

LONG-TERM STUDY OF NANO-ENGINEERED MERCURY VAPOUR SENSOR TESTED UNDER SIMULATED ALUMINA REFINERY CONDITIONS

Sabri YM¹, Ippolito SJ¹, Harrison I², Myers L², Rosenberg S³, Boom E³, Bhargava SK¹

¹ *Industrial Chemistry Group, School of Applied Sciences, RMIT University, Melbourne, AUSTRALIA*

² *Alcoa World Alumina, AUSTRALIA*

³ *Worsley Alumina Pty Ltd., AUSTRALIA*

Abstract

Mercury (Hg) emission reduction targets set by industry and regulators have spurred attempts to develop real-time monitoring technologies for evaluating the efficiency of Hg removal processes in alumina refineries. This work reports on the long-term stability of newly developed quartz crystal microbalance (QCM) based Hg vapour sensors which have been tested in simulated streams containing common interfering gas species found in alumina refinery stack gas. The developed sensors employ highly orientated nano-engineered gold surfaces formed via a novel electrodeposition process which significantly increase the sensitivity, selectivity and repeatability of the sensor towards Hg vapour over a non-modified (Au control) QCM. The modified QCM sensors were observed to have ~3 times higher sensitivity than the Au control QCM towards Hg concentrations between 1 and 10 mg/m³ in the presence of humidity, ammonia, acetaldehyde, acetone, dimethyl disulfide and methyl ethyl ketone when operated at 89°C. These conditions were chosen to represent the typical conditions of digestion and evaporation exhaust streams within the Bayer process. The coefficient of variance (CoV) of the modified and Au control based QCMs were found to be 2.8% and 7.8% respectively following 10-days of continuous operation. The modified QCM was found to have Hg detection limit of 30.72 µg/m³, which is ~50% better than the Au control QCM. Furthermore, the modified sensors were observed to have significantly larger dynamic range which resulted in better accuracy and performance over the non-modified Au control sensor. The promising results of the developed sensor indicate their high potential for use as a cheap alternative to Hg monitoring techniques currently employed by the alumina industry which generally involve long sampling and offsite analysis procedures.

1. Introduction

Mercury is a toxic by-product which can be unintentionally released in to the environment from large industrial based mining and refining processes. It is well known to have serious effects on the brain, kidneys and the central nervous system of humans (Stokstad, 2004). Around 70% of the environmental contamination of Hg pollution results from anthropogenic emissions such as industrial discharges, burning fossil fuels, smelting, waste disposal and mining. Australia, for example, is a leading producer of mining commodities which form a large share of its exports. The Australian National Pollutant Inventory indicated the alumina industry was responsible for approximately 6.6% (1.6 tonnes) of Australia's total Hg vapour emissions in the year span 2007-2008 (Government, 2009).

Alumina refineries generally use the Bayer process for refining bauxite to smelter grade alumina (Al₂O₃) feedstock. It is well established that significant levels of Hg can build up within various of its processes, which include: oxalate kilns, digestion, calciners, evaporation, as well as in other minor sources such as liquor burner and boilers (Dobbs et al., 2005a). Depending on the origin of the bauxite ore, Hg contents of 50 mg (Hind et al., 1999), 431 mg (Kockman et al., 2005) and up to 1500 mg (Dobbs et al., 2005a) per tonne of bauxite have been reported. As the digestion and evaporation of the Bayer process involve flash evaporation/cooling, equilibrium within the heat exchange process is established between the condensate and the gaseous vapour stream. Significant concentrations of volatile organic compounds (VOCs) and Hg are present in this vapour. The Hg in the gas phase is predominantly in the elemental form due to the chemically reducing nature of the digestion and evaporation processes with Hg emission concentrations ranging from 0.003 – 32 mg/m³ at temperatures of 20 – 200°C (Dobbs et al., 2005b). During the

refinery process much effort is made to capture the Hg before it is emitted into the environment, however measurable quantities of Hg are still emitted in the vapour phase for every metric tonne of alumina produced.

In order to better understand emission sources, migration, and environmental and societal impacts of Hg vapour, continuous emissions monitors (CEMs) located at strategic points within the Bayer process are imperative. For example, such systems could be located at the digestion or evaporation stacks, or at the output of a regenerable thermal oxidizer (RTO) to allow operators to determine the primary process where Hg is most likely to escape in the gas phase. However, the initial purchase and operating expenses associated with most commercially available CEMs are far too high for most emitters. Commercially available instrumentations are typically based upon fragile atomic absorption (AAS) or atomic fluorescence (AFS) spectroscopy and lack the robustness required for many CEM installations. Furthermore, both AAS and AFS systems are susceptible to cross-interference by other gases within the many industrial process streams, such as SO₂, NO₂, H₂O, O₃ and carbonyl containing VOCs such as benzene, toluene and acetone, as these gas species absorb the same wavelength as Hg (253.7nm) and can therefore produce misleading results (Weissberg, 1971, Windham, 1972, Sholupov et al., 2004, Logar et al., 2002). In order to overcome the presence of such gases, solid sorbent bed/s (i.e. Appendix K) or sampling train (i.e. Ontario Hydro) methods are sometimes used in conjunction with the AAS and AFS systems for determining lower concentrations of Hg. Mercury vapour is trapped within the sorbent beds or trains and later released in an argon carrier gas for detection. This allows the ventilation of interfering substances from the gas stream before measurement. However, thermodynamic problems may occur

while releasing Hg from the solid sorbent beds for analysis, which is disadvantageous (Caron et al., 1999). In the case of the sampling trains, the trapped Hg is chemically reduced to its elemental state using the cold vapour (CV) technique. Unfortunately such methods require highly qualified operators as well as trapping and pre-treatment of industrial stream gas prior to analysis. Hence, there is a need for a new technology to be developed which is less expensive to operate, maintenance free, robust and capable of accurately measuring Hg in a variety of different types of industrial flue gas stream environments. Such a technology would benefit both legislators and plant operators alike, and would allow plant operators to make informed decisions concerning their control technology requirements as well as provide them with feedback for advanced process control technologies (IDS-Environment).

In this work, we describe a highly selective Hg vapour sensor based on a quartz crystal microbalance (QCM) using nanostructured gold sensitive layers. The low-cost fabrication method is described, which increases the sensitivity of a standard Au electrode based QCM to have a 390% and 180% increase in sensitivity towards 10.55 mg/m³ of Hg vapour at operating temperatures of 28°C and 89°C, respectively. The QCM is based on the linear relationship (equation 1 below) between the resonance frequency (Δf) and the mass of a substance adsorbed onto the surface (Δm) of the QCM electrode surface;

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\mu_q\rho_q}}\Delta m = -S_f\Delta m \dots\dots\dots (1)$$

where, f_0 is the resonant frequency of the fundamental mode of the crystal, A is the active area of the electrodes in cm², ρ_q is the density of quartz crystal being 2.648 g·cm⁻³, S_f^q is the shear modulus of quartz (2.947·10¹¹ g·cm⁻¹·s⁻²) and S_f is the integral mass sensitivity or Sauerbrey constant (Sauerbrey, 1959).

2. Experimental

The two faces of the optically polished AT-cut QCM substrates (7.5 mm diameter, 10 MHz resonant frequency, Hy-Q Crystals, Australia) were deposited with a 10 nm Ti adhesion layer and 150 nm Au (4.5 mm diameter) using e-beam deposition (BAK 600) at 22°C and 2 x 10⁻⁵ Pa. After patterning these are referred to as non-modified Au control QCMs. Thereafter the surfaces of several QCMs were further modified by electrodeposition technique as discussed in subsection 2.2.1, which are referred to as the modified QCM sensors.

2.1 Materials

Analytical grade HNO₃, HCl, H₂SO₄, KMnO₄, Pb(C₂H₃O₂)₄ and HAuCl₄·3H₂O were purchased from Sigma-Aldrich. Elemental Hg permeation tubes were purchased from VICI, TX, USA. Water vapour was generated using a V-Gen relative humidity generator from InstruQuest, USA, and interfering gases were sourced from specialty gas mixes provided by Coregas, Australia.

2.2 Methods

2.2.1 Preparation of sensing layers

The electro-deposition of gold nanostructured thin-films was performed in an electrolyte solution (total volume 75 mL) which contained 2.718 g/L HAuCl₄·3H₂O and 1.77 g/L Pb(C₂H₃O₂)₄. A schematic of the two electrode electrodeposition process is shown in Figure 1a. A potential of -2 V was applied at room temperature, between an Au-QCM crystal (cathode) and an Au foil (anode) spaced 25 mm apart, for an electrodeposition time of 150 seconds. This insured that Au nano-structures were formed on both Au electrodes of the QCM. The potential was applied using an Agilent arbitrary waveform generator (Model 33220A) and the current was recorded using a Keithley digital multimeter (Model 2001). The cyclic voltammetry (CV) trace for the electrolyte was later performed using a three electrode system (CH Instruments, CHI 760C) in order to study the electrochemical properties of the ions in the electrolyte and is shown in Figure 1b.

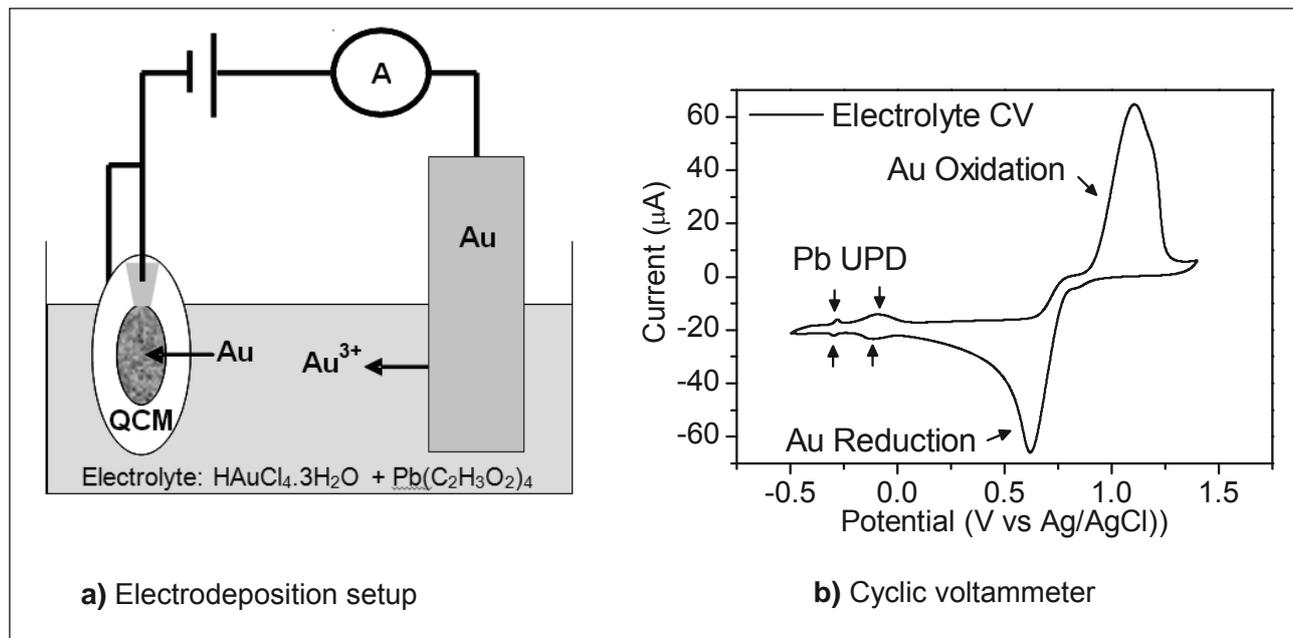


Figure 1: a) Electro-deposition set-up and b) the electrolyte cyclic voltammeter measurement (CV) which was performed using a three electrode setup. The Pb UPD and the Au oxidation and reduction regions are indicated by arrows.

The CV trace in figure 1b shows the Au oxidation and reduction regions as well as the Pb under potential deposition (UPD) regions. UPD is a phenomenon in electrodeposition that usually refers to the reduction of a metal cation at a potential less negative than the equilibrium potential for the reduction of that particular metal (O'Mullane et al., 2009). The CV trace provided insight into the range of currents and voltages (relative to the Ag/AgCl reference electrode) that may be used to form the nanostructured surfaces and confirmed that the voltage applied during the 2 electrode depositions would not have reduced Pb ions in the electrolyte solution on the QCM electrode surfaces.

2.2.2 Mercury vapour sensing

The modified QCM along with a non-modified (Au control) QCM were tested towards Hg vapour in the presence of common interfering gases found in alumina refinery stacks in a Teflon chamber with a 0.5 L volume. Mercury permeation tubes were used to generate various concentrations of Hg vapour in a highly controllable manner in order to calibrate the Au control and nanospikes based QCMs. Hg vapour concentrations in the test stream were calibrated using acidic KMnO₄ wet trapping method (similar to the Ontario Hydro method) and inductively coupled plasma mass spectroscopy (ICP-MS) analysis of the trapping solutions (Laudal et al., 1997). This calibration method was used on a regular basis to ensure that correct Hg concentrations were generated over the entire testing period. ICP-MS measurements were performed using HP4500 series 300, ShieldTorch System.

An Agilent (53131A) frequency counter with a resolution of ± 0.1 Hz over an integration period of 4 seconds was used to measure the resonant frequency change (Δf) of QCMs. All sensing tests were conducted using the following procedure: The QCMs were exposed to a gas stream containing a known concentration of Hg vapour for 1 hour. Thereafter, the sensors were regenerated with N₂ flow for another hour (unless otherwise stated). This step is referred to as a pulse. The total gas flow rate in the cylindrical shaped Teflon chamber housing the QCM sensors (volume 0.5 L) was kept constant at 200 standard cubic centimeters per minute (sccm) using a specially developed 8 channel gas calibration system employing mass flow controllers (MFCs). The operating temperature was maintained at $89 \pm 1^\circ\text{C}$ throughout the experiments. The sensors were continuously used to monitor the concentration of Hg in the presence of different interfering gases over a 3-day preliminary test, a 50-day long-term test and a 10-day industry simulated testing period. The 3-day preliminary test involved exposing the sensors towards five Hg pulses of concentrations 1.02, 1.87, 3.65, 5.70 and 10.55 mg/m³ ± 0.05 mg/m³ (balance N₂) in increasing order, repeatedly for six consecutive sequences.

In order to determine the long-term stability of the modified QCM, the sensors were tested towards Hg vapour with and without the presence of humidity (7.6 to 10.4 g/m³) and/or ammonia (1180 to 1770 mg/m³) over a 50-day period using two different test patterns. The purpose of the first test pattern was to study if the sensor had any memory effects by testing the effect of previous exposures of Hg towards subsequent Hg vapour exposure at a different Hg concentration. The test pattern is referred to as the Memory-test and required a total of 25 pulses to achieve each combination. The purpose of the second test pattern was to study the effect of different concentrations of interfering gases (such as humidity and ammonia) while exposing the sensor towards continuous pulses of one concentration of Hg vapour, referred to as the Interference-test. The interfering gases were only exposed to the sensors during the 1 hour Hg exposure period of each pulse in the sequence.

To further test the cross-sensitivity of the electrodeposited surface a separate modified QCM was exposed to Hg vapour in the presence of additional interfering gases for a 10-day period. The

testing was performed in a separate cuboid shaped stainless steel (SS) chamber (volume of 0.1 L) which, unlike the Teflon chamber had an external heating element which was not in contact with the gas stream, thus enabling additional interfering gases such as acetaldehyde, acetone, dimethyl disulfide and methyl ethyl ketone to be introduced. The additional interfering gases chosen to be tested were based on the combination of chemicals that are most commonly found in alumina refinery stacks (Forster and Grocott, 1996, Mullett et al., 2007, Mullett, 2005), which also exhibit functional groups that may have undesirable chemical interactions with gold surfaces (Bilic et al., 2002, Tanida and Hoshino, 1990, Finklea et al., 2002, Rocha et al., 1998, Richton and Farrow, 2002, Kay et al., 1989, Surplice and Brearley, 1975, Nuss and Jansen, 2006, de Vooys et al., 2001, Mirsky et al., 2002, Meyer et al., 2004). Table 1 list the interfering gases which were added to a modified version of the Interference-test which was based on the one used in the previous 50 day test. It should be noted that the water vapour was also significantly increased to 23.5 g/m³, which is ~ 2.5 times more than the concentrations used for the 50-day long-term test. The increase in water vapour is also more in line with real world conditions (100% humidity at an operating temperature of 50°C) once a 1:3 dilution is done with the sample gas and dry nitrogen.

Table 1: Interfering gas levels in the mixture to which the QCMs were exposed.

Interfering gas	Concentration	
Water vapour	23.5	g/m ³
Ammonia	270	mg/m ³
Acetaldehyde	560	mg/m ³
Acetone	18	mg/m ³
DMDS	6	mg/m ³
MEK	100	mg/m ³

3. Results

3.1 Characterization

SEM characterisation of the electrodeposited nanostructures on QCM electrodes was performed in order to determine the size and shape of the resulting nanostructures. Figure 2.1a shows the SEM image of a 100 nm Au thin-film which was e-beam deposited to form the QCM electrode of the (non-modified) Au control sensor. The SEM image clearly indicates a relatively flat surface with well dispersed Au clusters. Figures 2b show the SEM images of Au-coated QCM crystals after subsequent electrodeposition of Au from a solution containing AuCl₄⁻ ions in the presence of Pb₂⁺ ions for 150 seconds. The 150 second deposition period provided homogeneous nanostructures resembling nanospike type structures which uniformly cover the entire electrode surfaces of the QCM based sensor.

In order to study the crystal orientation of the electrodeposited surface, both the modified and Au control QCM electrodes were characterised using X-ray diffraction (XRD). The XRD analysis of the electrodeposited samples reveals the preferential growth of face centred cubic (fcc) Au nanospikes along the (111) crystallographic plane as shown in Figures 2c. It is clear from the XRD patterns that the Au electrodeposition under the conditions employed here, resulted in a significant enhancement of the (111) peak. The growth of nanospikes along the (111) crystallographic plane is also evident from the intensity ratios of the (111) and (200) diffraction peaks, observed to be approximately ~ 32 whereas the ratio of standard Au (JCPDS file reference) is a ratio of 3 (Sun et al., 2005).

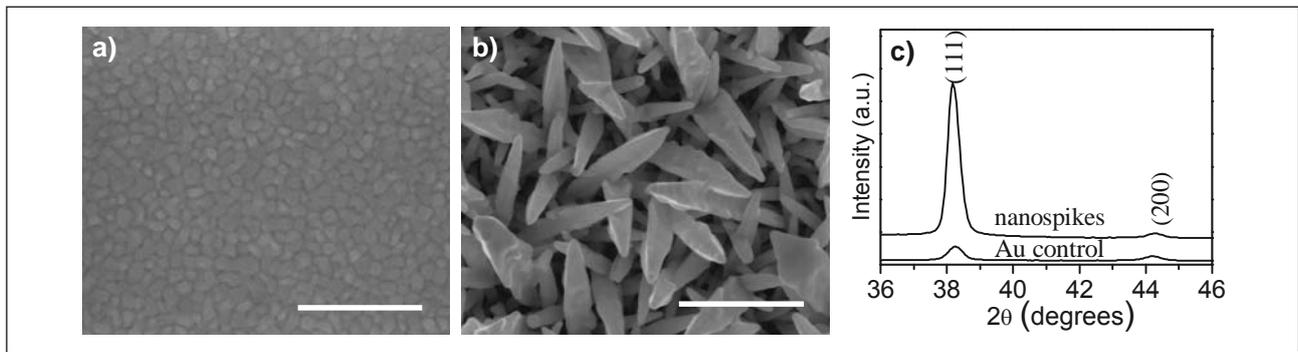


Figure 2: SEM images gold thin films a) before Au electrodeposition (Au control), b) following 150 seconds of Au electrodeposition and c) XRD pattern of Au control and modified surfaces. Scale bars in SEM images represent 500 nm.

3.2 Sensing Experiments

The modified and Au control QCMs were tested in three separate experimental stages. These stages were the 3-day preliminary test, a 50-day long-term limited interference test and a 10-day simulated interference testing period.

3.2.1 Preliminary Testing

A 3-day preliminary test was performed in order to determine the difference in performance (i.e. repeatability and sensitivity) between the Au control and nanospikes based QCM sensors. The response curves for both sensors are shown in Figure 3a. This Hg exposure sequence was repeated six times over the 3-day preliminary testing period which resulted in 6 pulses for each of the 5 tested Hg concentrations. It is evident that the modified QCM shows significantly higher response magnitudes towards

the 5 tested Hg vapour concentrations in comparison with that of the Au control QCM. For instance, the modified QCM is observed to have ~2.8 times the response magnitude of the Au control QCM when exposed to a Hg concentration of 10.55 mg/m³. The drift of the Au control QCM was found to be 0.28 Hz/h with a peak-to-peak noise floor of ±0.59 Hz. On the other hand, the modified QCM had similar drift but with only ±0.08 Hz of noise. In addition, the modified QCM was observed to achieve a 90% response (t₉₀) in ~18.5 minutes; more than 10 minutes quicker than the Au control QCM. Both sensors showed to have good repeatability over a 3-day preliminary testing period with the maximum coefficient of variance (CoV) or spread of the data observed to be ~1.6% and ~3.6% for the modified and Au control QCMs, respectively (Figure 3b). This shows a good repeatability of the modified QCM and indicates that the precision of both sensors were highly repeatable over the 3 day testing period.

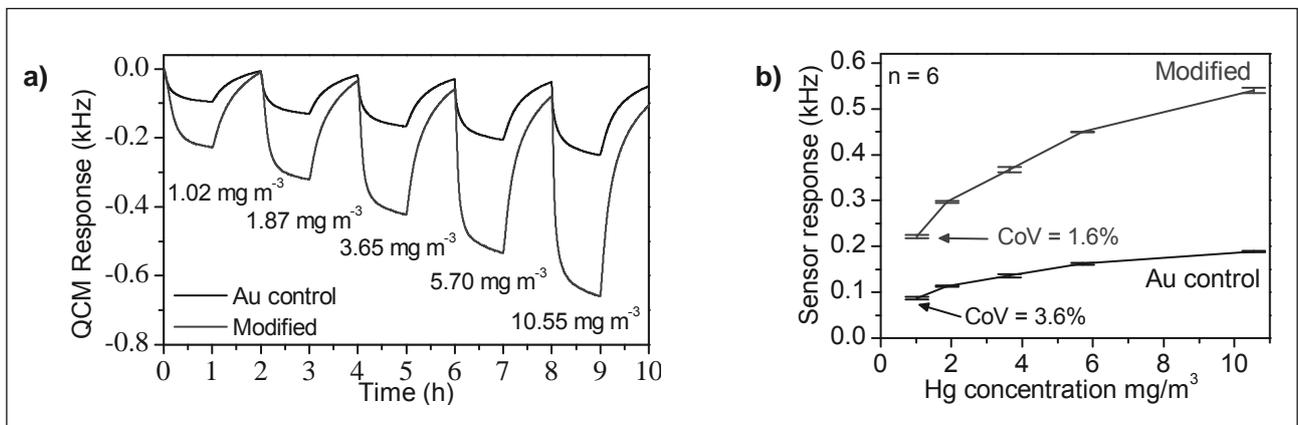


Figure 3: a) Response of modified and Au control QCMs towards Hg pulse sequence, with Hg concentrations ranging from 1.02 to 10.55 mg/m³ and b) Degradation over a 3-day continuous testing period. The number of data points (n) used to calculated the CoV for each point was n = 6.

3.2.2 Long-term sensor performance

A 50-day test was performed in order to determine the long-term stability of the modified and Au control QCM sensors, as well as investigate their cross-sensitivity towards humidity and ammonia. The QCMs were tested using the Memory-test and Interference-test patterns during the 50 day period. Figure 4 shows the dynamic response of the modified sensor from the first Memory-test sequence where only the Hg concentration (x_n) was varied. This test sequence was performed in five different variations which either were conducted using a balance of dry N₂, in the presence of humidity, in the presence of ammonia or a mixture of both humidity and ammonia.

The purpose of the Interference-test pattern was to study the cross-sensitivity of different concentrations of humidity and ammonia while exposing the sensor towards continuous pulses of single concentration of Hg vapour. Figure 5 shows the data gathered for the modified QCM sensor when performing an Interference-test at a Hg concentration of 3.65 mg/m³ (or x₃) with the interfering gas levels being varied at every Hg pulse. The clean Hg pulses are shaded while those performed in the presence of the interfering gases are marked by arrows. This test sequence was performed once for each of the five Hg vapour concentrations tested (ranging from x₁=1.02 to x₅=10.55 mg/m³).

The change in frequency (Δf) and the rate of change of the frequency ($\Delta f/\Delta t$) were calculated for each test sequence. The comparable pulses were used to gather degradation data (i.e. reduction in response magnitude versus age of the sensor) over a 50 day period.

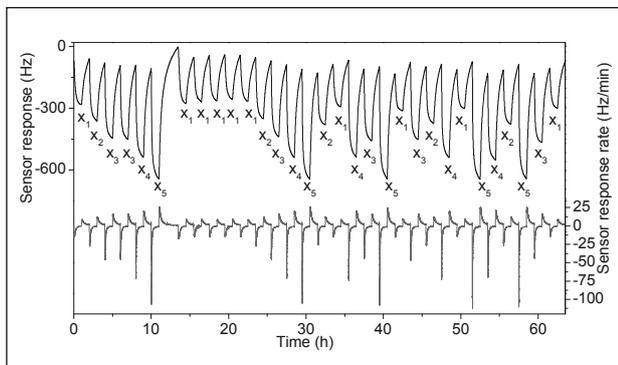


Figure 4: Response of the modified QCM during a memory-test. The top curve (left axis) is the QCM response and the bottom curve (right axis) is the QCM response rate data. The exposed vapour pulses were $x_1 = 1.02 \text{ mg/m}^3$, $x_2 = 1.87 \text{ mg/m}^3$, $x_3 = 3.65 \text{ mg/m}^3$, $x_4 = 5.70 \text{ mg/m}^3$ and $x_5 = 10.55 \text{ mg/m}^3 \pm 0.05 \text{ mg/m}^3$ Hg balanced in dry nitrogen.

A summary of the performance of each sensor over the entire 50 day period is shown in Figure 6a and Figure 6b for the sensor response (Δf) and sensor response rate ($\Delta f/\Delta t$), respectively. The number of data points, n , for each of the five tested Hg vapour concentration range from 42 to 62 for both test patterns combined.

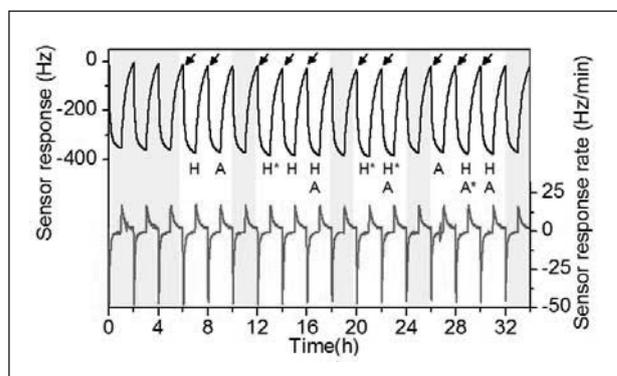


Figure 5: Response of modified QCM towards an Interference-test pattern at a Hg concentration of $x_3 = 3.65 \text{ mg/m}^3$ (where H = $4.2 \text{ g/m}^3 \text{ H}_2\text{O}$, H* = $7.6 \text{ g/m}^3 \text{ H}_2\text{O}$, A = $590 \text{ mg/m}^3 \text{ NH}_3$, A* = $1180 \text{ mg/m}^3 \text{ NH}_3$).

The performances of both the modified and Au control sensors were observed to be exceptional throughout the 50-day testing period. However the data spread in Figure 6 for the modified QCM is shown to significantly outperform the Au control QCM in terms of increased response magnitude, selectivity and dynamic range for both the Δf and $\Delta f/\Delta t$ data. The maximum CoV calculated taking the data from the the entire 50 day testing period was observed to be $\sim 6.6\%$ and $\sim 14.3\%$ for the modified and Au control QCMs, respectively. Additionally there is significant overlap in two standard deviation (2σ) certainty bars for the Au control QCM when compared to the data obtained from the modified QCM. For example, for the Au control QCM, a Δf of 90Hz could either be read as Hg concentration of 1.01, 1.87 or 3.65 mg/m³ if a certainty of 2σ

(95% confidence in variation of data from the mean) is required or reported, whereas the modified based sensor responses do not show any overlap between the five Hg concentration levels that were tested over the 50 day testing period. This clearly demonstrates the ability of the modified QCM to differentiate between different Hg concentrations in the presence of ammonia and water vapour at levels below 1180 mg/m³ and 4.2 g/m³ respectively. Furthermore, analysis of the data from 10.55 mg/m³ Hg pulses during the course of the 50 day testing period revealed that the response magnitude of the modified QCM towards Hg degraded by only $\sim 9\%$ while the Au control QCM degraded by up to 23.3% as summarised in Table 2.

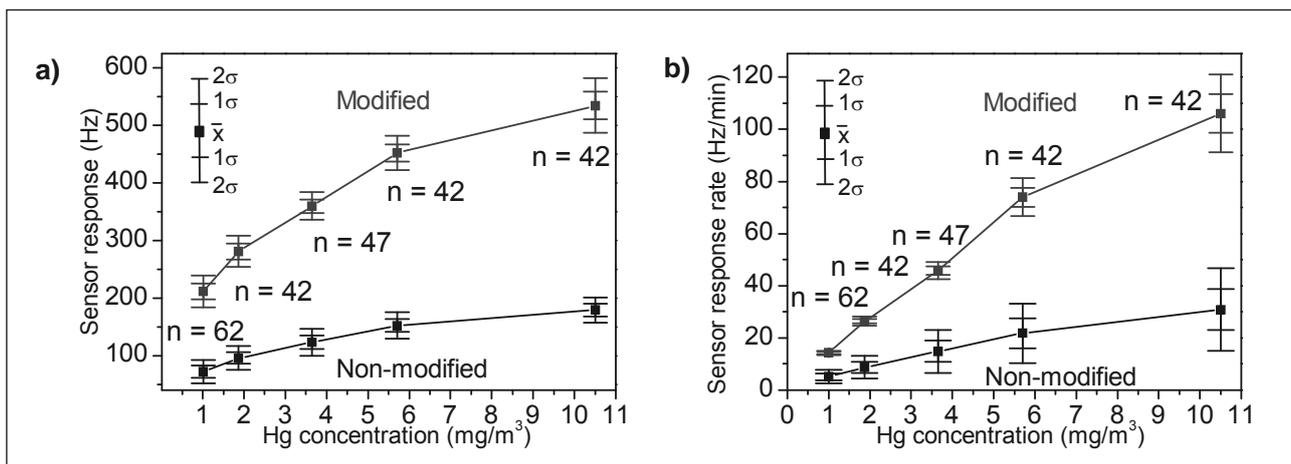


Figure 6: Change in a) sensor response and b) response rate for both the modified and Au control QCMs. Each bar represents one standard deviation (σ) from the mean.

Table 2: QCM data showing response magnitude and % degradation for both the modified and Au control QCMs tested over a 50 day period.

Day	Response (Hz)		Degradation (%)	
	Modified	Au control	Modified	Au control
1	579.7	213.0	-	-
15	527.7	184.2	-9.0	-13.5
29	532.3	163.4	-8.2	-23.3
50	544.9	168.6	-6.0	-20.8

The response characteristics of the Au control sensor showed a considerable reduction in response magnitude with the Au control QCM having ~23% lower response magnitude for Hg on day 29 when compared to that of day 1 of the 50 day testing period. On the other hand the modified QCM appears to be more stable with only a 6% reduction in affinity towards Hg on day 50 when compared to day 1. The data implies that the nanopikes surface could potentially enable the sensor to operate for at least 50-days of continuous testing without a recalibration unless a higher accuracy is required. The results presented are considered

a critical step forward to obtaining an accurate on-line Hg vapour sensor system capable of determining elemental Hg vapour concentrations in the presence of fluctuating humidity and ammonia concentrations.

3.2.3 Industry simulated Testing

In order to study the feasibility of the nanopikes surface as a sensitive layer for a Hg vapour sensor suitable for the alumina industry, a 10-day test was performed as described in Section 2.2.2. This test utilised a specially built stainless steel sensor chamber which enabled the addition of acetaldehyde, acetone, dimethyl disulfide and methyl ethyl ketone to the interference-test. The sensitivity S and limit of detection (LoD) of the QCMs at 89°C in the SS chamber was calculated and presented in Table 3. The CoV is given as a percentage, and represents the precision/selectivity of the sensor. The sensitivity of the sensors is Hg concentration dependent and is given as a/x_n where a is constant and x_n represents Hg concentration, with $n = 1, 2, 3, 4$ and 5 refers to Hg vapour concentrations of 1.02, 1.87, 3.65, 5.70 and 10.55 mg/m³, respectively.

Table 3: Sensitivity and detection limit of the Au control and modified QCMs at an operating temperature of 89°C in Teflon and stainless steel chambers.

Sensor	Teflon chamber			SS chamber		
	$S, a/x_n$ [Hz/(mg/m ³)]	LoD (µg/m ³)	CoV (%)	$S, a/x_n$ [Hz/(mg/m ³)]	LoD (µg/m ³)	CoV (%)
Modified	149.2	316	4.5	96.9	30.72	2.8
Au control	40.2	171	9.6	34.7	45.31	7.8

In the Teflon chamber, it was found that the Hg vapour sensitivity of the modified and Au control QCMs was Hg concentration dependent; the modified QCM was observed to have ~4 times the sensitivity of Au control QCM towards Hg vapour. In the SS chamber, the modified QCM was observed to have better selectivity towards Hg vapour (low CoV) and ~3 times the sensitivity of the Au control QCM. Although the response magnitude and sensitivity of the modified QCM has reduced in the industrial chamber due to the chamber's differing size, shape and construction, both the Au control and modified QCMs are observed to attain the advantage of lower CoV and LoD. This indicates that using the modified QCM in the smaller stainless steel chamber results in better selectivity

and the detection of lower Hg concentrations down to 30.72 µg/m³, as shown in Table 3.

The response graph of the modified and Au control QCMs towards a Hg concentration of 1.87 mg/m³ at an operating temperature of 89°C are shown in Figures 7a and 7b, respectively. It may be observed that although both QCMs respond relatively well to Hg in the presence of interfering gases tested, the modified QCM response contains a relatively higher signal to noise ratio than the Au control QCM. Similar data was obtained for all Hg vapour concentrations tested (1.02, 1.87, 3.65, 5.70 and 10.55 mg/m³).

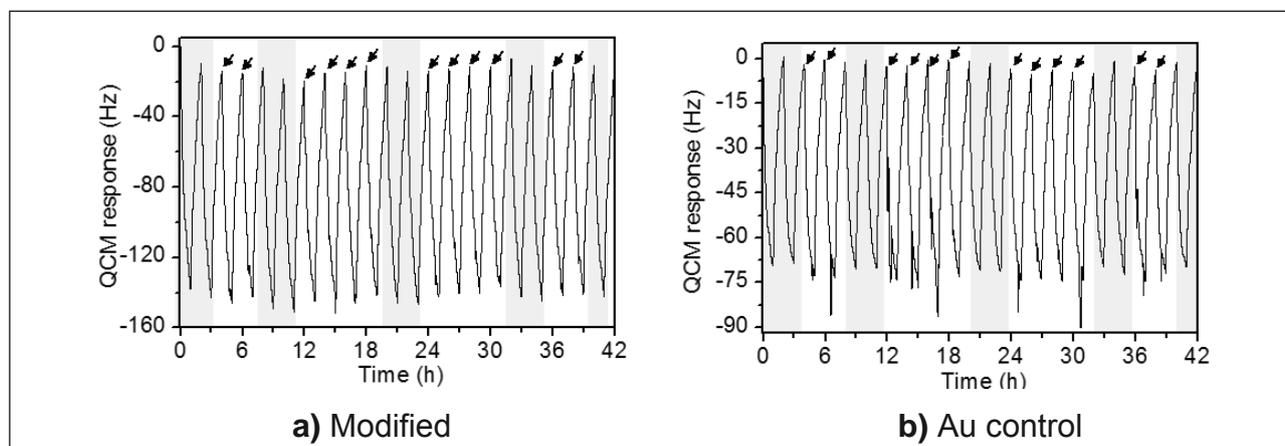


Figure 7: Response dynamics of a) modified and b) control QCMs towards Hg concentration of 1.87 mg/m³ at 89°C in the presence of interference gases (black arrows) listed in Table 1.

A summary of the performance of both sensors towards the five Hg vapour concentrations is presented in Figure 8. The number of data points, n , collected throughout the 10 day period for each of the tested Hg vapour concentrations is also shown.

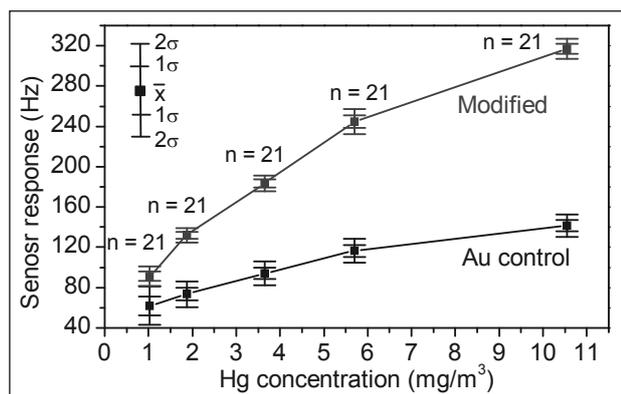


Figure 8: Sensor response magnitude for modified and Au control QCMs. Note the significant overlap in the 95% confidence level in response magnitude (2σ bars) of the Au control when compared to the modified QCM.

It is observed that there is a high separation (dynamic range) between the response magnitudes of the different Hg vapour concentrations for the modified QCM when compared to the Au control QCM. This clearly demonstrates the ability of the nanopikes-sensitive layer to be potentially not influenced by the interfering gases present in alumina refinery stack gas. It is also worth while noting that the response magnitude of the modified QCM in the stainless steel chamber is lower than that observed in the Teflon chamber (see Figure 6a). This is due to the different experimental parameters that were used in the preliminary and the 50-day testings as compared to the tests conducted in the stainless steel chamber. The main difference was that the pre-treatment of both QCMs was performed at temperatures of up to 170°C prior to conducting the 10 day test. In contrast the data presented in sections 3.2.1 and 3.2.2 used QCMs which were only pre-treated at lower temperature of $\sim 134^{\circ}\text{C}$ inside the Teflon chamber. Additionally, the volume and residence time of each gas chamber is different, as is the heat transfer from the chamber to the gas molecules, the diffusion of the gas molecules and consequently Hg sorption on the Au sensitive layers. However, overall, the data obtained from the modified QCM in the stainless steel chamber clearly demonstrates the potential of the nano-modified QCMs to be used as an online Hg vapour sensor for industrial effluent streams such as those found in alumina refineries.

4. Conclusions

It is clearly evident from the mercury sensing studies that Au nanopikes directly electrodeposited onto a QCM sensor can act as an excellent selective Hg vapour sensor in a simulated alumina refinery stack. The Hg vapour sensors were successfully used to continuously monitor the concentration of Hg vapour in the presence of different interfering gases that are present in alumina refinery stack over a 50-day long-term and a 10 day interference tests. The modified sensors were observed to have better selectivity towards Hg vapour (CoV of $\sim 1.6\%$, 6.6% and 2.8% during the 3 day, 50 day and 10 day tests, respectively) with around 3 to 4 times the sensitivity of the non-modified Hg sensors. The increase in both selectivity and sensitivity is attributed to the unique nanostructure gold film which was deposited over the QCM electrodes. The QCM based sensors presented may potentially be developed as an in-situ online monitoring for industrial Hg vapour sensing applications.

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