chamber a 9V suction pump (SKC Model No. 222-2301) was connected to the sensor housing to draw gas samples from the chamber directly into the flowcell. This ensured rapid delivery of gas samples to the device to promote a quick response time. The injected acetic acid was dispersed throughout the enclosure by a 9 V fan. The fan served to keep the chamber is environment homogenous and ensures a quick change in the acetic acid level through the chamber is environment when a sample was introduced.

2.4 Electronic Setup

The LEDs were wired through the side of a chamber in an air tight fashion, and were controlled externally by a control board and a pre-programmed microprocessor. The control board relayed sensor values back to the PC via a serial port. The detector LED is operated by first charging its internal capacitance and then discharging it. In the current setup, the discharge rate is proportional to the amount of light falling on it. This charge and discharge happens at a frequency of 50 Hz**.** It was our intention to have a high sample rate as possible, because at a low sampling rate, it's possible to miss key events. However when the sampling rate is too high it quickly saturates the input buffer of the recording software (Matlab in this case). It was found that at max sampling frequency, the recording software's buffer when specified to be large still saturated over the duration of long tests. The sampling rate was lowered to accommodate this. The controlling microprocessor employed in this case was an MPP430F449 equipped with an 8 MHz crystal. This crystal ensured a greater resolution over lower frequency chips because all hardware instructions are based on the main clock in this setup and the arithmetic logic unit is no exception. The processor then measures the speed of each discharge which is an indirect measurement for the light falling on it. The light falling on it is modulated by the colorimetric film meaning a simple gas sensor is realised.

The emitter LED used in this setup was a Kingbright 5 mm green LED with a λ_{max} at 565 nm (Radionics, Ireland Part No. 451-6537) and the detector LED used in this study was a 5 mm red LED with a λmax at 660 nm (Digi-Key, Ireland Part No. 67-1612-ND). The wavelength of the emitter LED is matched with the λmax of the dye so one can monitor the change of the prominent peak change as the dye changes from its protonated to deprotonated states. It was first established by Lau *et al.*, [17] that when using an LED as a detector, in this manner, it can sense wavelengths at and below its emission wavelength. Therefore by choosing a 660 nm LED, one can detect the absorbance λ max waveband, i.e. 565 nm of the pH indicator. A more detailed explanation can be found in [17]. The emitter in this setup was powered via a 3.3 V regulator (National Semiconductor LM1068 series CT-3.3), and smoothed using 3 capacitors in parallel (10 µF, 100nmF, 100 nF). A variable resistor was placed in serious to optimise and control the light intensity. The following procedure describes the implementation of a P.E.D.D. detection system, described fully in [17] for our platform.

1. I/O output, set to output mode.
2. Charge the LED's internal capacitance cathode, by setting the I/O output register high (i.e. 3.3v)
3. Switch the I/O register to input mode once the LED capacitance is charged.
4. Set the software counter variable to 0.

5. Check over a certain number of processer counts (in this case 1400) if the discharge has crossed the logic threshold.
6. Repeat to step #1.

The signal was not amplified nor filtered on the control board, the IO values were read into a Matlab connected through a serial RS232 connection. Here the post processing of the data was carried out where the time values were calculated and applied and a floating point average was applied. The timings of the experiments were carried out manually (manual injections*)*. The altering of the sensor preparation coupled with the introduction of the new flowcell has improved the performance characteristics of the sensing platform. These improvements are detailed in the next section.

3. Results and Discussion

3.1 Repeated Hit/Purge Cycle

Testing began with the test chamber being purged with ambient air for 10 minutes to establish a baseline. After this, the enclosure was sealed. Then 7 µL of 100% acetic acid was injected into the chamber which was dispersed by the fan, creating a concentration of 0.54 mg/L acetic acid in air. Once the sensor has been exposed to the acetic acid for 10 minutes it was then purged for 15 minutes by drawing ambient air through the chamber. This purge and injection sequence was repeated three times in total. The procedure generated a clear positive response (Figure 3), with a relative standard deviation (RSD) of 1.2%.

This optical detection method relies on the measurement of very small amounts of current and is therefore very sensitive to disturbances. However it is in fact this sensitivity that allows one to achieve measurement ranges in the ppb region (a classic trade off in many sensing systems e.g. electrochemical sensors). The spikes visible in the figures are evident when the external safety chamber was disturbed at times to allow access to the injection port. The noise will be addressed by introduction a filtration step and /or by ruggedizing the system from its current development/research phase to a more finalised/commercial phase.

The results also demonstrate that the sensor has a low-signal-to noise ratio (SNR) calculated from the baseline of test 3.1 as 99:1. This low level of electrical noise has been achieved through effective grounding of the system. The speed of the response of the sensing platform was calculated from the time it takes the sensor to reach 95% of its steady-state response. In this case it was evaluated to be 6 minutes 52 seconds from the average of the three responses in test 3.1. This response time is the response time of the entire system; which includes sample dispersion throughout the chamber, establishment of equilibrium between the chamber and the sensor, the movement of the gas through the testing flowcell, and the diffusion of the sample into the sensor film.

The speed of response of the colorimetric film was evaluated separately by injecting acetic acid into a custom miniaturized flowcell containing a detector and emitter LED and a coated slide. The flowcell's small internal volume and the direct injection insured that the sensor is immediately exposed to the acetic acid. The speed of response of the coated slide was calculated from time it took the slide to reach a 95% response to a 7 µl 100% acetic acid injection which equates to a concentration of 268.81 mg/L acetic acid in air, the evaluated time response value was 27 seconds and was an average of three runs.

3.2 Calibration of Sensor

A ten point calibration was carried out using acetic acid and repeated a total of three times with three separate sensor slides. It was carried out by increasing the sample concentration in 0.1 mg/L steps up to 1 mg/L. An initial 10 minute baseline was established, followed by 10 sequential injections of 0.1 mg/L of acetic acid. After each injection, a 10 minute period was allowed for the sensor to reach a steady state response (Figure 4). From this plot a calibration curve was generated for each of the three slides.

As expected the 0.1 mg/L steps are clearly defined at under 0.3 mg/L, and from the graph we can see that the sensor response is linear over the 0- 0.2 mg/L acetic acid range (Figure 5).The clarity of definition is reduced above this level and is due to the non-linear nature of the sensor. It is also worth noting that at higher concentrations of acetic acid the signal to noise ratio is decreased which causes a slight distortion of our readings. From the calibration curve plot (Figure 5) the device is sensitivity has been calculated from the slope of the linear section of the calibration curve as 43.6 units / mgL^{-1}.

From these simple tests the performance characteristics of the sensing platform can be effectively deduced. The limit of detection (LOD) has been calculated as three times the standard deviation of the base line in our calibration plot (Figure 4). The average of the three calculated limits of detection was 0.001145 mg/L or 12 ppb which is a significant reduction on many published similar sensing devices [10, 11, 18].

A relatively low variance of 14% was seen in the calculated LODs of the three sensor slides. This shows a level of reproducibility which is an improvement on drop casting direct onto the LED surface where sensors exhibited little reproducibility and produced a variance of 46% [10]. Further improvements could be made in terms of sensor reproducibility through the employment of inkjet printing as a fabrication technique which posses extremely low position repeatability and a low drop volume resolution which could be used to drop the variance further [10] and has been suggested in the future work section.

As well as showing favorable performance characteristics the newly designed flowcell provides practical system implications. The flowcell shrouds the sensor and detector LEDs from environmental light, which has been highlighted as a cause of noisy sensor signals in previous work [10, 11, 19] in the form of environmental light. This improvement has manifested itself in a more easily identifiable, clearer response. Importantly, the flowcell also acts as a protective barrier between the chemically coated slide and potential harsh external conditions.

3.4 Effect of Water Injection

In gas sensors, cross-response to humidity is a common issue. In these particular sensors, the response mechanism depends on proton transfer between the sample molecules and the dye. This transfer is effectively modulated by water, and we therefore investigated the effect of humidity on the sensor response while the temperature was regulated at room temperature (ca. 20°C). Testing began with a 10 minute purge to establish a baseline prior to injection of 7 µl of water (the same volume of acetic acid injected in test 3.1) was delivered to the test chamber. After 10 minutes the chamber was purged with ambient air. This resulted in a change in the humidity of the chamber with the humidity rising from 47.2% up to 48.8% before returning to 47.2% after the purge (Figure 6b). This change did not manifest itself as a recognizable effect on our sensor response with it continuing to stay at a steady state throughout the injection (Figure 6a). This has validated our responses in test 3.1 as a response to the pH change and not the humidity change.

4. Conclusions

In this work an optical pH has been developed upon pre-existing work. The developed sensor tested with acetic acid has exhibited good sensitivity, high reproducibility between exposures, had a minimal range of values distorted by noise and possessed a low range ppb LOD. Through collection of humidity data the sensor response has been validated as a response to the acetic species and not a response to the induced humidity change.

Through the application of a simple 10 point calibration it has also been shown that the sensor response is a linear one at acetic acid levels under 0.2 mg/L. This result coupled with the flowcell which serves to shield the delicate chemically coated slide the potential deployment lifespan of the device has been increased. This facilitates the potential development of the sensing device as a standalone low-cost low-power real world pH trace sensor. Potential application areas include air ventilation, landfill sites, environmental monitoring (ammonia), industrial parameter fencing, and horticultural monitoring (acetic acid).

Suggested Future Work

The authors also believe that the study would benefit from the following work being carried out in the future;

1. The development of full system circuitry onto a PCB.
2. A study of the use of a faster microcontroller crystal for higher resolution sensing against the resulting increased power draw.
3. A study of the behavior of PEDD sensors over a large temperature range.
4. The development of a larger range of pH sensing through the use of multiple dyes covering multiple ranges. expanding with multiple dyes for larger pH ranges
5. Investigating the sensing performance of PEDD sensors and comparing and contrasting them against other available optical sensors and other traditional sensing methods.
6. Through use of a coating slide the potential exists for highly reproducible techniques like Inkjet Printing being used in order to effectively batch calibrate large groups of sensors.
7. A study of the effect of gas speeds over a sensor slide, to investigate the effects of faster or slower flowrates.

Acknowledgements

The authors also gratefully acknowledge financial support from Science Foundation

Ireland (SFI) under the CLARITY: Centre for Sensor Web Technologies Award (07/CE/1147).

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Biographies

Dylan Orpen received his honours degree in Medical Mechanical Engineering from Dublin City University in 2008. His research interests include computational modelling of microfluidic systems and the area of cardiovascular stenting. He was previously employed by Boston Scientific Ireland and is currently a postgraduate student with the Clarity research group.

Stephen Beirne received his PhD (Development of a Low Power reactive Wireless Chemical Sensing Network) from Dublin City University in 2008. Since 2003 he has worked with the Adaptive Sensors Group (ASG) as part of the Adaptive Infomation Cluster and Clarity: Centre for Sensor Web Technologies, Dublin City University, on projects concerning wireless sensor devices. His research interests include wireless sensing devices, environmental sensors, and field deployable sensing systems.

Cormac Fay received his honours degree in Mechatronic Engineering from Dublin City University in 2005. He went on complete a M.Eng in telecommunications in 2007. He is currently pursuing a PhD within the Clarity Research Group. He has a wide range of research interesting ranging from gas sensing and environmental monitoring to video compression and video analysis.

Brian Corcoran received his doctorate degree in mechanical engineering in 2003 from Dublin City University, Ireland. Since then he has supervised research in high purity water systems, wireless sensor networks, CFD and micro-fluidics. He is currently a lecturer in mechanical and manufacturing engineering at DCU.

Kim Lau received his Ph.D. from Birkbeck College, University of London (Biochemical sensors 2002). He has published over 60 peer-reviewed papers in international journals, is a named inventor in 10 patents. Dr Lau was awarded the DCU Research Fellow 2007-2009. He is currently the Beaufort Scientist at Dublin City University, associate lecturer in School of chemical and biological studies and visiting professor of NorthEastern University of China, School of Chemistry. Dr. Lau is the co-founder of the China-Ireland Centre for Advanced Materials and Sensor Development in Northeastern University that includes members from 4 universities form china and DCU. His research interests include materials research, sensors and biosensors, low-cost sensing platform development for environmental and healthcare applications.

Dermot Diamond received his Ph.D. and D.Sc. from Queen's University Belfast (Chemical Sensors, 1987, Internet Scale Sensing, 2002), and was VP for Research at Dublin City University (2002-2004). He has published over 200 peer-reviewed papers in international journals, is a named inventor in 13 patents, and is co-author and editor of three books. He is currently director of the National Centre for Sensor Research (www.ncsr.ie) at Dublin City University, and a Principle Investigator in CLARITY (www.clarity-centre.com/), a major research initiative focused on wireless sensor networks. In 2002 he was awarded the inaugural silver medal for Sensor Research by the Royal Society of Chemistry, London and in 2006 he received the DCU President's Award for research excellence. Details of his research can be found at www.dcu.ie/chemistry/asg.

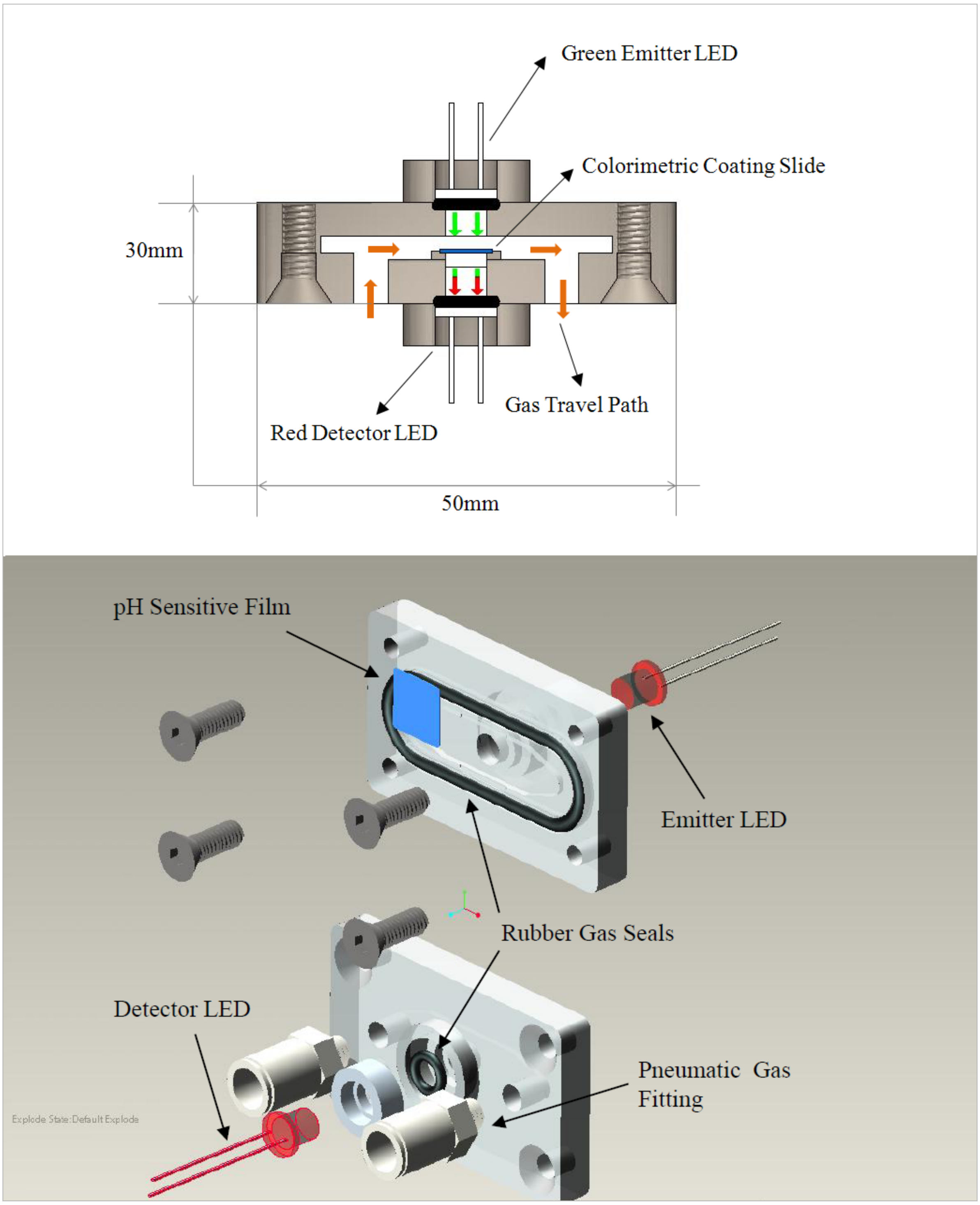

Figure 1. Top view is a horizontal cross section of the sensor flowcell, bottom is an exploded view of the flowcell and the sensor components.

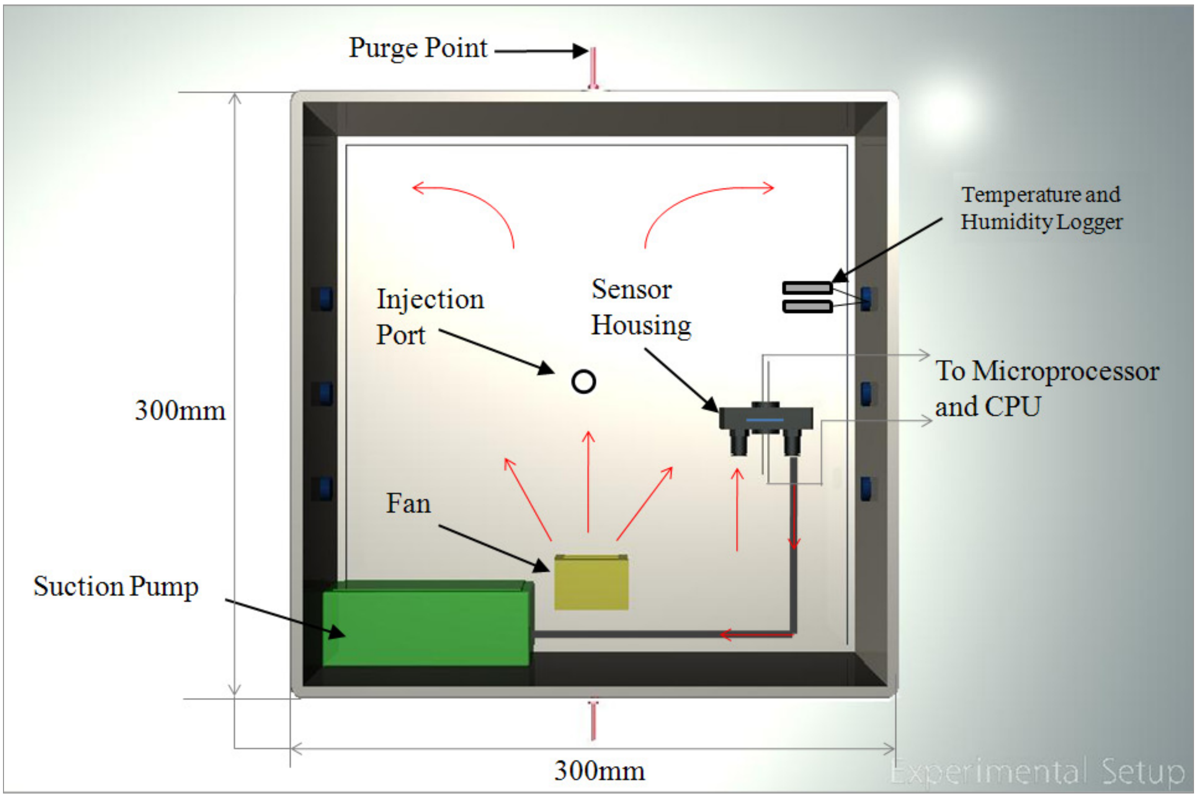

Figure 2. Test chamber configuration. (plan view)

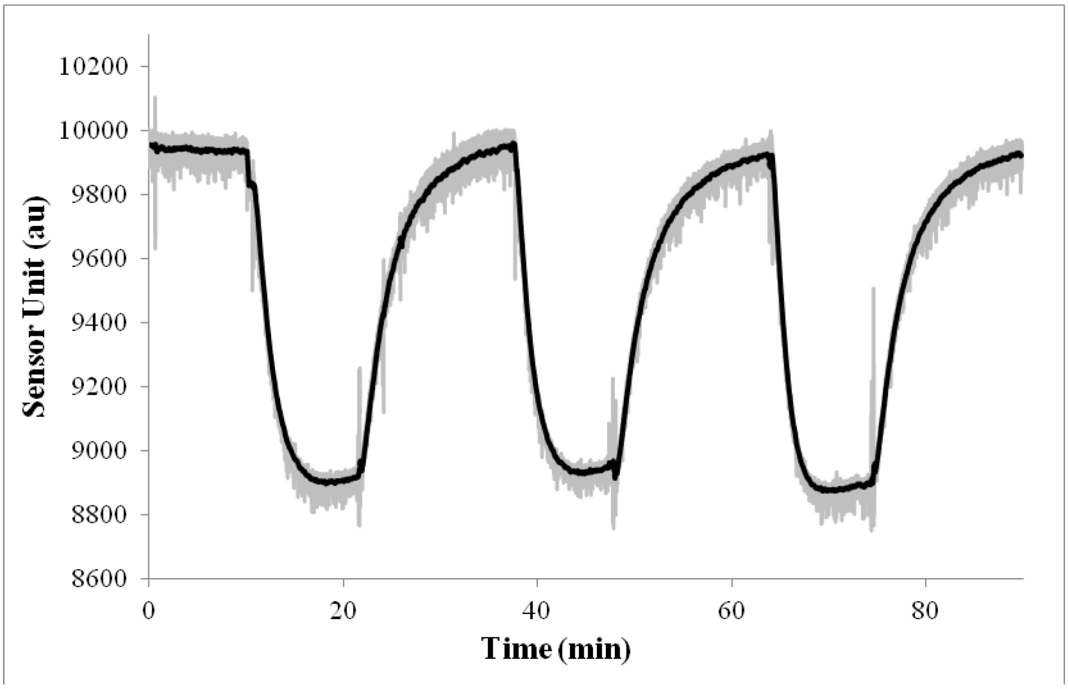

Figure 3. Sensor raw data (gray background) and smoothed data plot (black foreground), generated from test 3.1.

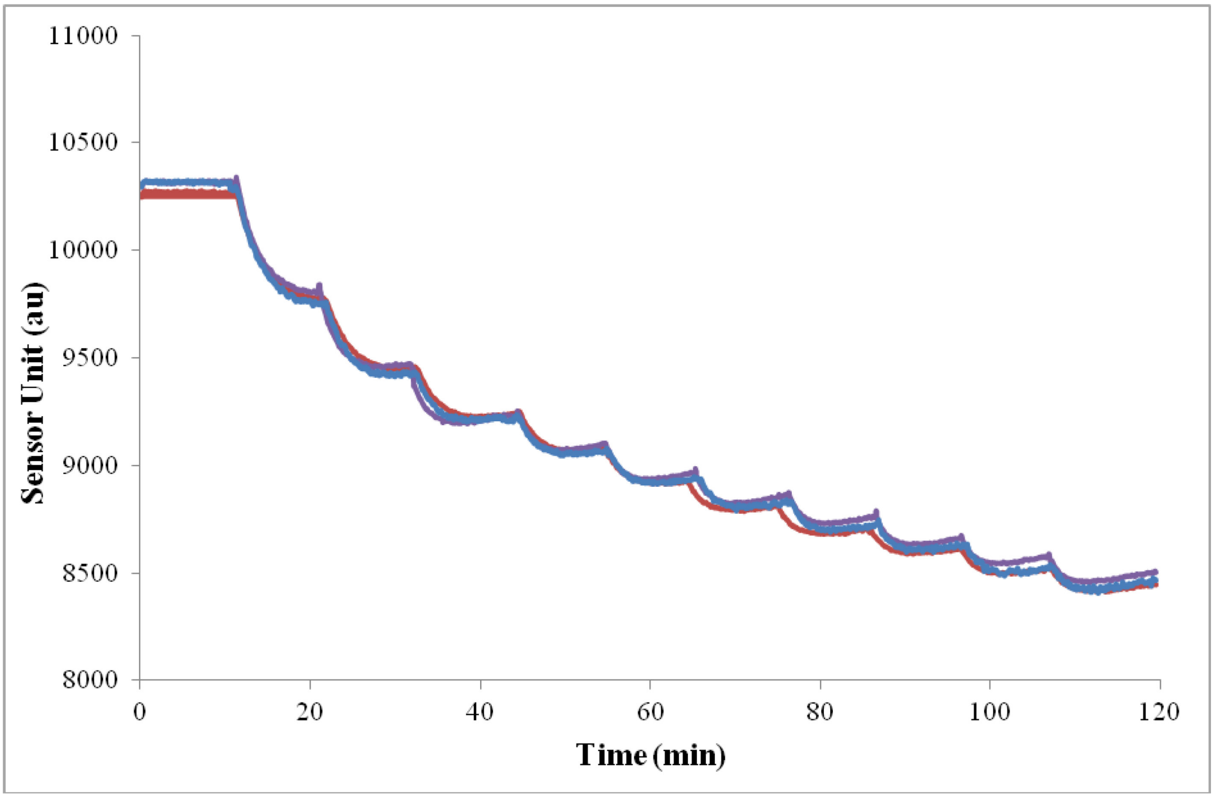

Figure 4. 10 cumulative 0.1 mg/L injections, results from three different slides overlaid

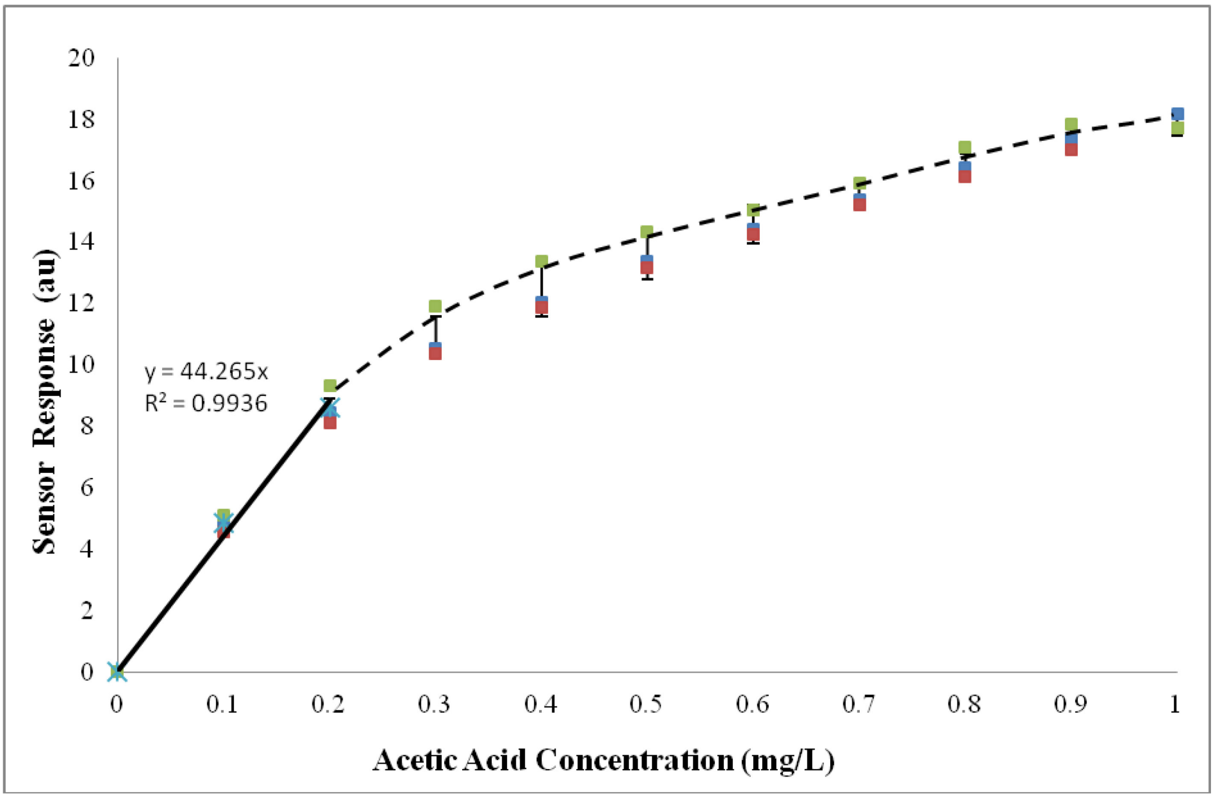

Figure 5. 10 point calibration curve developed in steps of 1 mg/L concentrations of acetic acid in air. Plot shows results from three separate sensor slides with associated error bars (n=3).

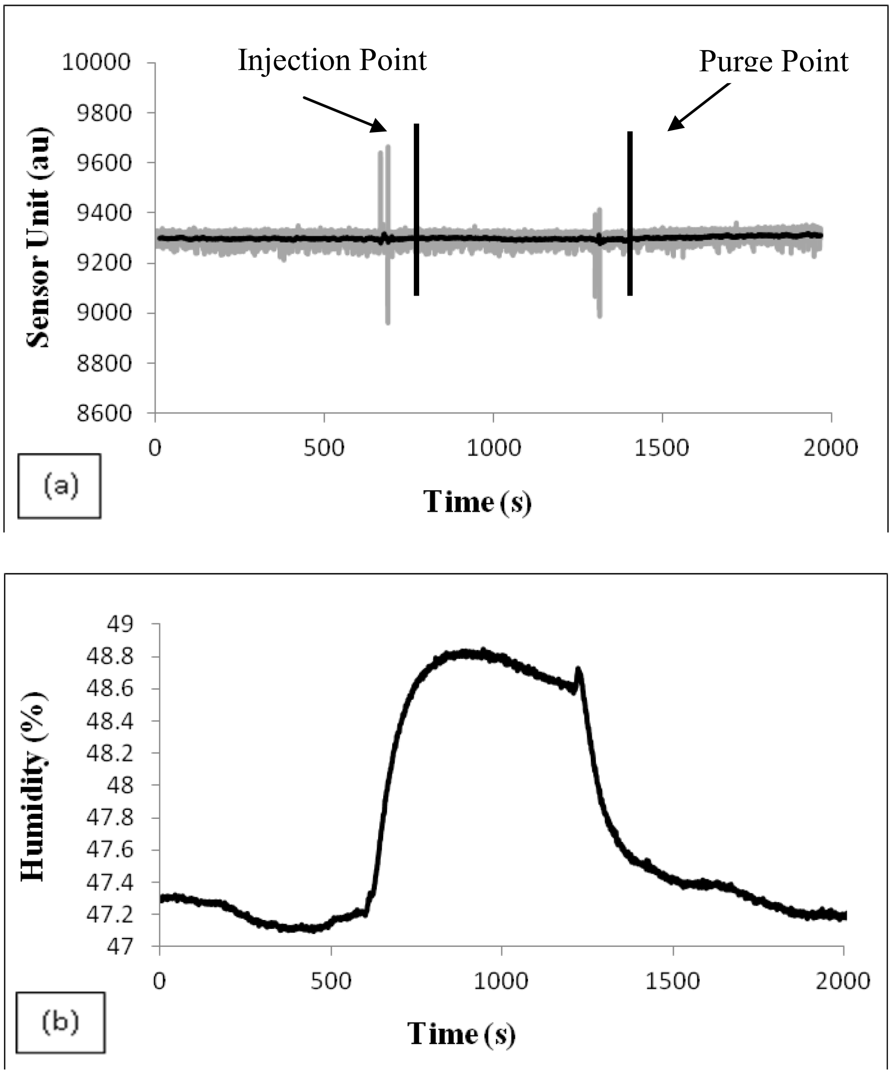

Figure 6. (a) Shows the sensor response over the delivery of a water injection to the test chamber. (b) Shows the change in humidity over the duration of the test.