Landfill Odour Detection using Quartz Crystal Microbalance (QCM)

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Abstract

Odour is considered as the main environmental pollution in Malaysia. Eventhough the standard permitted level has not been set for Malaysia as for air and water, but still the odour has been considered as one of the environmental pollution as the people started to concern about the odour. Conventionally, the odour was detected by the olfactometry, which used human as its panel. But, the human panels are fatigue and unable to produced a consistance result, especially for the continuous monitoring. In this study, the quartz crystal microbalance (QCM) was used as an odour detector. The QCM is basically a mass sensitive device with the ability to measured a very small change on a quartz crystal resonator in real time. This system is basically comprises of an array sensors as well as data acquisition and components analysis. A principle component analysis (PCA) was used to defined three distinct regions, according to the time of the samples being taken and hence to allow the landfill odour differentiation.

Keywords: Odour, Quartz crystal microbalance (QCM), Principle Component Analysis (PCA)

Introduction

The development of the odour detection equipment is still a major problem because of a lack of technical solution. Although the odour is recorded utilizing language expression, it is still difficult for us to associate actual odour with the expression and regenerate it again by only using that expression. It is important to establish the electronic method for odour recording.

In the 1964, the study by King demonstrated that quartz crystal could be used as sorption detectors (mass sensitive devices) by coating the crystals with liquid Gas Chromatography (GC) stationary phases [1]. Nowadays, there's a growth interest on the use of quartz crystal as gas sensor for identification of odour, fragrance and aromas [2].

Following are some of the previous study of which show successful examples of the application of the sensor system based on the quartz crystal microbalance.

Chay and Shih had detected organic vapour by using multichannel piezoelectric quartz crystal. By applying an artificial neural network, they recognized organic and demonstrated the distinction between these organic vapour [3].

Ulmer et al. [4], used a polymer coated quartz microbalance as one of the their sensors to identify odours and flavours. They optimised the quantitative analysis of known gases mixture. Cui et al. [5], made use of quartz crystal microbalance with deposited polypyrole for odour mapping. Better odour discrimination was achieved using this system. Moreover, odorants could be clearly distinguished by their particular position.

The quartz crystal microbalance (QCM) sensor is an example for a very sensitive detector of mass change [6]. Quartz crystal is an earth mineral that is used as the basic materials of the sensors. Figure 1 shows the experimental set up used to analyze the odour produced from the landfill area.

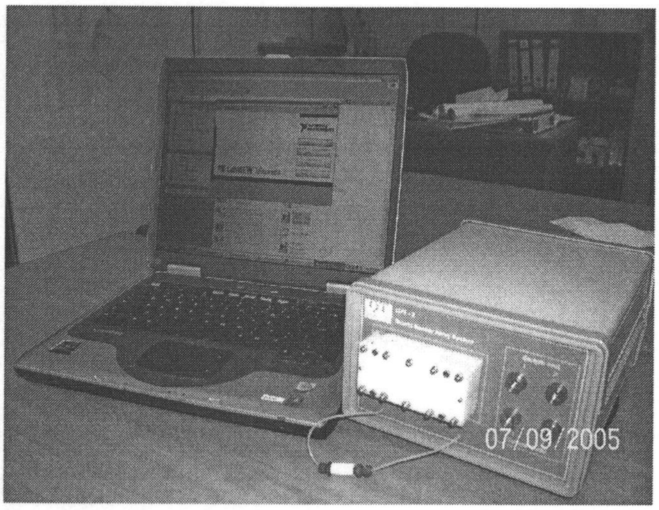

Fig 1 Experimental set up for odour detection

Many studies had shown the application of the QCM sensors for odour detection. Among those are gas mixture analysis [6], solvent vapour detection [3], detection of organic vapour in the environment [7, 8], determination of single odour substances in various types of botanical species such as fruit and flower [9], detection of odour emission from composting facility [10], etc.

The QCM were developed by using lipid blended with PVC as sensing material. Upon excitation by application of a suitable A.C voltage across the 2 electrodes, the device can be made to oscillate at a characteristic resonant frequency. As the mass being adsorbed or placed onto a quartz crystal surface. Then the oscillate frequency will start to change and it can be shown by Sauerebrey Equation [11]:

$$\Delta f = -2.3 \times 10^6 f_o^2 (m/A)$$

where,

Δf = sensor frequency change (Hz)
f_o = oscillation frequency of quartz crystal (MHz)
m = mass change of the adsorbed analytes (g)
A = area of the crystal surface

The method for determining mass and measuring the change in the oscillation frequency of a quartz crystal is extremely sensitive, since this type of crystal has a sensitivity of about 10^{-9} gram [12].

Analytes that are present in the surrounding space (i.e. in sample bags) of the QCM sensors will interact with the sensitive coating materials. The adsorption or absorption of the analytes by the coating materials results in a mass change on the sensor surface. Consequently, the mass change on the sensor surface is converted to the frequency changes.

The QCM are rugged, low power, easily miniaturized and capable of direct chemical sensing in liquids. Moreover, QCMs can be adapted for many different uses by developing coatings that response to different target molecules, adding to their versatility.

Experimental Setup

Sensor Preparation

The quartz crystal was an AT-cut piezoelectric with fundamental frequency of 10 MHz, 8.0 mm diameter, with gold electrodes of 4.0 mm in diameter on both sides (Quartz Technology Ltd UK)

In this experiment, 8 quartz crystals were used as sensors. Each quartz crystal was coated with polyvinyl chloride (PVC) blended lipid on the sensing membrane. 10 mg of PVC was blended with 100 mL of liquid and 5 mL of tetrahydrofuron. The lipid membrane used in this study as shown in table 1 below.

Sensor	Lipid Used
1	Decyl alcohol (DA)
2	Oleic acid (OA)
3	Dioctyl phosphate (DOP)
4	DOP: TOMA = 5:5 (D:T = 5:5)
5	DOP: TOMA = 3:7 (D:T = 3:7)
6	Trioctyl methyl ammonium chloride (TOMA)
7	Oleyamine (OAm)
8	DOP:TOMA = 9:1 (D:T = 9:1)

Table 1 Lipid membrane used in this experiment

5 mL of this solution was coated on both sides of the quartz crystal by spin coating method at 1500 rpm. The coated crystals were then dried for a few minutes. The frequency of the quartz crystals sensor due to coating process was measured by using home-build data acquisition system. The frequency shifts of the coated quartz crystal varies from 1000 Hz to 8000 Hz, depending on the lipid coating materials.

Odour Sampling

Air samples from the landfill area were collected for the analysis by QCM. A battery power mini piston air sampling pump (Cole-Parmer) was used to collect air samples in Tedler Bags. The air samples taken at the landfill area was in the morning and evening for a period of 5 days. The samples of fresh air was also collected for comparison.

Odour Measurement

Figure 2 below shows the experimental set up for the odour measurement.

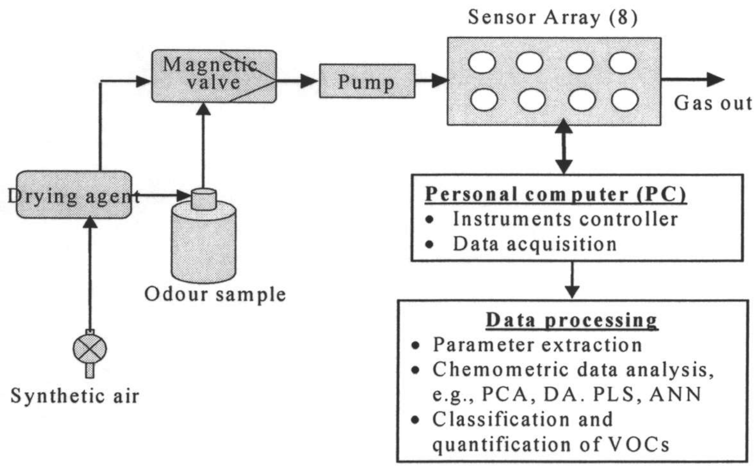

Fig 2 Experimental set up for odour detection

The measurement procedure were as follow. First the valve was switch opened and the pump was turned on. The cell was then supplied with the compressed air without the odourants from the air samples. Then, the routing valve was activated to supply the sample vapour and the resonant frequency shift was measured. Finally, the routing valve was deactivated and the cell was purged for the cleaning purposes. The flowrate of the gas is set at 230 mL/min. The frequency shift was measured for 30 s when the odour sample was supplied to the flow cell. The cleaning process time was set for the duration of 150 s.

Result and Discussion

The baseline frequency shift reading of all sensors were recorded for 5 days, during the data acquisition measurement in August 2005. From the figure 3 below, it shows that the sensors were stable, except for sensor DOP:TOMA, which was drifted to lower vales as days goes by.

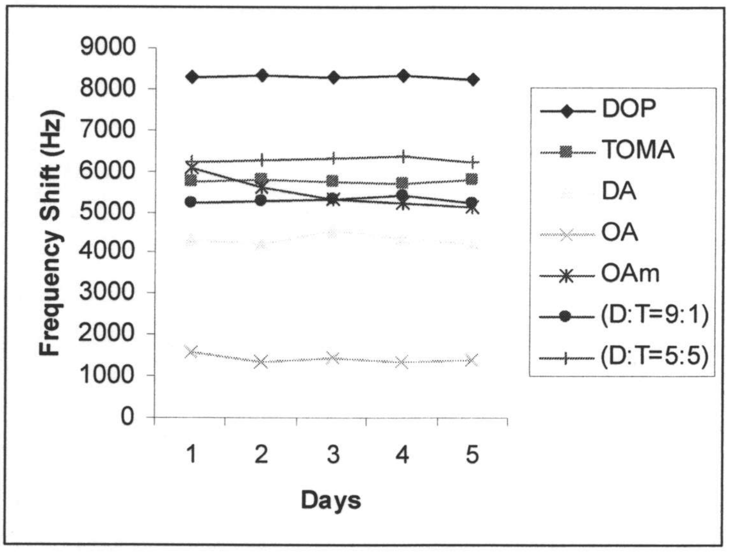

Fig 3 Baseline frequency shift during data acquisition (August 2005)

The PCA now was used to access clustering within the data. PCA is a linear method that has been proven to be efficient to distinguish the response of QCM.

The result of the PCA is shown in figure 4. The result of the PCA shown that all sensors are collerated, as nearly 90% of the variances of the data are contained within the first principle.

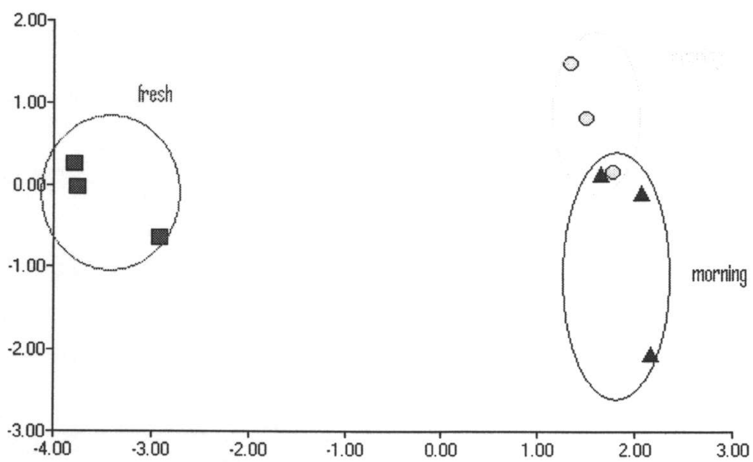

Fig. 4 The scores plot of the principle component analysis

Conclusion

Although a great deal of work still needs to be done, the first results are very promising. QCM can recognize and quantify the odours released by the landfill site. The technique of using one electronic nose as a measuring device for the chemical background noise is totally new and possibly a solution to the problems usually encountered when working in ambient atmosphere with such devices. Aging and replacement of sensors need to be investigated and considered while developing the sensor for odour monitoring.

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