A Real-time Sensor for Monitoring Organic Contaminants in Groundwater

by

Hoi Yee Jacqueline Ng (CL)

Fourth-year undergraduate project

in Group D, 2011/2012

"I hereby declare that, except where specifically indicated, the work submitted herein is my own original work."

30th May, 2012

Hoi Yee Jacqueline Ng

A Real-time Sensor for Monitoring Organic Contaminants in Groundwater

Technical Abstract

Introduction

Traditional lab-based analysis of groundwater quality can generally identify a wide range of contaminants accurately. However the turnaround time can be long and sample integrity may be lost during transportation and storage process. Also the instruments and manpower involved can be costly. Hence there is a need for a sensor that is able to provide instant and reliable analysis. However there is yet to be an established technique in the market that can provide real-time monitoring of organic contaminants in groundwater.

Project Aims

This project aims to develop a real-time sensor that is easy to fabricate, has a fast response time and can detect volatile organics, in particular MTBE and toluene, at a low concentration level. Also an indoor air quality sensor was purchased and tested alongside for comparison.

Theory

A solid state sensor was developed which was a conductive backing material with TiO_2 coating. TiO_2 works as a photocatalyst that indirectly degrade volatile organics whilst generates free electrons which can induce a current. With a suitable circuit design, the current can be converted and amplified into a voltage signal proportional to the concentration of contaminants in the water. The indoor air quality (IAQ) sensor is an electrochemical sensor which transforms a chemical/physical change into an electrical signal relative to the concentration of volatile organics in air. By Henry's law, the vapour concentration of a volatile organic is linearly correlated to its aqueous concentration at a fixed temperature.

Preliminary Experiments

From preliminary experiments some preferred fabrication methods were found for different backing materials. Suitable apparatus (e.g. UV source, plate holders) and experimental techniques were selected for better performance of sensor and more accurate results.

Method

Different fabrication methods and materials were used to coat TiO_2 onto backing materials. The sensors were then tested with standard solution and/or incrementally increasing concentration methods to see how they respond to MTBE and toluene.

Results & Discussion

It was found that the best fabrication method is to coat a stainless steel plates using ethanol slurry. Figures 1 & 2 show that the relationship between the sensor's output readings and

concentration of MTBE and toluene can be linearised by taking logarithms and modelled by natural logarithms respectively. The IAQ sensor's reading forms a linear correlation with the vapour concentrations of both MTBE and toluene. The low detection limits of MTBE of both sensors have an order of magnitude of 0, whereas of toluene, the order of magnitude of IAQ sensor is 2 orders greater than solid state sensor. The response time of solid state sensor is almost instantaneous whereas IAQ sensor varies with the concentration of chemicals.

Figure 1: Solid state sensor's response to MTBE

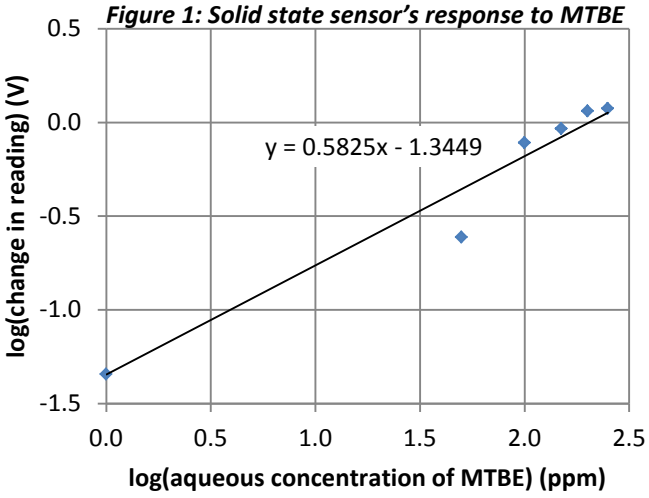


Figure 2: Solid state sensor's response to toluene

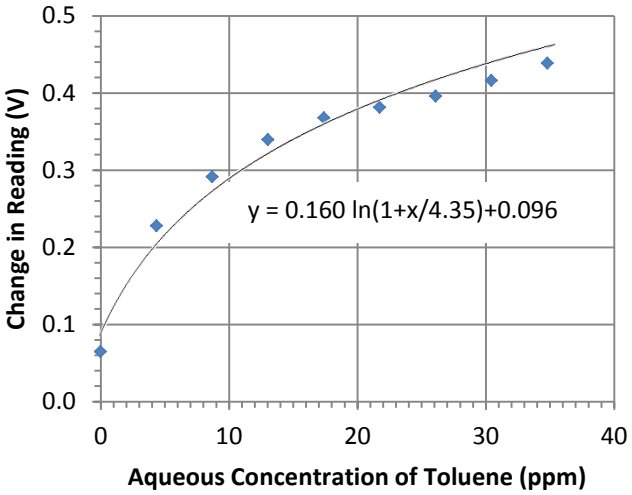


Figure 3: Indoor air quality sensor's response to MTBE

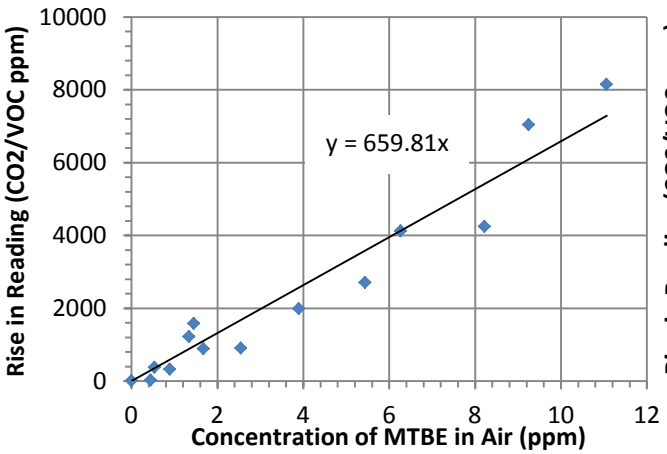
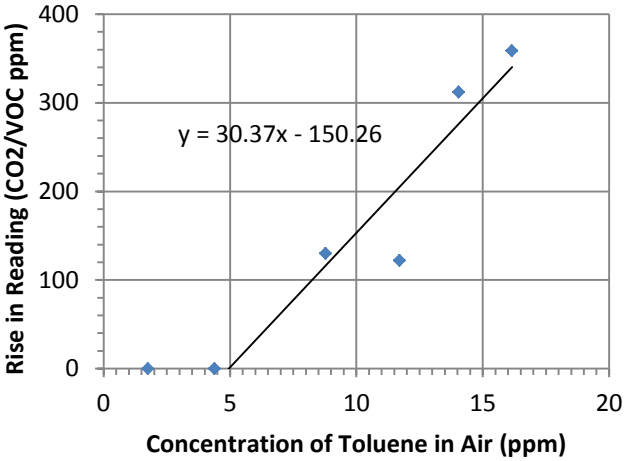


Figure 4: Indoor air quality sensor's response to toluene



Conclusions

A real-time solid state sensor made of ethanol slurry stainless steel plate was found to be easy to fabricate and has fast response time. It can detect a minimum of 3ppm MTBE and 0.5ppm toluene in water, which is better than IAQ sensor (7ppm MTBE and 30ppm toluene in water). Future work is required especially on improving the adhesion issues with TiO_2 coating and hence the durability of the sensor.

Content

1. Introduction

1.1. The Need for a Real-time Sensor

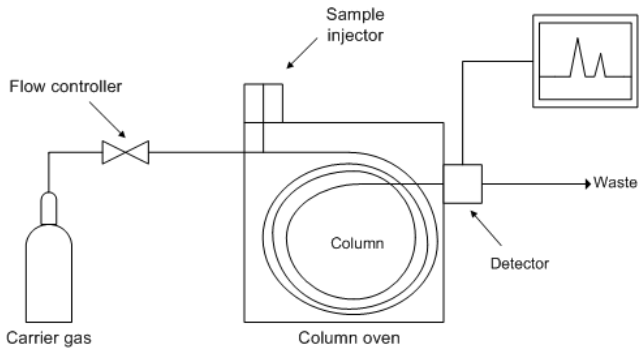


Figure 1: Diagram of a gas chromatograph *(from Wikimedia)*

Traditionally the analysis of groundwater quality is performed in a laboratory. The entire procedure involves collecting discontinuous batches of water samples manually and transporting to the laboratory. They may as well be put into storage before being analysed. Gas chromatography is a technique often used to analyse organic pollutants in groundwater. A sample is first injected into a flowing stream of helium gas. It is then heated and passed through a thin tube called a capillary column which is coated with a material attractive to organics. A gas chromatograph separates and detects the organic compounds according to their volatility (or boiling point).

The main advantages of lab-based methods are that the analysis can be very accurate, different contaminants can be identified and there are a wide range of techniques available. Nevertheless the procedure is time consuming and the integrity of samples may be lost prior to the analysis, such as volatile contaminants may change in concentration during the transportation stage. Also the involvement of manpower (e.g. manual sampling) and the analytical instruments used tend to be expensive.

Therefore there is a need of an instant analysis, in which samples are taken directly to analysis without the need of transportation or storage. This shortens the turnaround time and preserves the integrity of sample, avoiding any changes in vapour/aqueous concentration. The cost of some techniques can be fairly inexpensive as well. In practice, quick response times can influence where to take the next sample and help to choose the most effective sampling point. A portable gas chromatograph is commonly used in the field for detecting volatile organics. It has an oven incorporated and works best with very volatile organics such as benzene, toluene, ethylbenzene and xylene which have low boiling temperatures.

1.2. Comparison of Different Types of Sensors

Currently there are different types of sensors under research and a literature review has been done in my technical milestone report (see Appendix 10.2). Below is a table summarising the

principle, merits and demerits of different types of sensors. (Arshak et al. 2004; Ho et al. 2001)

Types of Sensors		**Principle**	**Advantages**	**Disadvantages**
Piezoelectric Sensors		Change in the mass of sensor coating	Fast response time	Poor signal-to-ratio. Complex and expensive circuitry
Electrochemical Sensors		Transform a chemical / physical change into an electrical signal	Easy and cheap to reproduce.	Sensitivity and selectivity susceptible to temperature
Optical Sensors	Fibre Optic	Change in the light intensity inside optical fibres	Low power consumption. Low detection limit.	Sensitivity decreases over transmitted distance. Coatings degrade over time.
	Colorimetry	Change in colour intensity of sample and reagent solution	Portable. Simple to use. Not susceptible to interferences.	Limited sensitivity to volatile organics. Cannot be used in-situ.
	Infrared (IR)	Change in infrared radiation	Easy to identify specific gases with unique IR absorption spectra. Durable. Require little maintenance.	Expensive. Susceptible to humidity, water, dust and dirt.
Conductivity Sensors		Change in resistance of electrode coating	Quick response and recovery time for inorganics. Can be small and cheap to fabricate.	Susceptible to poisoning and humidity. Response drifts with time. Cannot detect organics.

Table 1: Comparison of Different Types of Sensors

However there is yet to be an established technique that provides continuous and reliable monitoring of organic groundwater pollutants which leads to this project – to develop a real-time sensor to monitor organic contaminants in groundwater.

1.3. Project Aims

This project is aim to develop a real-time sensor that is easy to fabricate and reproduce and is sensitive to a low concentration (ppm) of volatile organics, in particular MTBE and toluene.

It should have a fast response time so that a small change in concentration can be detected fairly quickly. The sensor was based on a solid state sensor developed earlier by Vaidya (2006-7) in her fourth year project which is explained in detail in 2.1. Also an air quality sensor which fits into a USB port of a computer was bought for comparison. It was designed to give an indication of indoor air quality. A possible application of a real-time sensor would be to assess a remediation process, for example to determine whether contaminants are being removed.

1.4. MTBE

Methyl *tert*-butyl ether, MTBE, is a volatile organic compound which was used to be a fuel addictive to replace lead in fuel in order to improve combustion and air quality. However due to its very high water solubility, leakage of MTBE from underground storage tanks becomes a huge issue, as it causes groundwater contamination. A few ppb of MTBE can destroy the taste and odour of water. It is a potential human carcinogen at high doses and it has been banned across the world. In addition since MTBE is not easily decomposed and it spreads very fast in groundwater, it is essential to monitor and remove MTBE from the groundwater in order to minimise its health risk to receivers.

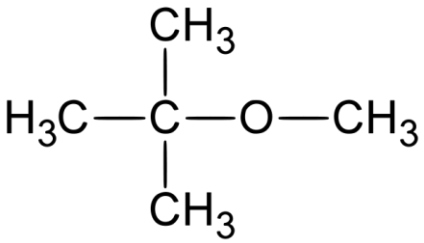


Figure 2: Chemical structure of MTBE *(from Wikimedia)*

1.5. Toluene

Apart from MTBE, the sensitivity and selectivity of sensor to toluene were also tested in this project as both chemicals are soluble organics in water. Toluene, also known as methylbenzene, is an aromatic hydrocarbon. It is a clear colourless and volatile liquid. Toluene occurs naturally in crude oil and is usually produced in the process of making gasoline in a catalytic reformer. According to US ATSDRC and UK EA, gasoline typically contains 5-7% of toluene by weight in the U.S. and 5-11% in UK respectively; hence by knowing the concentration of toluene, the amount of petroleum hydrocarbons present can be estimated.

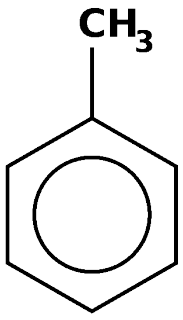


Figure 3: Chemical structure of toluene

Because toxicity of toluene is much lower than benzene, it is a common replacement of benzene as a solvent in the production of paints, adhesives and as a petrol additive to improve octane rating. Toluene may enter the soil and groundwater due to localised spills of petroleum and solvent products from historical use, e.g. near petrol station or refineries.

Toluene can pose a significant health concern such as to the central nervous system if one has a medium/long-term inhalation exposure (e.g. adhesives manufacturers). In this case, appropriate control measures should be taken to minimise the risks and so it was tested only in an enclosed space.

2. Theory

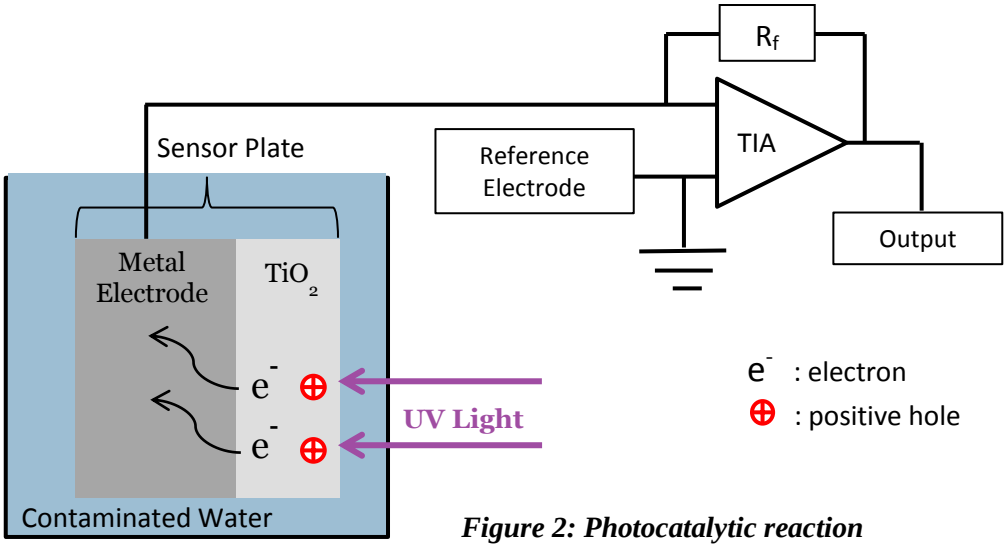


Figure 2: Photocatalytic reaction

2.1. Solid State Sensor

The sensor used in this project is based on the solid state sensor designed by Vaidya (2006-7) which was shown to work on MTBE. Figure 2 above shows how the sensor works via photocatalytic reaction.

The sensor plate consists of a metal electrode coated with titanium dioxide, TiO_2. Under UV light, TiO_2 becomes a photocatalyst and generates electron-hole pairs. Water molecules react with the holes to form hydroxyl radicals (·OH) which in turn degrade MTBE into carbon dioxide and water. In the meantime, free electrons drift to the metal electrode which can induce a small current if connected to a circuit.

The overall MTBE photocatalysis reaction is: $C_5H_{12}O + 7.5O_2 \rightarrow 5CO_2 + 6H_2O$

The design of circuit includes a reference electrode, a feedback resistance (R_f) and a trans-impedance amplifier (TIA). This circuit compares the current from both sensor plate and reference electrode and converts it to voltage. The output signal is amplified by the R_f and the TIA. Thus current generated from the degradation of MTBE is proportional to the concentration of analyte present in the contaminated water. Moreover, this process is

reversible. Reduction in MTBE concentration decreases the number of holes required. The extra holes generated will recombine with the free electrons and so the current will drop.

2.2. Indoor Air Quality Sensor

In addition to the solid state sensor, an indoor air quality sensor (Voltcraft CO-20, Figure 3a) was purchased for comparison. As shown in Figure 3a, this sensor is in an USB-stick format so the power supply can be supplied from a computer. It is claimed to be able to detect volatile organic compounds (VOCs), carbon dioxide and any unpleasant odours. Also the provided data logging software allows the measured data to be plotted (Figure 3b) and recorded onto the computer, in the unit of CO_2/VOC ppm. It should be noted that this sensor is designed for monitoring the air quality of indoor areas, living and office spaces for instance, instead of accurate laboratory or field analysis. Therefore high concentration of MTBE or toluene was avoided in the experiments to prevent damaging the sensor.

In contrast to the solid state sensor, this sensor uses metal-oxide semiconductor sensor technique to detect VOCs, which is likely to be an electrochemical sensor as described previously in Table 1. It should be noted that one of its disadvantages is being susceptible to operating temperature, which would also affect the equilibrium of VOC concentration in the solution and in the headspace. This is further explained in the next section.

Figure 3a: Voltcraft CO-20 USB gas measuring

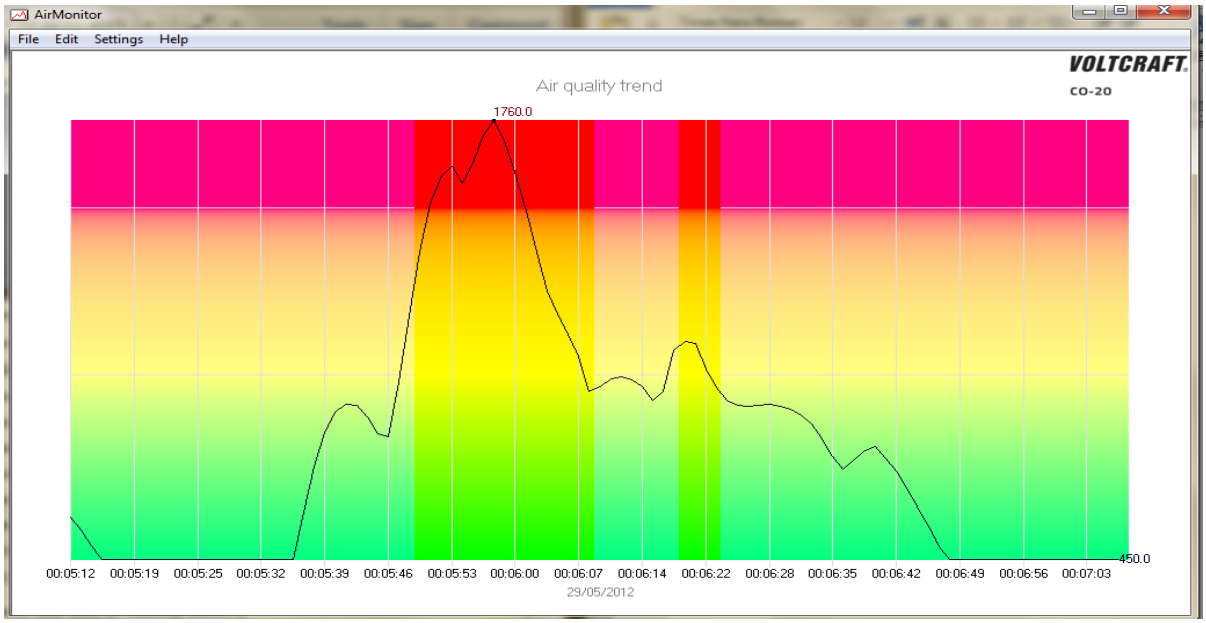


Figure 3b: An example of a real-time graph provided by the software

2.3. Henry's Law

Henry's law states that at a constant temperature, the solubility of a gas in a particular solvent is proportional to the partial pressure of the gas. The proportionality constant for this relationship is given by Henry's law constant which depends on the temperature and comes in different forms and units. For simplicity, the dimensionless Henry law's constant, k_H, is considered in this report, which is the ratio of concentration of gas in solution to the concentration of gas, i.e. k_H = air content / water content

Fischer and Muller (2003) found that the dimensionless Henry's law constant of MTBE varies with temperature exponentially as given in Table 2 and Figure 4.

Temperature (°C)	Henry's Law Constant $C_{(gas)}/C_{(aq)}$
3.0	0.009
5.0	0.011
10.0	0.012
15.0	0.018
20.0	0.022
25.0	0.029

Table 2: Dimensionless Henry's law constants of MTBE at different temperatures

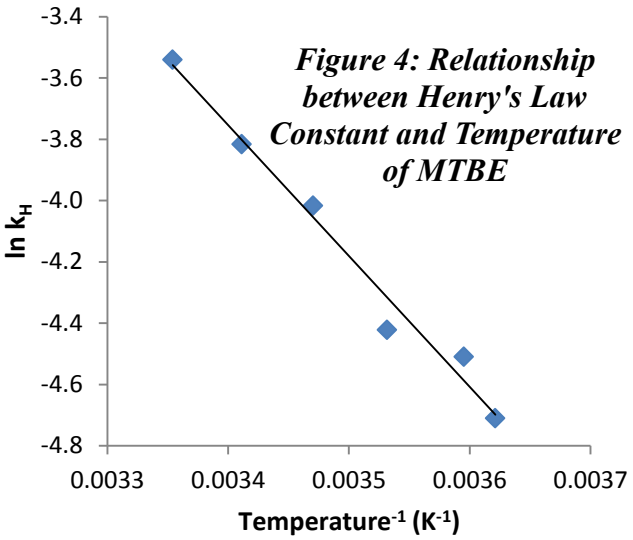


Figure 4: Relationship between Henry's Law Constant and Temperature of MTBE

Since the solid state sensor measures the aqueous concentration whereas the indoor air quality sensor measures the gas concentration, it is important to keep the temperature of experiment constant in order to allow equilibrium to establish. Therefore Henry's law can be applied and both sensors can be compared fairly.

3. Solid State Sensor

3.1. Preliminary & Design of Experiment

Several preliminary experiments were conducted in order to identify different variables and to improve the final experiment. Figure 5 illustrates the initial setup of the experiment.

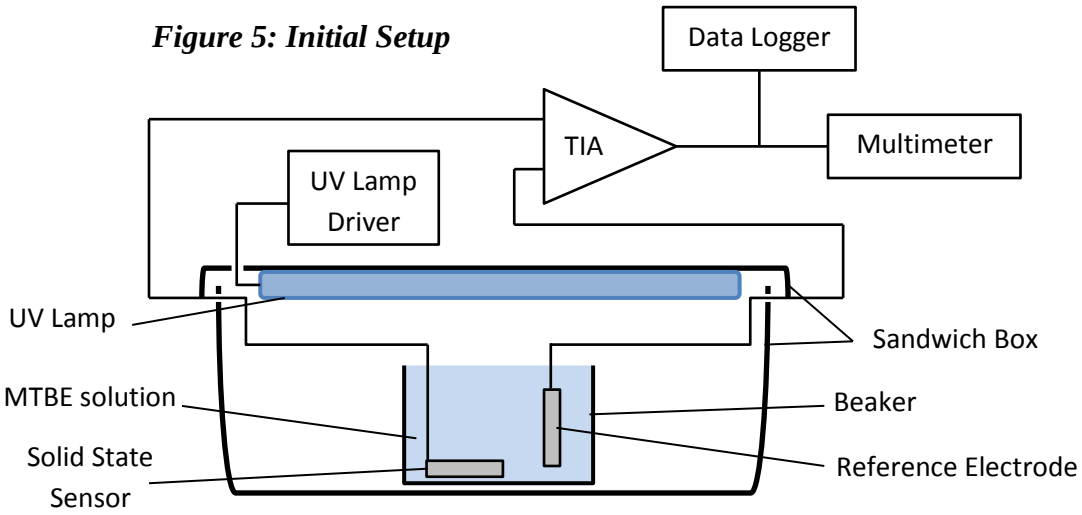
Certain concentration of MTBE solution was first made up and poured into the beaker. Solid state sensor plate and reference electrode were then placed into the beaker and connected to the TIA as in Figure 5. The lid was closed and the UV lamp was not turned on until the

readings stabilised. Again the readings were allowed to settle before the UV lamp was turned off. Since the initial reading varied with experiments when the UV light was off, change of reading, ΔV, was calculated. This was found by:

ΔV = (average of *stabilised* readings when UV is on) – (average of *stabilised* readings when UV is off)

Detailed method and calculations used in the final experiment are explained in 3.2.3.

Figure 5: Initial Setup



3.1.1. Stainless Steel

Initially 30mm x 50mm stainless steel plates were used as backing material. At first the method of Vaidya's (2006-7) was followed using TiO_2/water slurry (see 3.2.3.1 for detailed method of making). However the coating did not seem to adhere very well and there was a lot of cracking. After the first experiment more than half of the coating has already fallen off. This is illustrated in Figure 6 which is very undesirable as the sensor is not durable at all. Therefore TiO_2/ethanol slurry was tried instead. This time in attempt to alleviate the cracking problem, the stainless steel plate was first cleaned with acetone to remove any dirt and grease. Then a thinner slurry was made using ethanol instead of water and applied onto the plate. It was again allowed to air-dry. This seemed to work and the adhesion was better (see Figure 7). Although there was still fall-off, it was not as significant as using TiO_2/water slurry. Thus this fabrication method was used as a basis for comparison in the final experiment.

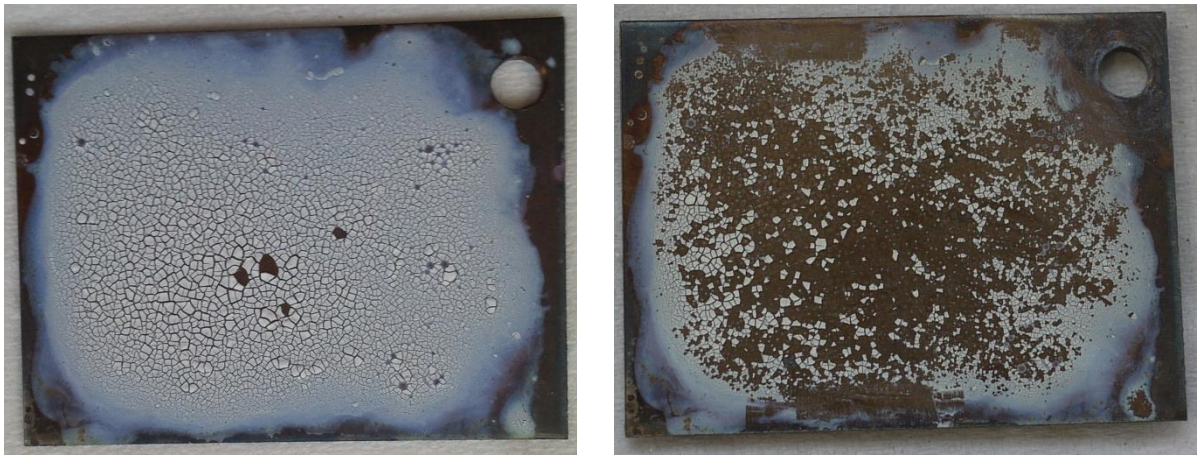


Figure 6: TiO_2/water slurry - before (left) and after (right) testing

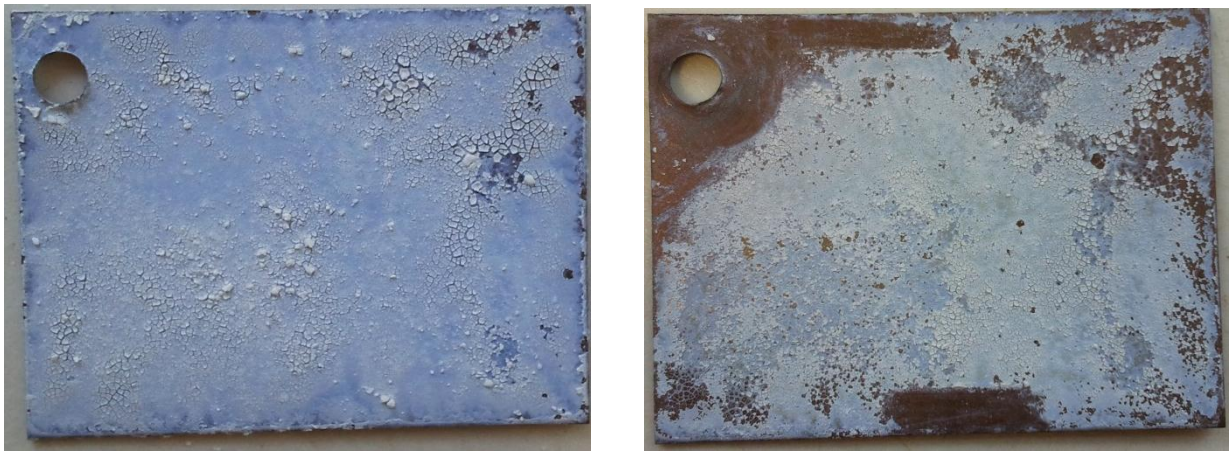


Figure 7: TiO_2/ethanol slurry - before (left) and after (right) testing

3.1.2. Unprinted Circuit Board

Unprinted circuit boards were also tried as backing materials, which were kindly provided by Dr Dukic from the Electronic Development Group. They are copper sheets laminated onto a plastic substrate, allowing one side of the plate to act as a sensor and the other side as a reference electrode. Hence there is no need for a separate reference plate, making the sensor smaller and more portable.

Initial testing with both ethanol and water slurry method was unsatisfactory. The coating was not attached firmly enough. Electronically conducting silver paint was included in the coating to see if it would solve the problem. Also diluted washing liquid was also added into the slurry as Shimizu *et al* (1999) found that surfactants could improve "the quality and the crystallinity of the films". Various mixtures were tested on the same unprinted circuit board as shown in Figure 8a. After they were dried, the coating was slightly scratched and soaked in water for 10 seconds to check how well the coating was bonded. In Figure 8b, it seems that areas 1 and 3 (top & bottom right hand corner) performed the best which were coated with

slurry made of ethanol, TiO_2, silver paint with or without surfactant. These two fabrication methods were tried again in the final experiment.

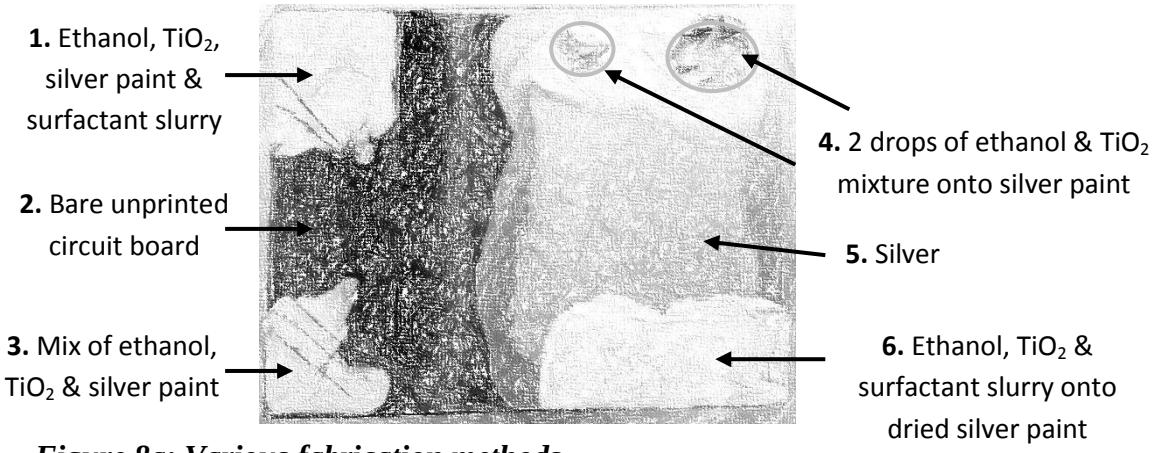


Figure 8a: Various fabrication methods

Figure 8b: Before (left) & after (right) soaking in water for 10 seconds

3.1.3. UV Light Source

A UV lamp from Philips Cleo (15W, no reflector) was used. It is attached to the bottom side of the sandwich box lid, so UV light is always shining downwards, preventing any undesirable eye contact and damage due to UV leakage. This also keeps the distance between the UV source and the solid state sensor constant, ensuring the amount of UV light exposed to sensor constant and controlled.

A UV light emitting diode, LED, was later proposed to replace the original UV lamp as it is small and gives direct radiation. The UV LED available at the laboratory is 395nm in wavelength. As shown in Figure 12, turning the UV LED on and off did not affect the reading. Afterwards it was found that because the UV absorption spectrum of TiO_2 is <388nm, TiO_2 cannot work as a photocatalyst at 395mm UV light. Hence MTBE was not decomposed and there was no significant change in reading.

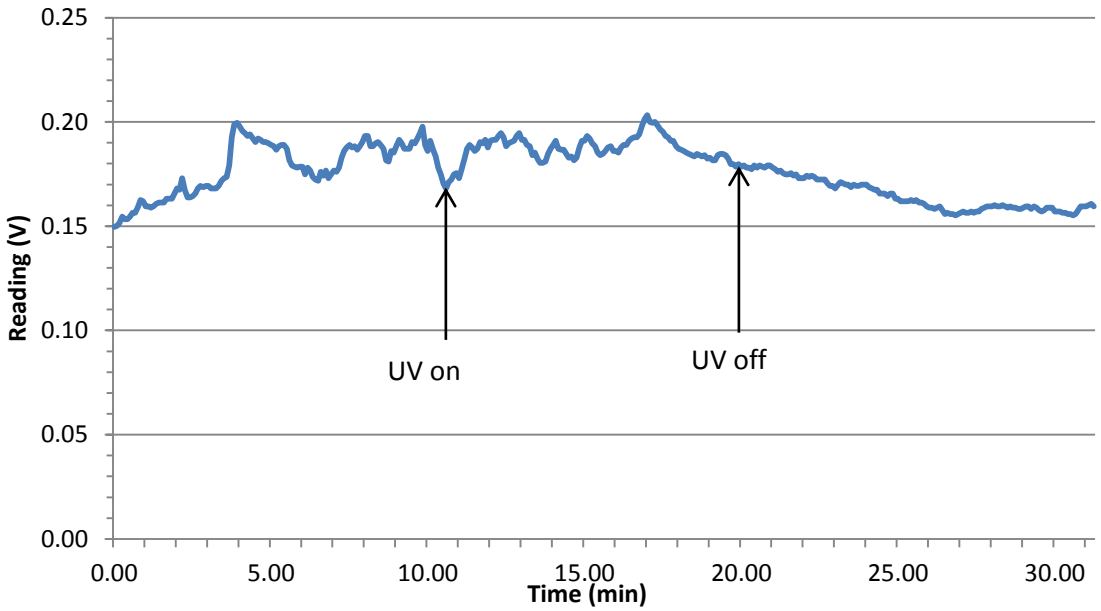


Figure 12: Sensor plate response to 0.2% MTBE under a UV LED

3.1.4. Data Logger

Readings output to multimeter were at first recorded manually every 30 second which incurred human reading errors and was very time consuming. It was then replaced with a data logger which is accurate up to 4 decimal places and records readings every 5 seconds.

3.1.5. Reference Electrode

A silver/silver chloride (Ag/AgCl) reference electrode was used at first but it was later on found out that UV light can decompose AgCl to Ag according to Rodgers, 2011. Therefore a clean uncoated stainless steel plate was used instead. This was also suggested by Vaiyda, 2006-7, for future improvement on reference electrode, because this would also reduce any relative metal potential.

Figure 8 compares using either Ag/AgCl electrode or an uncoated metal plate (same material as sensor) as a reference electrode which were tested in 10g/L of MTBE solution. The noise of Ag/AgCl electrode (~0.08V) is about twice greater than the uncoated metal plate (~0.04V). Also the larger change in reading of the uncoated metal plate suggests that it would be able to provide greater sensitivity, i.e. lower detection limit of MTBE. Hence an uncoated metal plate was used as a reference electrode in the final experiment.

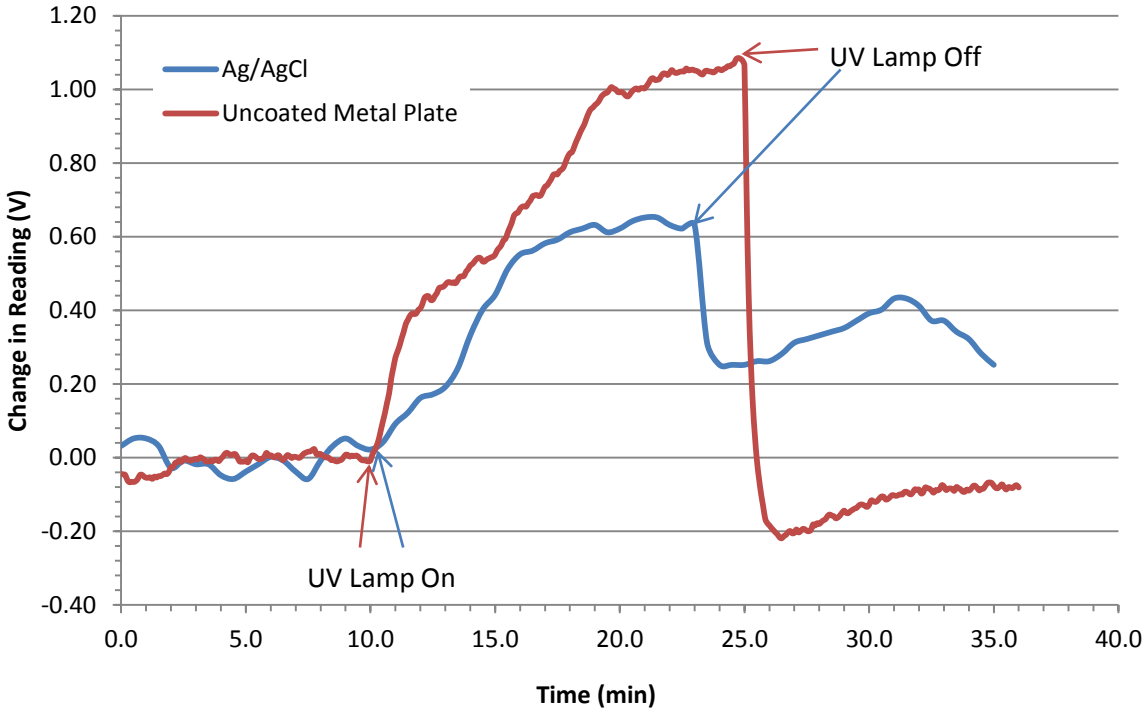


Figure 8: Comparison between Ag/AgCl electrode and an uncoated metal plate as a reference electrode

3.1.6. Distance of Plate Separation & Effect of Stirring

Experiments were carried out to investigate if stirring and the spacing between the sensor and the reference plates may have an effect on the readings and the time for the readings to settle with the UV on. Stirring was introduced using a magnetic stirrer directly underneath the beaker inside the sandwich box and a magnetic bead inside the solution, whereas the distance between plates was varied approximately with the aid of tapes. The results are shown in Figures 9 & 10.

Figure 9 suggests that varying the spacing between plates does have some effect on the reading. Therefore the two plates should be kept fixed at a constant separation distance. Generally placing the plates closer together seems to increase the change in reading slightly. This should also improve the accuracy since the concentration of solution surrounding the reference electrode should better resemble the concentration around the sensor. However it is true that placing the two plates too close might turn the sensor into a capacitor.

Moreover Figure 10 shows that the settling time of readings when UV is on has decreased as distance between plates reduces. This implies the diffusion limit of the photocatalytic reaction is achieved more quickly, making the monitoring process more effective.

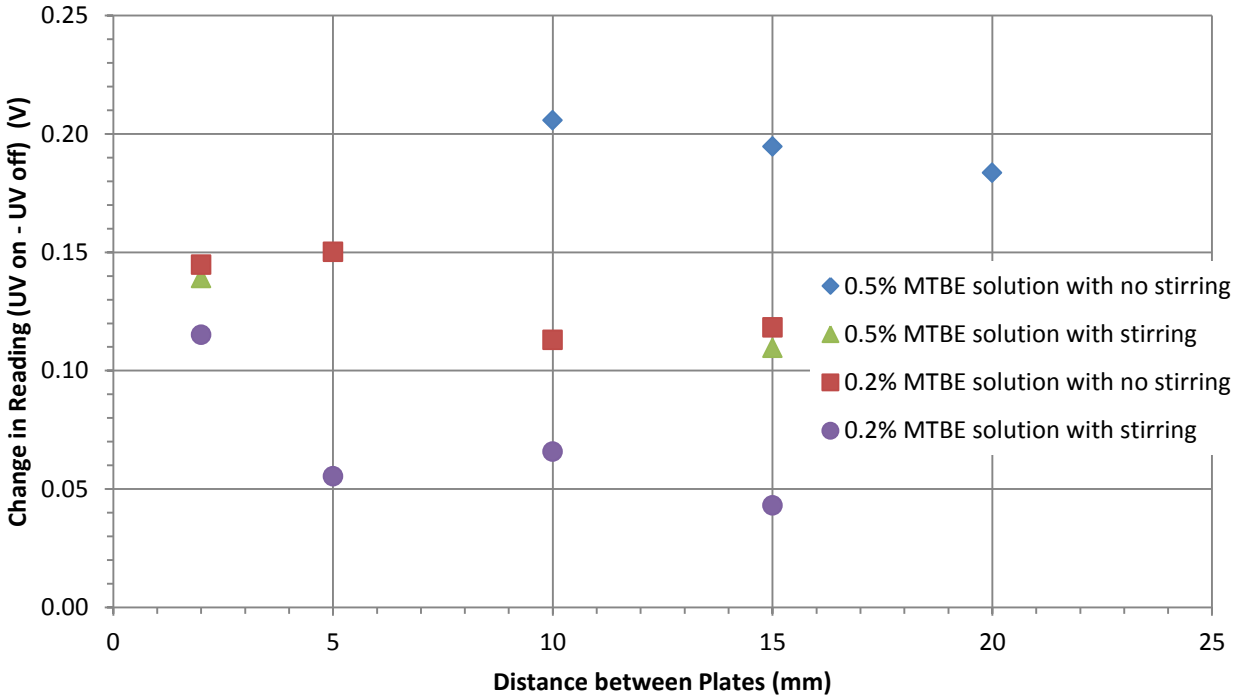


Figure 9: Effect of stirring and distance between plates on the change in reading

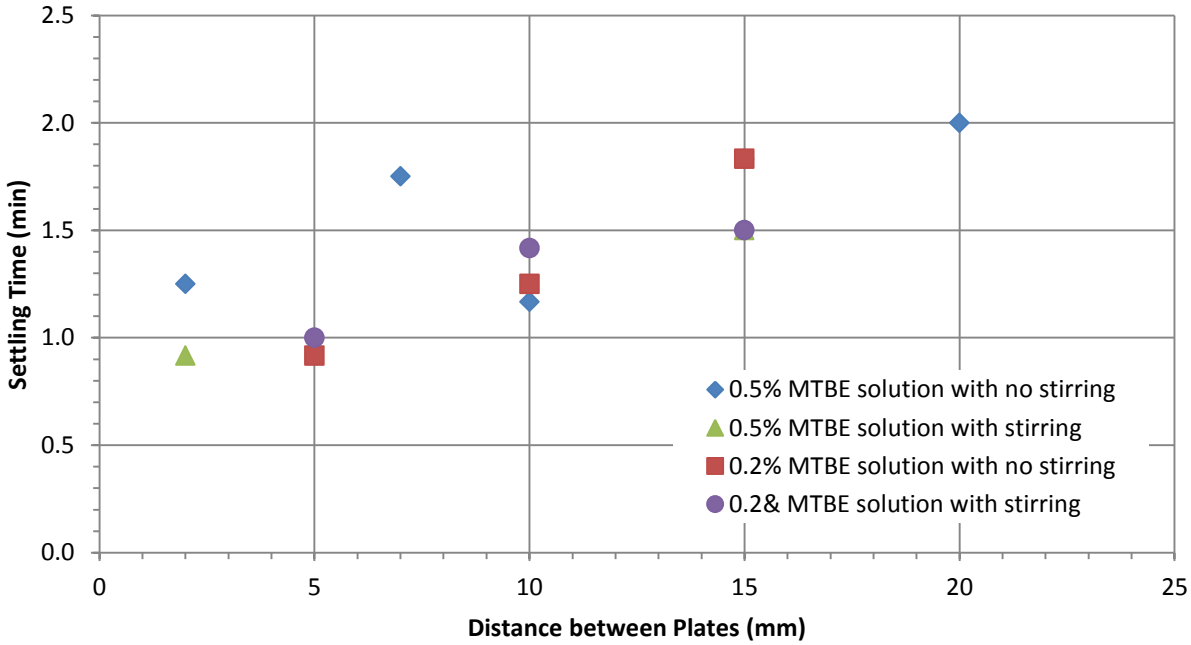


Figure 10: Effect of stirring and distance between plates on the settling time

The benefits of reducing the spacing between plates are demonstrated by both results, that the sensitivity and the settling time of sensor can be enhanced. Hence a pair of persepx plates holders were made as shown in Figure 11 below, which keeps a distance of 2mm between the sensor and reference plates. This would also reduce the overall space requirement by the sensor.

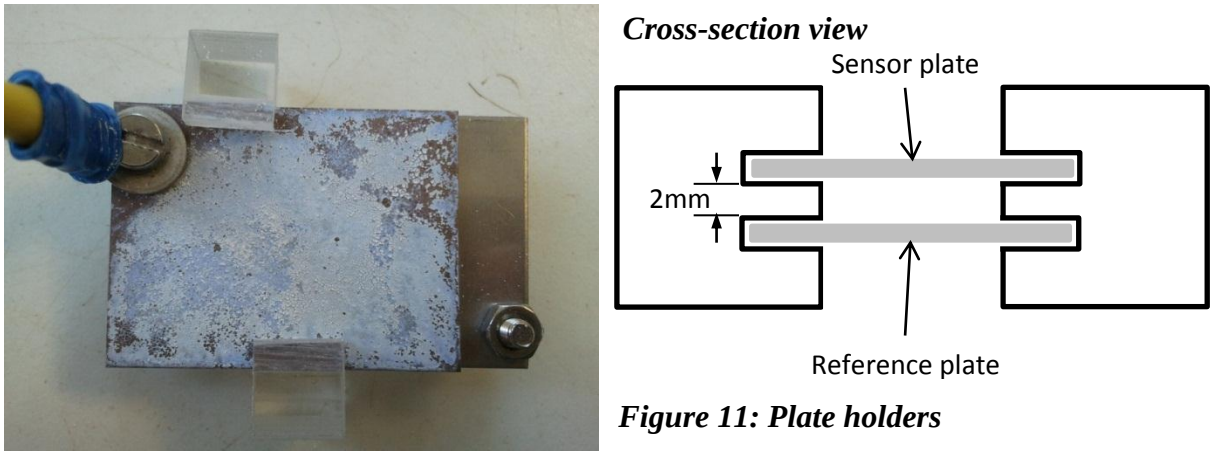


Figure 11: Plate holders

On the other hand, stirring seems to reduce the change in reading for some degrees, possibly because stirring limits the diffusion of MTBE towards the sensor. Thus the concentration near the sensor plate reduces. This would also suggest the settling time should be reduced. It agrees with the results in Figure 10 with higher concentration 0.5% MTBE, but settling time for lower concentration 0.2% MTBE is hardly affected. Overall the reduction in readings might make differentiating between a small change in concentrations difficult and it does not improve the settling time hugely, so stirring was not applied in the final experiment.

3.1.7. Experimental Techniques

Two different techniques were used to test the solid state sensor. The first one involves making a range of concentrations of standard solutions which were then tested against the sensor. However when measuring the mass of MTBE, the reading of the scale kept decreasing which might be due to the volatile nature of MTBE. Hence another technique was tried with both MTBE and toluene, as suggested by Dr Lynch. A drop of MTBE or toluene was continuously added to the beaker directly after the readings have stabilised so any vaporisation would stay within the sandwich box without losing. A step-wise increase in readings would be expected as well.

3.2. Method

3.2.1. Materials

- TiO2 powder from Evonik Aeroxide TiO_2 P25 (same as Degussa P25)
- Stainless steel plates, 35mm x 25mm
- 35mm x 25mm unprinted circuit boards
- 35mm x 25mm chromium plated glass
- Ceramic plate coated with carbon powder
- Silver varnish (Kemo Electronic)

- Nickel spray paint
- Methyl-tert-butyl ether (Fischer)
- Toluene (BDH)
- UV lamp (Philips Cleo, 15W, no reflector, 16mm diameter, 300mm long, 260nm light, optical power 2.1W)

3.2.2. Fabrication Method

Different backing materials and various methods were used in attempt to make a working solid state sensor.

3.2.2.1. 35mm x 25mm Stainless Steel Plates

Water slurry method: A few drops of water were added to the TiO_2. Two coats of the water slurry were applied on the plate surface which was allowed to air-dry in between. Then the plate was put into a non-preheated furnace and baked at 200°C for 5 min. It was allowed to cool down in the furnace overnight.

Ethanol slurry method: The surface of plates was first polished with silicon carbide paper 400 for better adhesion. Then it was cleaned with acetone to remove any leftover debris or grease. A few more drops of ethanol were mixed with TiO_2 to make thinner slurry. The plate was left soaked in the slurry and air-dried overnight. Another coat of slurry was applied onto the plate and let dry. The plate was baked at 500°C for 30min and cooled inside the furnace overnight.

Silver paint method: Electronically conducting silver varnish was painted on a clean plate. TiO_2 was sieved through a 90μm mesh fibre on the wet varnish immediately afterwards and allowed to try. The plate was then baked at 500°C for 30min and cooled inside the furnace overnight.

3.2.2.2. 35mm x 25mm Unprinted Circuit Boards

Zinc glue method 1: Zinc glue was mixed with TiO_2 and spread across the surface of circuit board. It was heated to about 600°C for 1min using a heat gun and let cool. The sides of the plates were abraded to remove any conductive materials such as the copper coating. Wires were soldered to the coated and uncoated side of the plates.

Zinc glue method 2: Zinc glue was first spread on the board surface. It was then heated to about 600°C for a while until melted. TiO_2 powder was immediately sprinkled over and allowed to cool and solidify.

Silver paint method: Ethanol, TiO_2 and silver paint were mixed together which was then painted onto the plate. It was allowed to dry overnight before testing.

Silver paint & surfactant method: Same as silver paint method with the addition of two drops of diluted washing liquids into slurry.

Nickel spray method: Nickel spray paint was sprayed over the surface of the plate. TiO_2 was quickly dusted over the paint while it was still wet. It was allowed to dry before testing.

3.2.2.3. 30mm x 30mm Carbon Coated Ceramic Plate

A carbon coated ceramic plate using powder coating was kindly produced by Dr Long. The TiO_2 coating was done the same way as the ethanol slurry method of stainless steel plates without the polishing and cleaning in the beginning.

3.2.2.4. 35mm x 25mm Chromium Plated Glass

The chromium plated glass remained from Vaidya's project (2006-7) was given by Dr Wilkinson. TiO_2 was coated onto the glass surface using the ethanol slurry method as for stainless steel plate. Electrically connection was made by using the clips from name badges (see Figure 23).

3.2.3. Standard Solution Method

Set-up of Experiment

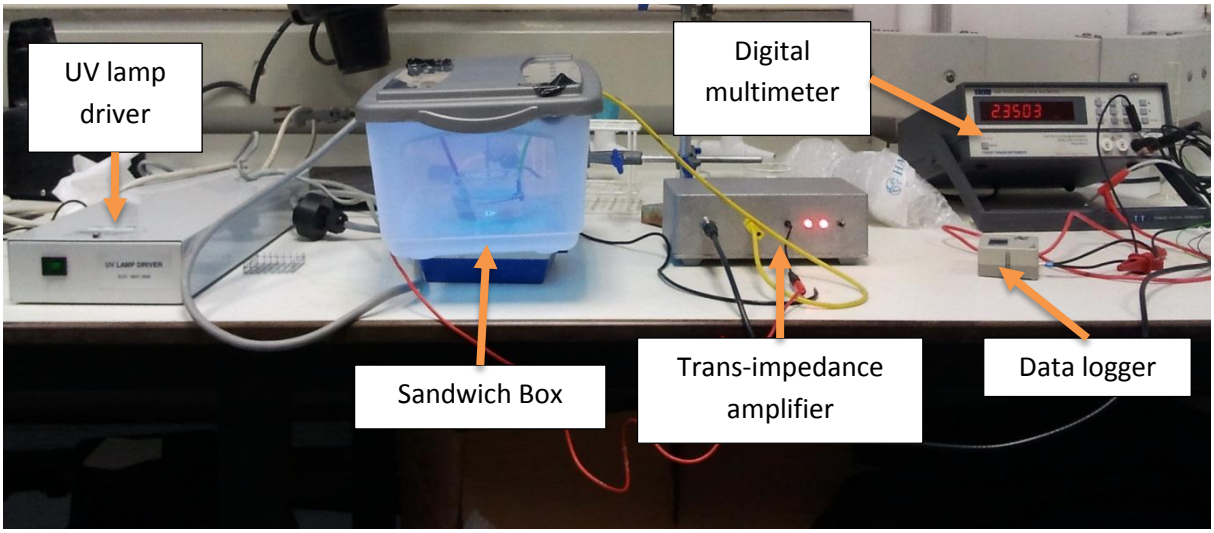


Figure 13a: Photograph of the set-up

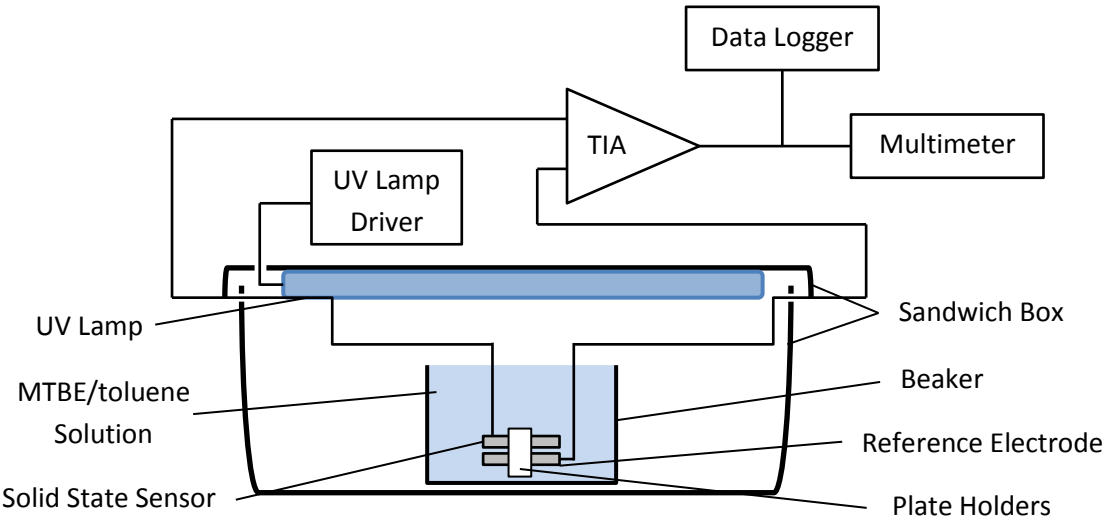


Figure 13b: Schematic diagram of the set-up

Procedure

Mass of MTBE ranging from 0 to 0.5g was weighed into a 100ml volumetric flask which was then filled with deionised water to make up various standard solutions. It was shaken well before pouring into the beaker for testing.

The experiment was set up as shown in Figure 13. Any openings or holes were blocked using a tape to prevent the leakage of MTBE. The UV lamp was kept turned off at first but the data logger and the multimeter was on. The voltage reading was allowed to settle. Then the UV lamp was turned on and the reading should start rising. The UV lamp was switched off once the reading had stabliised for around 5 minutes. The reading would be expected to fall back to approximately its initial value.

Calculations

As described previously, the change in reading, ΔV, is calculated by
(average of stabilised readings when UV is on) – (average of stabilised readings when UV is off)
which is illustrated in Figure 14.

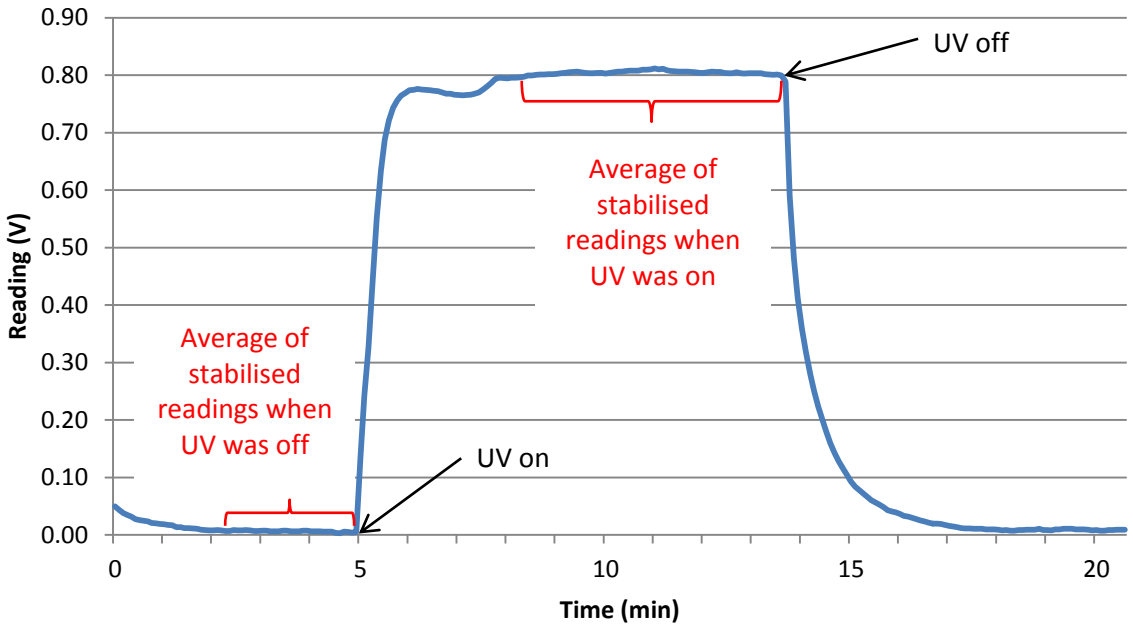
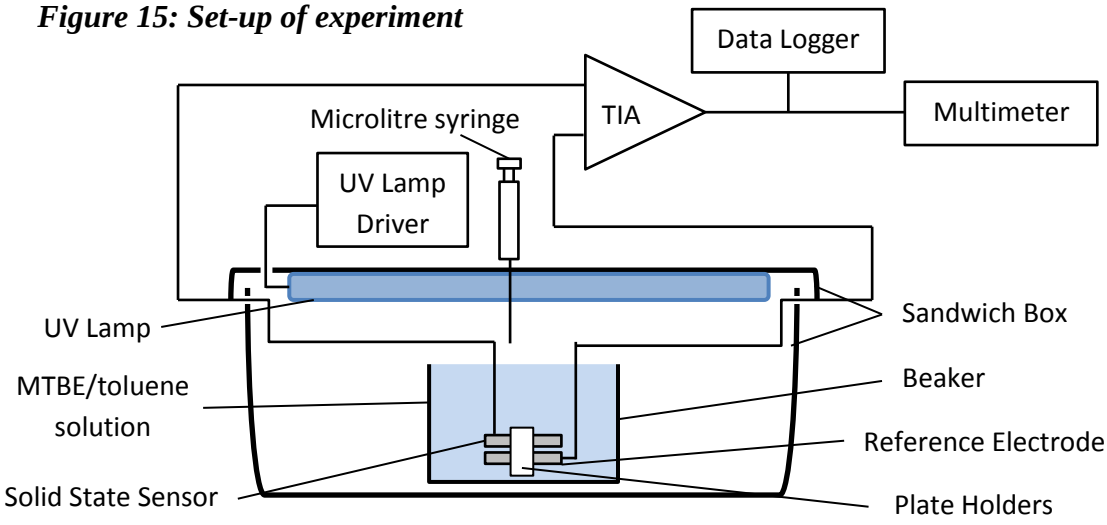


Figure 14: Calculation of change in reading

3.2.4. Incrementally Increasing Concentration Method

Set-up of Experiment

Figure 15: Set-up of experiment



Procedure

The apparatus was set up as in Figure 15 but the beaker was first filled with 100ml of deionised water only. The data logger and multimeter were switched on and the readings were allowed to stabilise before turning on the UV lamp. Once the readings had settled, using a microlitre syringe 5µl of MTBE or toluene was injected into the beaker. This process was repeated until desired concentration had been reached.

Calculations

The volume of MTBE or toluene was first converted into mass by taking the densities of MTBE and toluene as 740g/l and 870g/l respectively. The rest of caluclations are the same as the standard solution method in 3.2.2.

3.3. Results

3.3.1. Solid State Sensor Plates

Compared to the ethanol slurry method of fabricating a stainless steel plate into a solid state sensor, other methods either gave very poor adhesion between the backing material and TiO_2 coating, or did not produce a working sensor. Following photos (and Figures 6 & 7) are the sensors fabricated using different methods described previously.

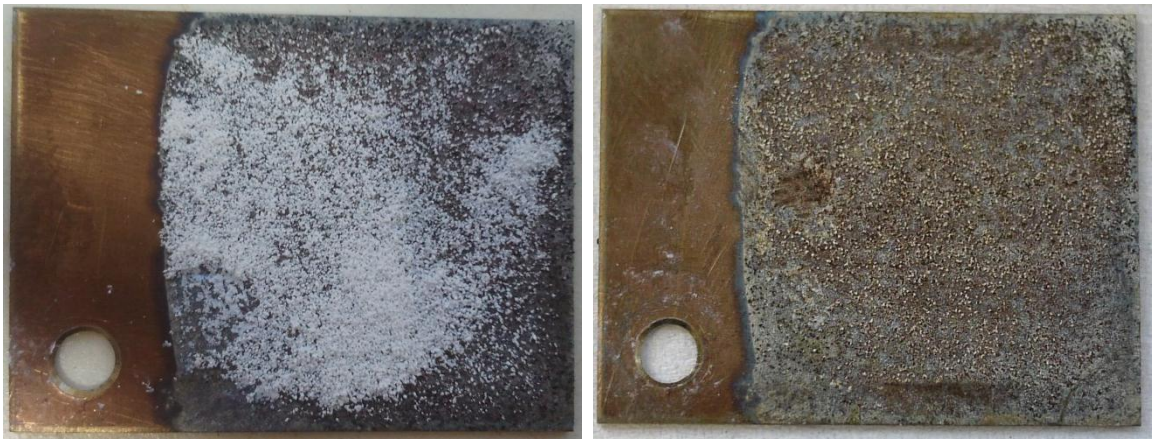


Figure 16: Stainless steel plates using silver paint method – before (left) and after (right) testing in MTBE solution

Figure 17: Unprinted circuit board using zinc glue method 1

Figure 18: Unprinted circuit board using zinc glue method 2

Figure 19: Unprinted circuit board using silver paint method – before (left) & after (right) after handled gently

Figure 20: Unprinted circuit board using silver paint & surfactant method – before (left) & after (right) soaking in water for 10 seconds

Figure 21 (right): Unprinted circuit board using nickel spray method

Figure 22: Before (bottom left) & after (bottom right) after baking ceramic plate

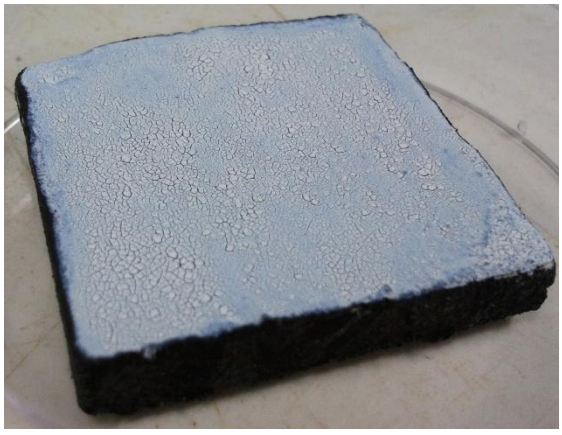


Figure 23: Chromium plated glass using ethanol slurry method and its connection clip

3.3.2. Testing of Different Sensor Plates in MTBE Solution

The following graphs, Figures 24-27, are the results of testing different fabricated sensor plates in MTBE solution using standard solution method.

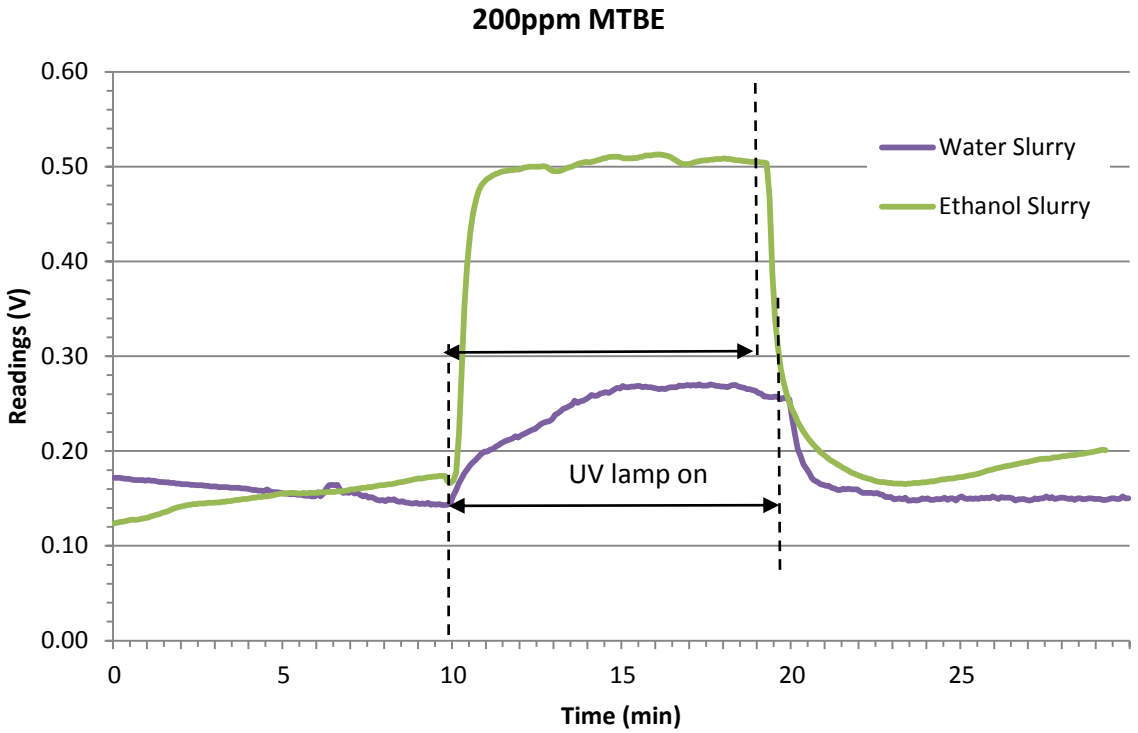


Figure 24a: Comparison of signal strength between water slurry and ethanol slurry methods in 200ppm MTBE

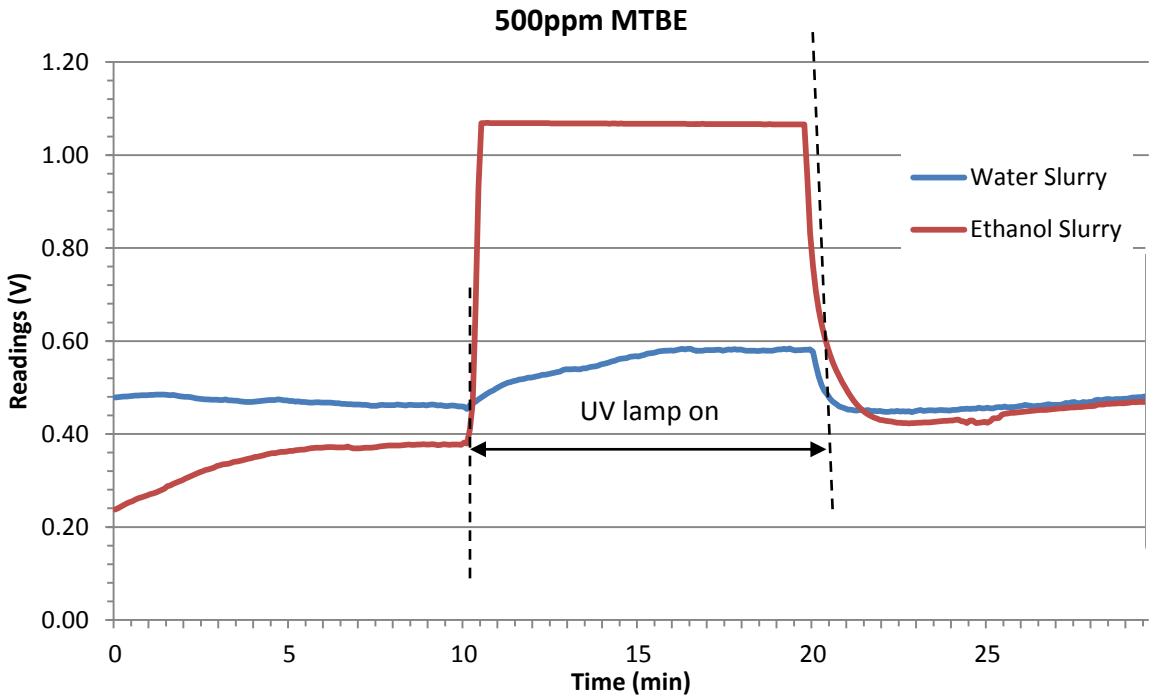


Figure 24b: Comparison of signal strength between water slurry and ethanol slurry methods in 500ppm MTBE

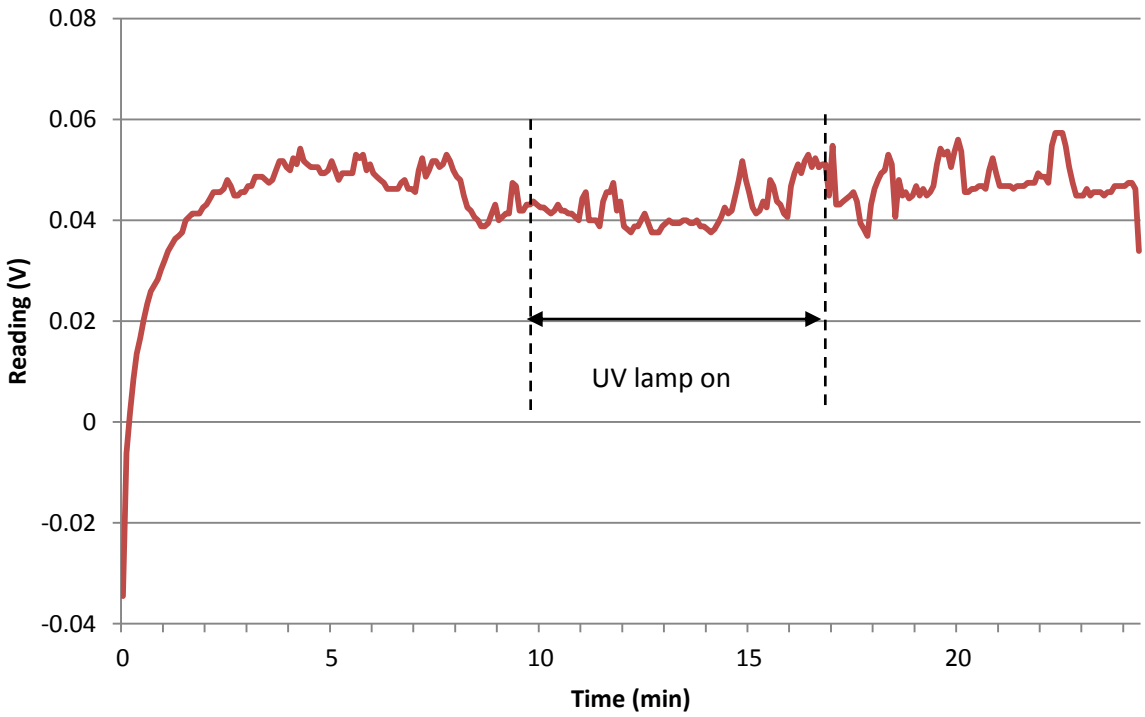


Figure 25: Stainless steel plate – silver paint method, tested in 1000ppm MTBE

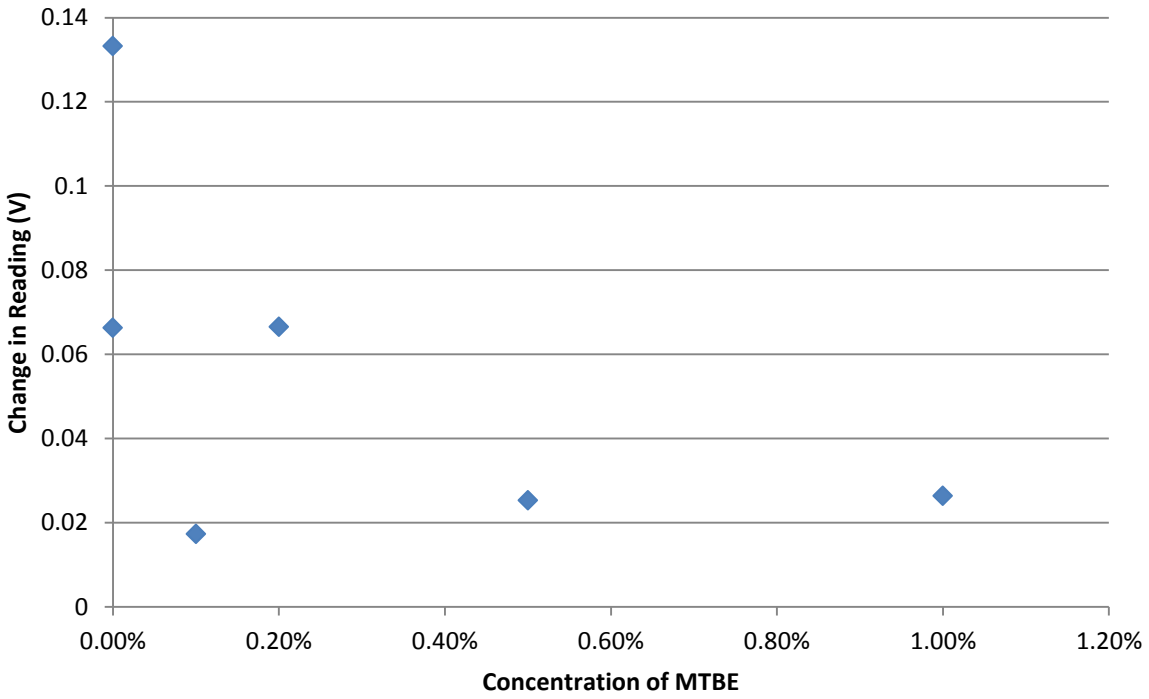


Figure 26: Unprinted circuit board – zinc glue method 1

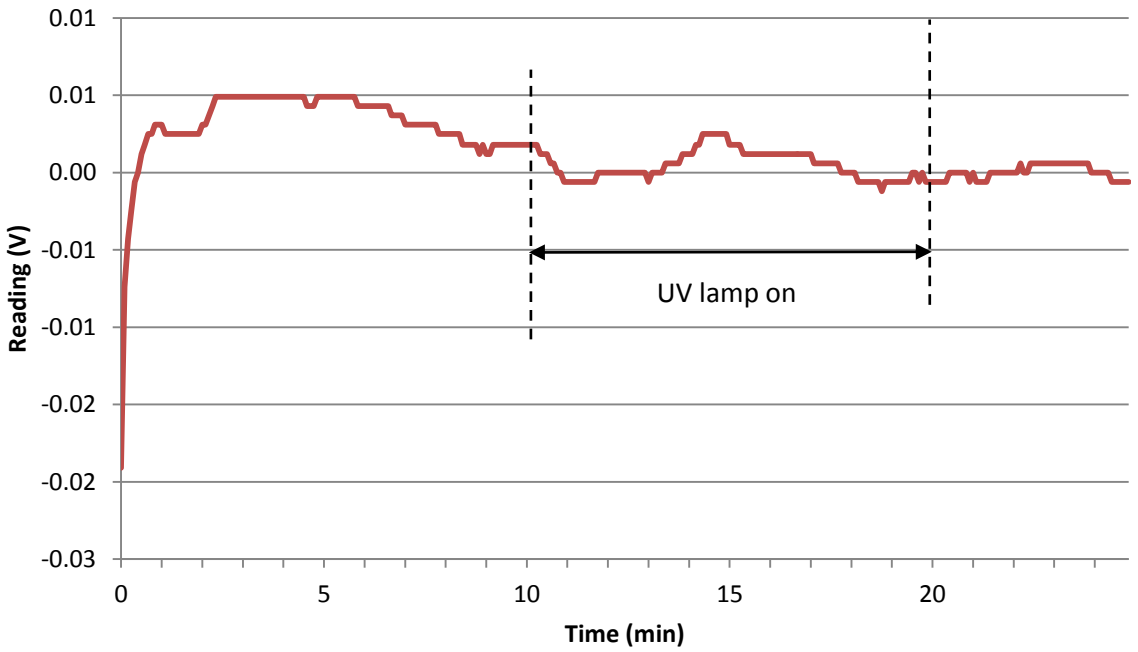


Figure 27: Chromium plated glass – ethanol slurry method, tested in 1000ppm MTBE

3.3.3. Response of Ethanol Slurry Stainless Steel Sensor Plate to MTBE & Toluene

Because the stainless steel plates coated with ethanol slurry method gave the best signal overall, it was further tested in a range of MTBE and toluene concentrations using both standard solution and incrementally increasing concentration methods. The results are shown in following Figures 28 - 30.

Figure 28: Solid state sensor plate response to MTBE

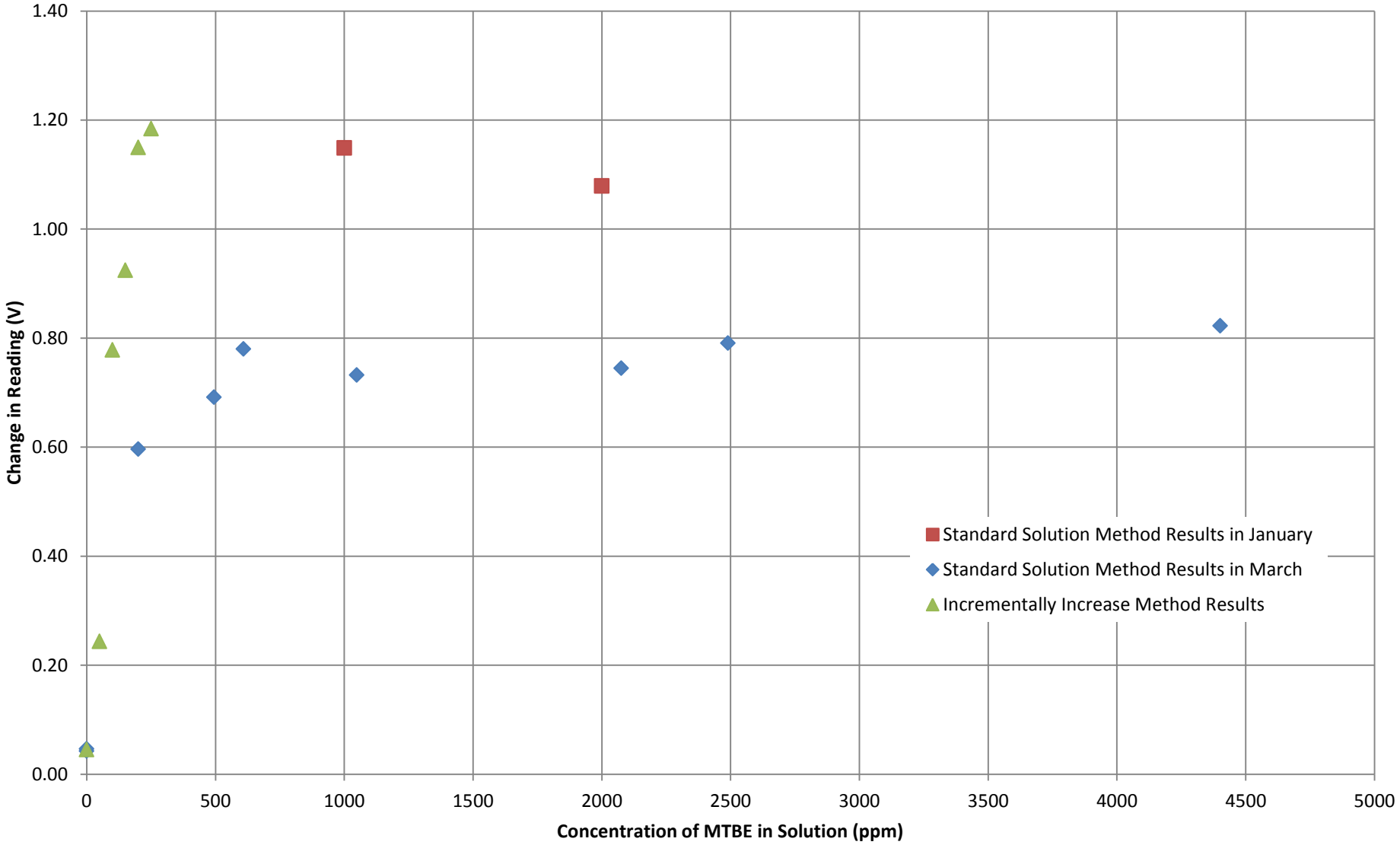


Figure 29: Stainless steel sensor plate response to MTBE - incrementally increasing concentration method

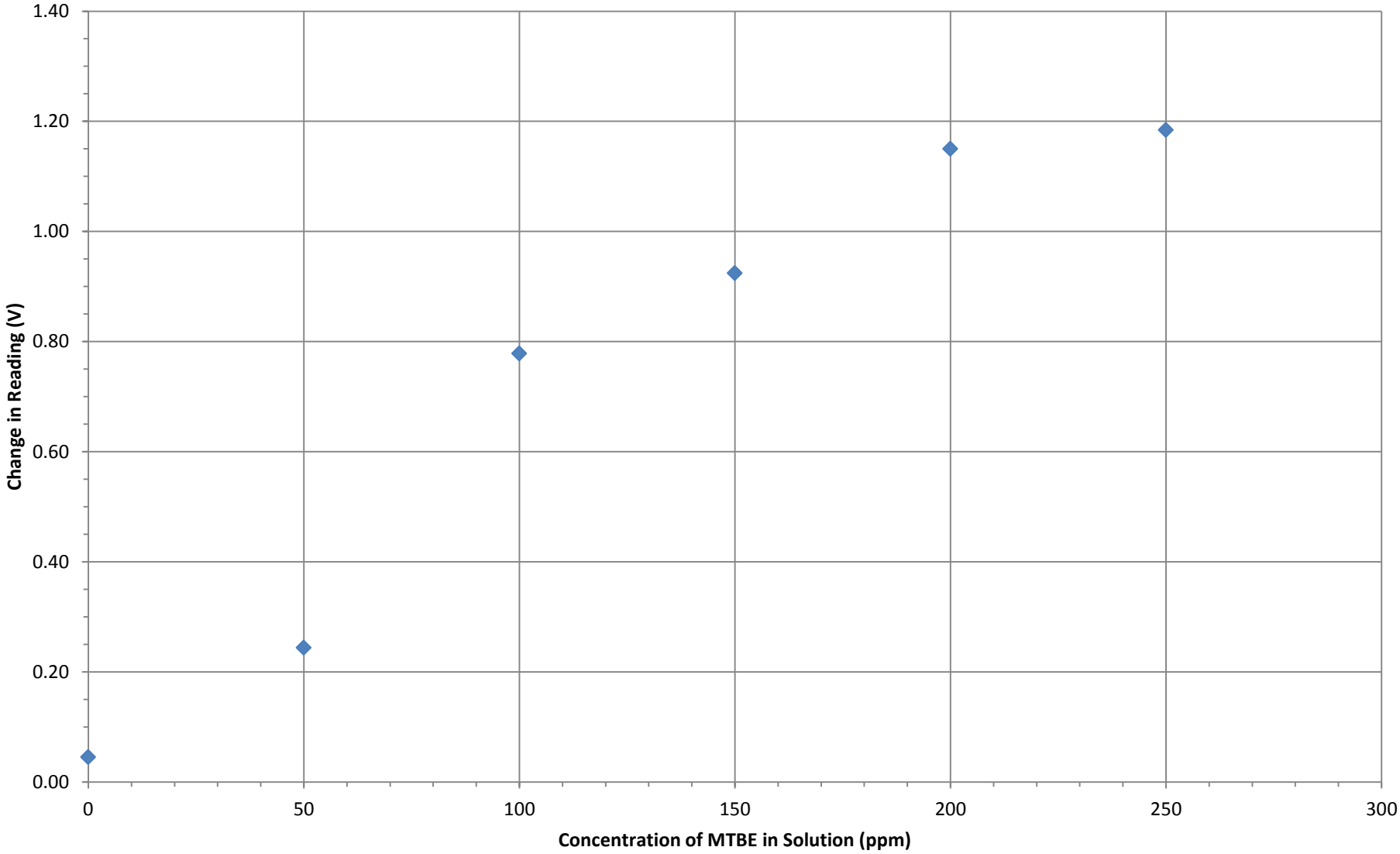
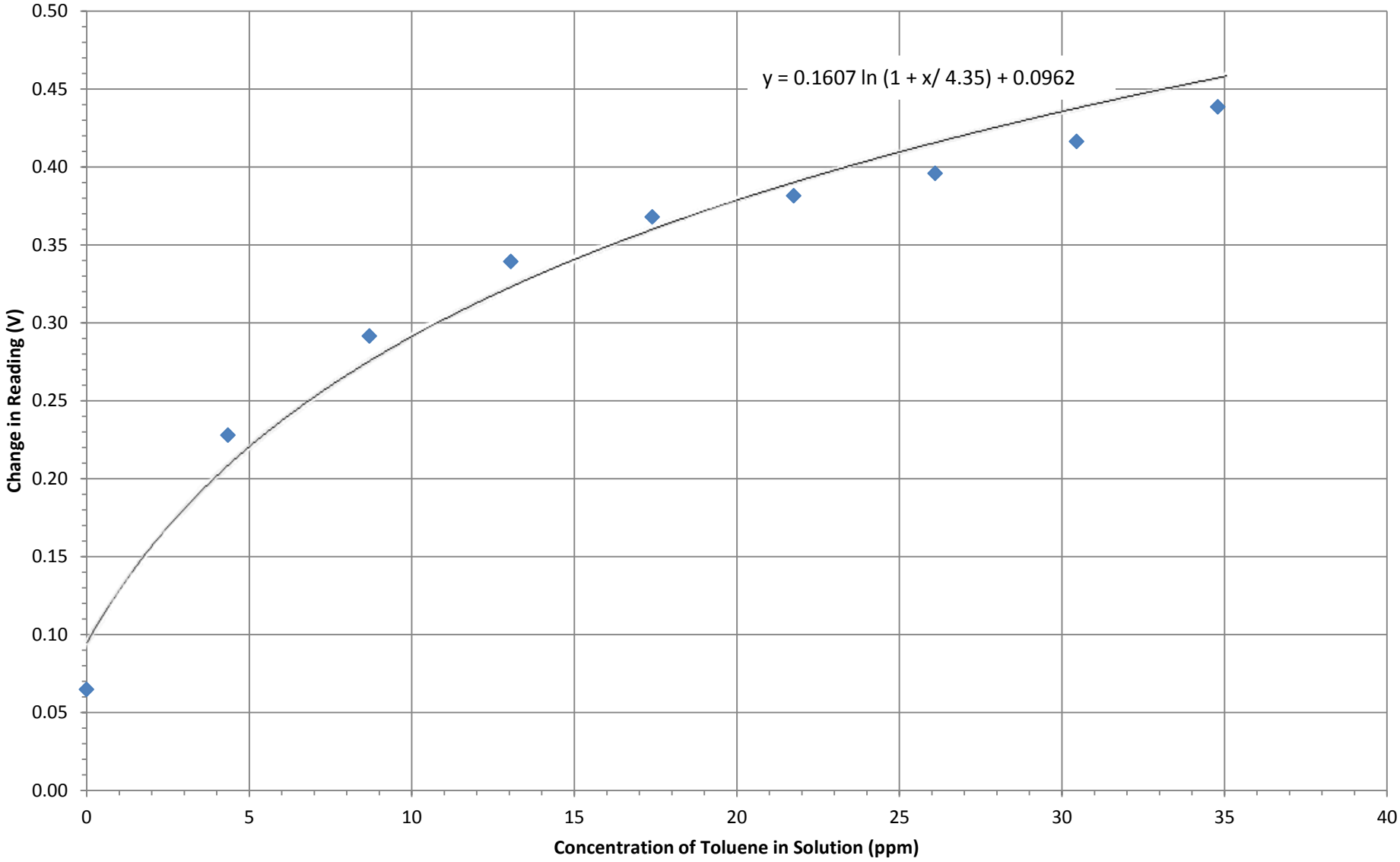


Figure 30: Stainless steel sensor plate response to toluene - incrementally increasing concentration method



3.4. Discussion

3.4.1. Comparison of Different Fabrication Methods

Backing Materials	**Method**	**Heating stage**	**Adhesion of TiO_2 Coating**	**Sensor signal**
Stainless steel plates	Water slurry	200°C for 5min	✓	✓
	Ethanol slurry	500°C for 30min	✓✓	✓✓✓
	Silver paint	500°C for 30min	✓	×
Unprinted Circuit Boards	Zinc glue 1	600°C for 1min	✓✓✓	×
	Zinc glue 2	600°C for a few seconds	×	Not tested
	Silver paint	None	(✓)	Not tested
	Silver paint & surfactant	None	(✓)	Not tested
	Nickel spray	None	(✓)	Not tested
Carbon Coated Ceramic Plate	Ethanol slurry	500°C for 30min	×	Not tested
Chromium Plated Glass	Ethanol Slurry	500°C for 30min	✓✓	×

Table 3: Comparison of solid state sensor fabrication methods

Table 3 summarises how different solid state sensors were made and their quality and performance as a sensor. Figures 24a & 24b shows that the strength of signal differs by more than 2 times between the stainless steel sensor plates made from water slurry and ethanol slurry methods. This could be because of the larger proportion of TiO_2 coating worn off from the water slurry plate in comparison to ethanol slurry one as seen in Figures 6 & 7. The less TiO_2 available for photocatalytic reaction led to the lower concentration of MTBE could be degraded and thus detected.

The two selected methods used on unprinted circuit boards, silver paint with/without surfactant, did not make a satisfactory coating as anticipated. There was still a significant amount of TiO_2 fall off as shown in Figures 19 & 20. All the coating methods tried on

unprinted circuit boards were rather poor (except zinc glue 1), suggesting that TiO_2 may not bind well with copper in general.

Overall, the coating made of a premix of TiO_2 and zinc glue (i.e. zinc glue 1, Figure 17) gives the best adhesion with no sign of fall off. However as shown in Figure 26 there is no correlation between the change in reading and the MTBE concentration, so it does not work as a sensor. This could be due to TiO_2 become securely bonded to the zinc and unable to act as a photocatalyst. Generally even though the adhesives used (i.e. silver paint, zinc glue and nickel spray), have low electrical resistivity (see Table 4), the main issues are that:

- they dry too quickly to allow TiO_2 to be attached (Figure 16, 18, 19 & 21)
- once they are dried they do not bind with TiO_2 (area 6 in Figure 8b)
- the presence of metal particles seems to inhibit the ability of TiO_2 as a photocatalyst

Hence, as illustrated in Figures 16 & 25 for example, insufficient amount of TiO_2 coated onto the backing material causes the sensor plate not responsive to the presence of MTBE even in a high concentration of 1000ppm in water.

Figure 22 shows that the carbon coating on ceramic plate did not seem to be able to withstand high temperature and could have vaporised, due to the absence of black coating after baking. Also the TiO_2 did not adhered very well that it fell off even with the plate gently shaken.

Ethanol slurry method on stainless steel plates gives the best overall adhesion and sensor signal. The same method on chromium surface gives quite good adhesion too but the chromium plated glass did not work as a sensor as shown in Figure 27. This might be because of the relatively lower electrical resistivity of chromium (see Table 4), which is at least 5 times smaller than stainless steel. In addition only a very thin layer of chromium was plated onto the glass, so its resistivity could be even greater in comparison to an entire sensor plate made of stainless steel.

Metals	**Typical electrical resistivity (Ωm)**
Silver	1.59×10^{-8}
Zinc	5.90×10^{-8}
Nickel	6.99×10^{-8}
Stainless Steel	6.90×10^{-7}
Chromium	1.25×10^{-7}

Table 4: Typical electrical resistivity values of metals (extracted from Wikipedia)

3.4.2. Response to MTBE

Both results from using standard solution (SS) and incrementally increasing concentration (IIC) methods are shown in Figure 28 & 29. It is noteworthy that the standard solution results taken in January are remarkably higher than March in Figure 28. The reason is likely to be due to the fall off of TiO_2 coating from the stainless steel plates, as shown in Figure 31. This causes a reduction in TiO_2 available for photocatalytic reaction, so less MTBE was degraded and lowered the change in reading in March.

Figure 31: Photos of sensor plate surface taken in January (left) and March (right)

Furthermore, the results from SS and IIC do not agree with each other in Figure 28. The values of change in reading for IIC are significantly greater, whereas SS values seem to level off around 0.80V. This could be due to the handling of volatile chemicals. MTBE was directly added into the solution in the IIC method whereas the process of making and pouring standard solutions is likely to involve the loss of MTBE due to vaporisation. Hence the actual amount of MTBE left in the beaker would be less than expected, reducing the reading change.

Concentrating on the more accurate results from IIC method in Figure 29, the relationship between concentration and change in reading can be linearised by taking the log of both variables, as shown in Figure 32. The low detection limit of MTBE can be estimated by:

3 * (peak-to-peak magnitude of noise in reading) + change in reading at 0% MTBE

This gives a reading of 0.0560V, which corresponds to a concentration of MTBE in solution of roughly 3ppm on Figure 32. The solid state sensor is quite good considering such a simple fabrication. The limit would be expected to be even lower if TiO_2 can be better and more strongly coated onto the stainless steel plates in the future.

However more data of higher concentrations of MTBE should be taken before the maximum detectable quantity can be determined accurately.

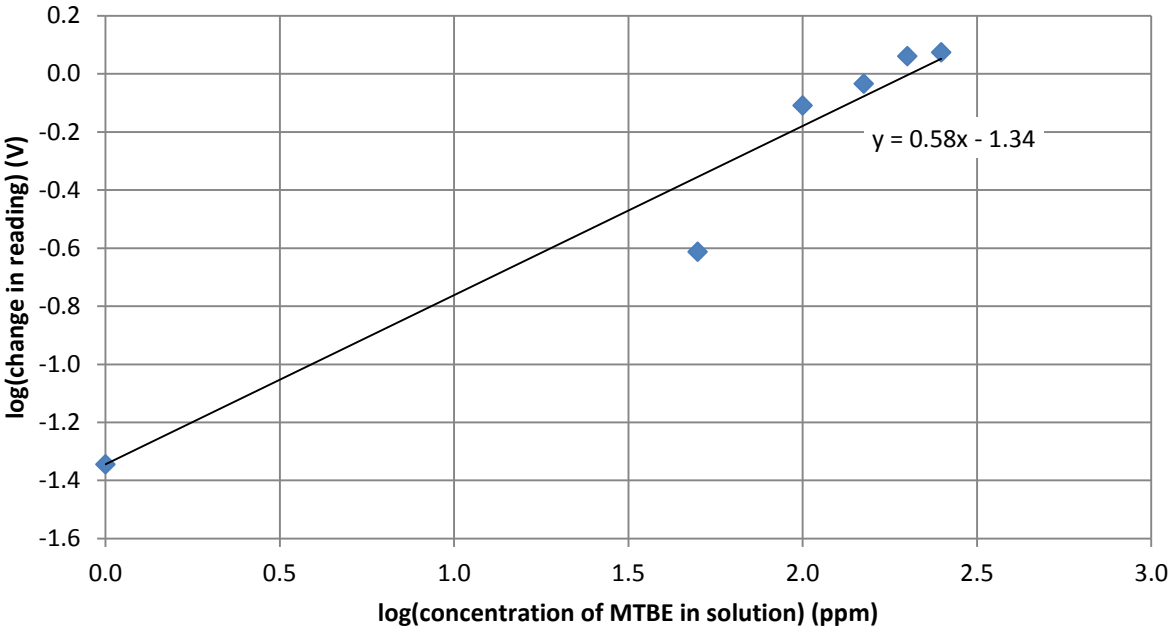


Figure 32: The relationship between change in reading and concentration of MTBE

3.4.3. Response to Toluene

Response of the solid state sensor to toluene was tested using the IIC technique as it seemed to be more appropriate and accurate from MTBE results. The relationship between the concentration and the reading change is not linear, but can be modelled by taking the natural log of the concentration as shown in Figure 30.

Using the same method of estimating the low detection limit as before, it gives a change in reading of 0.1238V. This corresponds to a toluene concentration of approximately 0.8ppm. This is very promising as it achieves one of the project aims – able to detect a low concentration (ppm) of toluene.

On the other hand, more data of higher concentrations of toluene should be taken before the maximum detectable quantity can be determined accurately.

4. Indoor Air Quality Sensor

4.1. Preliminary & Design of Experiments

4.1.1. Operating Temperature

Both solid state sensor and indoor air quality (IAQ) sensor were tested together at first using the incrementally increasing concentration (IIC) method for quicker and more accurate comparison. This involved the assumption of equilibrium being established so that by Henry's law, the vapour concentration measured by the IAQ sensor was proportional to the aqueous concentration measured by the solid state sensor. However it was noticed that the readings of IAQ sensor did not increase as the aqueous concentration increased. Also the temperature inside the box should have increased due to the UV lamp and caused more vaporisation, so high vapour concentration would be expected. Therefore another experiment was carried out to see how IAQ sensor responds to the temperature rise from switching on the UV lamp. The set-up of the experiment is shown in Figure 34 with the beaker filled with deionised water only. Since deionised water was used, it eliminates the concern of affecting the Henry's law constant of any volatile organics as described in 2.3.

The result is shown in Figure 33 which does imply that increase in temperature has an effect on the IAQ sensor. Therefore IAQ sensor was tested separately from the solid state sensor and the operating temperature was kept constant, close to the laboratory temperature, 20°C.

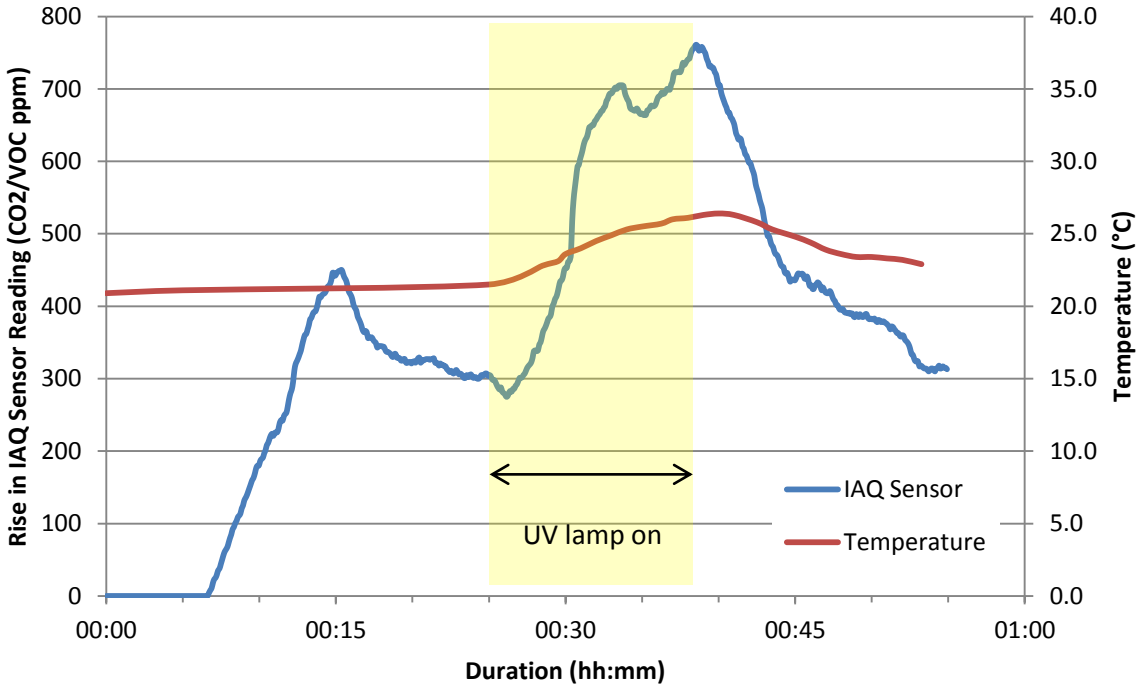


Figure 33: Response of IAQ sensor to temperature change

4.1.2. Experimental Techniques

Due to the limit of time, the IIC method which was preferred was not able to be tested with the IAQ sensor. Hence only the standard solution method was used.

4.2. Method

4.2.1. Materials

- Indoor Air Quality Sensor (Voltcraft CO-20)
- Methyl-tert-butyl ether (Fischer)
- Toluene (BDH)

4.2.2. Standard Solution Method

Set-up of Experiment

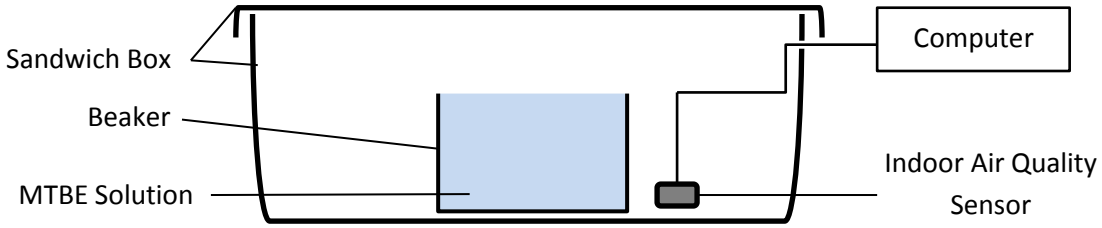


Figure 34: Schematic diagram of the standard solution method set-up

Procedure

MTBE was prepared using standard solution method, the same as solid state sensor. The IAQ sensor was taped onto the bottom of the box. Also it was ensured that both the positions of beaker and the sensor were the same throughout the experiments while testing with different concentrations of MTBE/toluene solution. Any openings or holes were blocked using a tape to prevent the leakage of MTBE/toluene.

The sensor was allowed to warm up for 1 minute in the beginning. Then the data logging was switched on and continued until the readings had stabilised for about 5 minutes. The sensor and the sandwich box should be left in open air for at least 30 minutes after each experiment, in order to allow MTBE to diffuse away and fresh air in.

Calculations

The rise in reading was calculated by (Figure 35):

(Average of stabilised readings) – Baseline reading (which is 450 in this case)

Since the IAQ sensor measured the vapour concentration of MTBE or toluene, the concentration of MTBE in solution was multiplied by the Henry's law constant to calculate the corresponding concentration in air. The dimensionless Henry's law constant for MTBE used was 0.022 according to Table 2 because the temperature of laboratory was around 20°C.

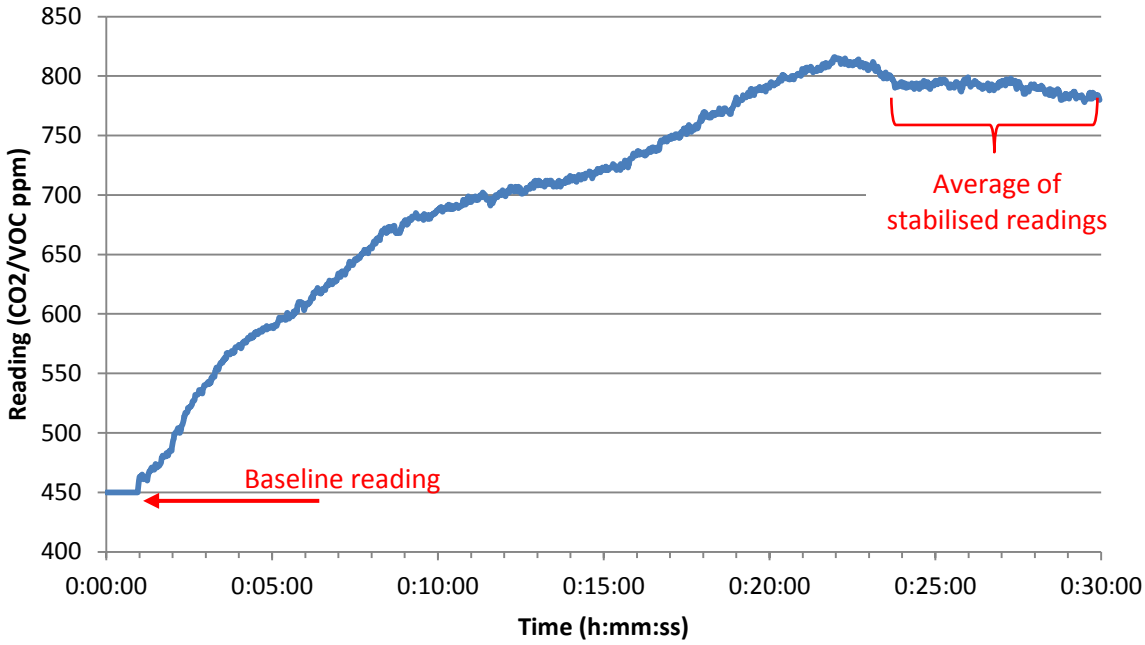


Figure 35: An example of calculating the rise in reading

4.3. Results

IAQ sensor response to MTBE and toluene are represented in Figures 36 and 37 respectively.

4.4. Discussion

4.4.1. Response to MTBE

The readings of IAQ sensor shows a fairly linear relationship with the concentration of MTBE in air, where every 1ppm MTBE in air gives rise to approximately 660 CO_2/VOC ppm reading on the IAQ sensor. This seems to suggest that the IAQ sensor is quite sensitive. Calculation of the low detection limit using the method described previously gives a rise of reading of 102 CO_2/VOC ppm, corresponding to 0.155ppm of MTBE in air or ~7ppm in water. It is unsure what the maximum value of the IAQ sensor reading can reach as it is not stated in the manual or the manufacturer's website. Since the maximum reading recorded in experiments is 8597 CO_2/VOC ppm, it is assumed the maximum detectable quantity of IAQ sensor is 10000 CO_2/VOC ppm, which is around 15.2ppm of MTBE in air or ~679ppm in water.

Figure 36: Indoor air quality sensor response to MTBE

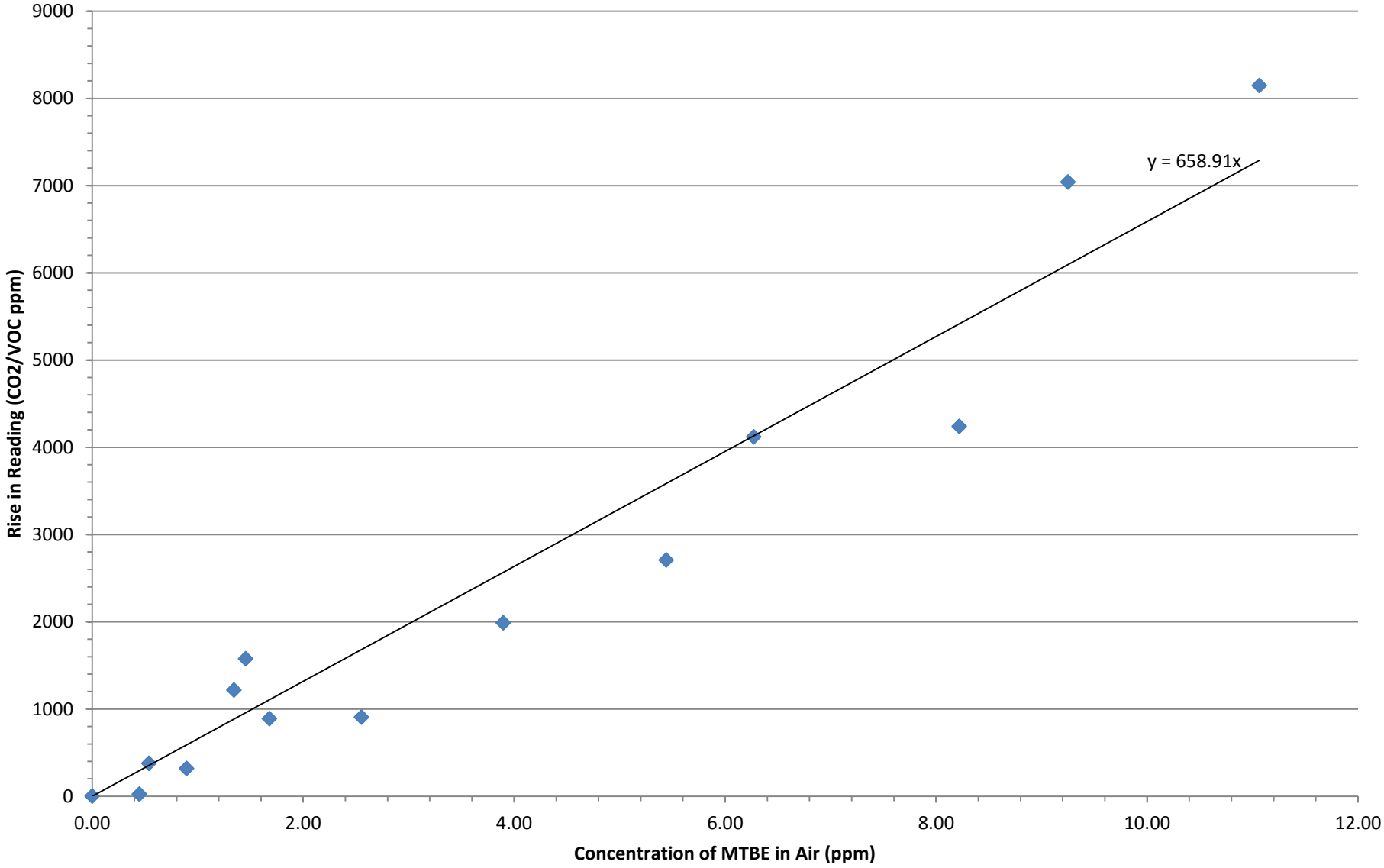
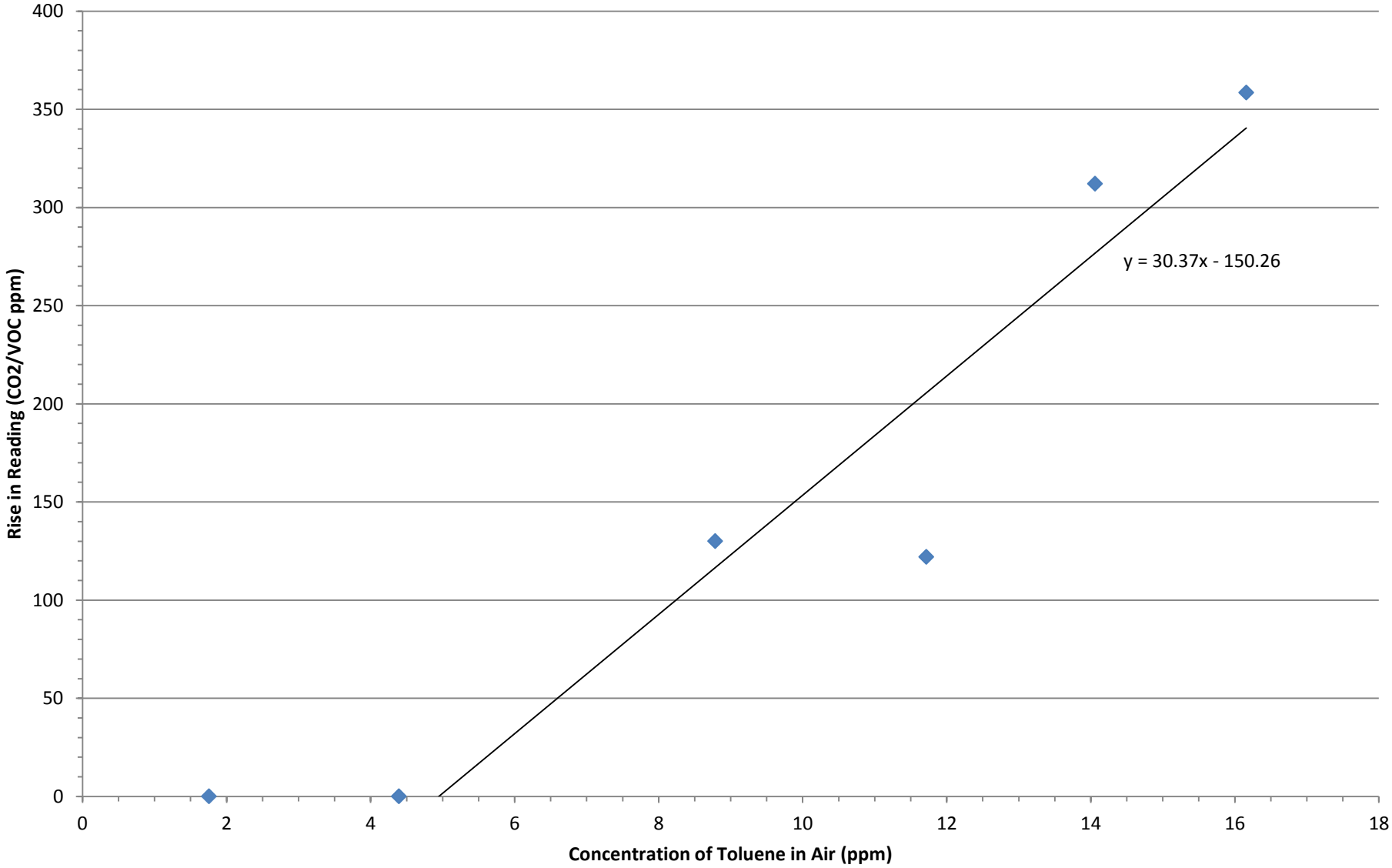


Figure 37: Indoor air quality sensor response to toluene



4.4.2. Response to Toluene

Again there seems to be a linear relationship between the IAQ sensor response and concentration of toluene in air. However the IAQ sensor is not as sensitive to toluene as to MTBE as the best-fit line suggests that every 1ppm increase of toluene in air gives rise to only around 30 CO_2/VOC ppm rise in reading, and that the minimum detectable quantity of toluene is about 5ppm (where it intercepts the x-axis). On the other hand the peak-to-peak noise level of IAQ sensor is relatively lower, so the resulting low detection limit is 36 CO_2/VOC ppm, which is equivalent to ~6ppm of toluene in air or ~30ppm in water. Again assuming the maximum reading of IAQ is 10000 CO_2/VOC ppm, this means the maximum detectable quantities of toluene in air and in water are 334ppm and 1655ppm respectively.

5. Comparison between Solid State Sensor and Indoor Air Quality Sensor

5.1. Response Time

Throughout the experiments, the response of solid state sensor to both MTBE and toluene was generally instantaneous after the UV lamp was turned on. This is desirable as it can also provide a quick check if the sensor is working or the circuit might have been connected wrongly. On the other hand, the response time of IAQ sensor varied with concentration. In general, the higher concentration of MTBE or toluene, the shorter the response time. This is partly because the IAQ sensor measured vapour instead of aqueous concentration, and it was placed next to the contaminated solution. It probably takes time for the volatile organics to establish equilibrium and diffuse towards the sensor. It may have been better if the sensor is placed right above the solution or a fan device is included in the box for quicker and more even distribution of contaminants.

5.2. Sensitivity to MTBE and Toluene

Table 5 below summarises the low detection limits of different sensors. It should be noted that the experimental methods and the operating medium for the two sensors are different, so the values were only estimations.

Sensor	Low Detection Limit (ppm in water)	
	MTBE	Toluene
Solid State Sensor	3	0.8
Indoor Air Quality Sensor	7	30

Table 5: Comparison of different sensor sensitivities

The solid state sensor has a very good sensitivity to both MTBE toluene which has an order of magnitude 0 and -1 respectively. The indoor air quality sensor, in contrast, does not detect toluene as well as the solid state sensor that its low detection limit is two orders of magnitude greater.

5.3. Overall Performance

The overall advantages and disadvantages of the solid state sensor and the indoor air quality sensor are described in Table 6 below.

	Advantages	Disadvantages
Solid State Sensor	• Cheap and easy to make • Fast response time • Good sensitivity to both MTBE and toluene	• Wear of coating over time • Requires extra power due to UV light
Indoor Air Quality Sensor	• Low power consumption • Good sensitivity to MTBE • Readily available with built-in circuit and software • Small in size	• Susceptible to temperature change • Unsuitable to prolonged high concentration exposure • Relatively poor sensitivity to toluene • Not designed for laboratory experiments or field work • Does not directly measure contaminants level in groundwater • Readings also take in account of CO_2

Table 6: Comparison of solid state sensor and indoor air quality sensor

6. Conclusions

A real-time sensor has been developed in this project which allows its voltage reading to be converted into concentration of volatile organics in water. Moreover it is able to provide a fast response and a low sensitivity to MTBE and toluene, satisfying the aims of this project.

6.1. Solid State Sensor

- Ethanol slurry coating method on stainless steel plate gives the best signal response
- It is able to detect a minimum of 3ppm MTBE and 0.5ppm toluene in water
- None of the methods provides satisfactory and durable TiO_2 coating

6.2. Indoor Air Quality Sensor

- It is susceptible to operating temperature
- It is able to detect a minimum of 7ppm MTBE and 30ppm toluene in water

7. Suggestion for Future Work

- Alternative coating method to improve the durability and adhesion of TiO_2 coating
- Use IIC method to calibrate the IAQ sensor in an empty and sealed enclosure – minimise the error when converting between aqueous and vapour concentrations
- Use a UV LED for more direct light source, allowing IAQ sensor and solid state sensor to be tested together
- Altering the position of IAQ sensor, such as right above the solution
- Investigate on the selectivity of solid state sensor, i.e. what other chemicals can be detected
- Investigate the effect of TiO_2 concentration
- Both solid state sensor and IAQ sensor to be tested alongside a groundwater clean-up project

8. Acknowledgements

I wish to thank my supervisor Dr R. Lynch for his consistent support through the project; Mr C.W. Knight for his technical assistance and Dr D. Dukic, Dr T.D. Wilkinson and Dr P.J.G. Long for their help on sensor fabrication.

9. References

Arshak, K., *et al*., 2004, A review of gas sensors employed in electronic nose applications, *Sensor Review*, vol 24, no.2, pp. 181

De Burca, R. *et al*., 2009, Soil Guideline Values for toluene in soil, *Science Report SC050021 / toluene SGV*, Environment Agency, UK,

Fischer, A., Muller, M., 2003, Interesting Properties of MTBE Water Solubility and Henry's Law Constant, *First European Conference on MTBE*, pp 144-150

Gehle, K, *et al*., 1993, Toluene Toxicity, *Case Studies in Environmental Medicine*, Agency for Toxic Substances and Disease Registry

Ho, C.K., *et al.*, 2001, Review of chemical sensors for in-situ monitoring of volatile contaminants, Sandia Report SAND2001-0643, 2001

Photovac, 2020ComboPRO, http://www.photovac.com/2020ComboPRO.aspx, accessed 26 May 2012

Rodgers, B., 2011, The Ag/AgCl Reference Electrode, http://www.consultrsr.com/resources/ref/agcl.htm, accessed 21 May 2012

Shimizu, K., *et al.*, 1999, Low-temperature Synthesis of Anatase Thin Films on Glass and Organic Substrates by Direct Deposition from Aqueous Solutions, *Thin Solid Films*, 351, pp 220-224

United States Environmental Protection Agency (US EPA), Temperature-Dependent Effective Solubility Calculator, http://www.epa.gov/athens/learn2model/part-two/onsite/es-temperature.html, accessed 26 May 2012

Vaidya, N., 2006-7, Ground Water Pollutant Sensor, Fourth Year Undergraduate Project, Cambrdige University Engineering Department

Wikipedia, Resistivity of various materials, Electrical resistivity and conductivity, http://en.wikipedia.org/wiki/Electrical_conductivity, assessed 29 May 2012

10. Appendix

10.1. Risk Assessment Retrospective

One of the main risks of this experiment was the UV light source. The submitted risk assessment mentioned is to perform the experiment in a sealed environment which was followed in the actual set-up. Because the UV lamp was attached to the bottom side of the lid in a sealed enclosure, UV radiation travelled downwards. Hence the severity of the risk was as anticipated – 1, minor. An additional control measure which should have been included is to always turn off the UV source before opening the lid.

Another major risk was the use of volatile organics, i.e. MTBE and toluene. The risk of inhalation was only expected when opening the lid of sandwich box. In the actual experiment, control measures should also be taken when making standard solution and throughout the experiment. Preparation of standard solution was performed in a fume cupboard. Since some holes were drilled on the sandwich box for insertion of syringe and wiring, the box was taped to air-seal, preventing the leakage of volatile organics.

10.2. Literature Review on Types of Sensors (Extracted from Technical Milestone Report)

Sensors for monitoring volatile contaminants can be categorised into four groups: piezoelectric sensors, electrochemical sensors, optical sensors and conductivity sensors. [1]

10.2.1. Piezoelectric Sensors

Piezoelectric sensors work on the principle of the change in mass of sensor coating. There are two main types of piezoelectric sensors: surface acoustic wave (SAW) device and quartz crystal microbalance (QCM). Both SAW and QCM sensors are coated with a gas sensitive membrane. A wave is produced which propagates along the surface of the SAW sensor or through the entire bulk of QCM sensor. Analyte is absorbed by the membrane and alters the (resonant if QCM) frequency of wave which is proportional to the concentration of analyte. Generally these sensors offer high sensitivity to organic vapours and fast response times, but they have a poor signal-to-noise ratio and require complex and expensive circuitry. [1]

10.2.2. Electrochemical Sensors

A typical electrochemical sensor involves a transducer device which transforms a chemical/physical change into an electrical signal. For example, a MOSFET (metal-oxide-semiconductor field-effect transistor) is used as a sensor. The gate material of MOSFET is usually made porous and gas sensitive, and coated with a catalytic metal which interacts with the analyte. Analyte can induce physical changes in the sensor and so alters the threshold voltage. The change in voltage can then be used to find the concentration of analyte. MOSFET sensors can be reproduced quite easily and at a low cost. However they may be prone to instability depending on the sensing material used. Also their sensitivity and selectivity are very susceptible to the operating temperature. [1]

10.2.3. Optical Sensors

Optical sensors can be sub-divided into three groups: fibre optic sensors, colorimetry and infrared sensors.

10.2.3.1. Fibre Optic Sensors

Fibre optic sensors use optical fibres to detect chemicals. Light generated from a light source is sent through an optical fibre and returns. Then it is captured by a photodiode. There are three types of such sensors. The first type involves the use of a spectrometer which analyses

the light that is reflected or emitted by the analyte. The second type consists of a fibre optic sensor with a thin film attached to the tip. Different formulated film interacts and binds with certain chemicals. The intensity of the colour/fluorescence of the thin film is related to the concentration of chemicals. The third type uses a flow injection method. A flow of contaminated water is introduced near the sensor where reagent is injected and mixed with the analyte. The products from resulting reactions (e.g. its intensity of colour) indicate the approximate concentration of contaminant. Fibre optic sensors require low power and are able it detect chemicals at very low concentration. However sensitivity may decrease over long transmitted distance and selectivity to organic pollutants may worsen if using UV-visible spectroscopy. Also the coatings used may degrade over time. [2]

10.2.3.2. Colorimetry

Test kits are used on site where a sample of water is taken. A particular reagent is added to the sample. The resulting colour is compared with a chart to give an approximate concentration. Colorimetric sensors are portable and simple to use. They are not susceptible to interferences. Nevertheless sensitivity to individual volatile organic chemicals is limited and they cannot to be used in-situ. [2]

10.2.3.3. Infrared Sensors

Infrared (IR) sensors are particularly useful for detecting gases which have unique IR absorption spectra. IR radiation is emitted through a path which is exposed to the target gas. Some energy is absorbed by the gas in the path and reduces the radiation received by the detector at the end of path. Concentration of gas can be determined by comparing with the radiation received without the analyte present. Due to the uniqueness of the IR absorption spectra, specific gases can be identified and quantified easily. IR sensors are also very durable, requiring little maintenance. However they can be expensive and can be affected by humidity and water. Response may also be impaired by dust or dirt on the surface of optic fibre. [2]

10.2.4. Conductivity Sensors

In conductivity sensors, sensing materials such as intrinsically conducting polymer and metal oxides are commonly used to coat the electrodes which form an electrical connection. The interaction between the sensing materials and analyte causes a change in resistance of the sensor. The relative resistance change can be used to find the corresponding concentration of analyte. Conductivity probes are popular choices for detecting inorganics because of the

quick response and recovery times. They also give good response to a range of analyte. In particular, metal oxide sensors are small and relatively inexpensive to fabricate. Nonetheless they suffer from poisoning (e.g. sulphur) and does not work for organics. Also, conducting polymer sensors are very sensitive to humidity and its response can drift with time. [1]

References

[1] K. Arshak, E. Moore, et al., 2004, A review of gas sensors employed in electronic nose applications, *Sensor Review*, vol 24, no.2, pp. 181

[2] C.K. Ho, M.T. Itamura, *et al*., 2001, Review of chemical sensors for in-situ monitoring of volatile contaminants, *Sandia Report SAND2001-0643*