

## **GAS-PHASE PRE-CONCENTRATION FOR A QUARTZ CRYSTAL MICROBALANCE BASED ELECTRONIC NOSE**

*Z. Ali<sup>1\*</sup>, D. James<sup>1</sup>, W. T. O'Hare<sup>1</sup>, F. J. Rowell<sup>2</sup> and S. M. Scott<sup>1</sup>*

<sup>1</sup>School of Science and Technology, University of Teesside, Middlesbrough, TS1 3BA, UK

<sup>2</sup>School of Health, Natural and Social Sciences, University of Sunderland, Sunderland, Tyne and Wear, SR2 7EE, UK

### **Abstract**

The effect of different relative humidity (RH) on the response of a six-polymer coated Quartz Crystal Microbalance (QCM) sensor based electronic nose (EN) was investigated, RH 30 and 50% respectively. Increases in the sensor responses were observed for an increase in RH. A stainless steel pre-concentration tube (PCT) containing Porapak-S and a nichrome heating element was developed to minimise the effect and allow for chromatographic pre-separation. Breakthrough times of chemical compounds through the PCT were experimentally determined and used to select a mixture of water and toluene as a suitable sample for pre-separation. The PCT was capable of separating the water from the toluene and the EN was competent at evaluating the concentration of toluene in the solution.

**Keywords:** electronic nose, chromatographic pre-separation, pre-concentration, relative humidity

### **Introduction**

Electronic noses (ENs) are devices used to measure headspace volatiles and odours, they are made up of an array of independently semi-selective chemical sensors which allows for reversibility. The array responses are analysed by a number of data analysis techniques, these provide the selectivity required for identification of the volatile substances. The major purpose of ENs is to provide a rapid and inexpensive headspace analysis of volatile organic compounds without the use of skilled technicians, which are required for other headspace analysis techniques such as GC-MS [1]. A variety of transducers have been used in EN applications including Metal Oxide Sensors (MOS) [2], Conducting Polymers (CP) [3] and Piezoelectric Quartz crystals (PZQ) [4].

Humidity is a major interferent in EN sensing. Zellers and Han [5] found using a SAW based nose that relative humidity (RH) was important for both polar and non polar coatings. It was found that several combinations of sensor coatings with vapour at differing RH resulted in significant changes in their sensitivities. Martín *et al.* [2]. minimised

---

\* Author for correspondence: E-mail: z.ali@tees.ac.uk

this effect in their discrimination of vegetable oils by carefully controlling the humidity of their carrier gas at 20% RH. Welle *et al.* [6] also investigated moisture management. They again showed that different moisture contents lead to changes in sensor discrimination. They suggested sample pre-treatment as a possible solution to the problem.

Numerous papers have been published combining pre-concentration with QCM and EN sensing [7–9]. Ali *et al.* [10] used a Denuder tube for sample pre-treatment of gaseous ammonia prior to detection by a single coated QCM. Although, as its name states pre-concentration is used to concentrate a specific or group of analytes in a sample, thus helping improve a detector response to it or them, they may also be used for the removal, or separation, of humidity. Groves *et al.* have used a PCT to analyse breath samples [11]. These samples contained high background levels of water. The absorbents used for the PCT were chosen so that the analytes to be detected were strongly retained, whereas the water would be weakly retained and pass through at an earlier time, thus separating the samples. Groves also showed that the breakthrough time ( $t_b$ ) of the analyte could be predicted by a modification of the Wheeler model [12] by Eq. (1).

$$t_b = \frac{W_e}{C_0 Q} \left[ W - \frac{\rho_B Q}{K_v} \ln \left( \frac{C_0 - C}{C} \right) \right] \quad (1)$$

where  $C$  is the concentration/mg mL<sup>-1</sup> downstream of the bed;  $C_0$  is the inlet concentration/mg mL<sup>-1</sup>;  $Q$  is the volumetric flow rate/mL min<sup>-1</sup>;  $W$  is the weight of absorbent/g;  $\rho_B$  is the bulk density of the packed bed/g mL<sup>-1</sup>;  $K_v$  is a rate constant/min<sup>-1</sup>;  $W_e$  is the absorption capacity/mg g<sup>-1</sup>;  $t_b$  is measured in units of minutes.

$K_v$  and  $W_e$  are generally experimentally determined, therefore  $t_b$  is commonly determined experimentally also.

Zellers *et al.* [13] continued this work by replacing the absorbent filled PCT with a porous-layer open-tubular capillary (PLOT) which are commercially available with wall coatings of different polymer and co-polymer. Heberle and co workers used a sensor array with a GC column for chromatographic pre-separation [14]. It was possible with this rig to discriminate between different beers independent of the ethanol content.

## Apparatus

A sensor array consisting of six QCMs with fundamental frequencies of 10 MHz was used (SES Piezo Ltd., Portsmouth, Hants, UK). Each QCM was coated with a commonly utilised gas chromatography stationary phase, each containing a different functional group to allow limited selectivity. The coated QCMs were housed in a 10 mL PTFE sensor chamber. The quartz crystals are offset to their neighbour to provide mixing of the sample in the chamber. A reference quartz crystal was used for differencing, allowing for compensation drift. A P.C. utilising a PC30AT interface card was used to acquire the data with software written in house in C/C++. Microsoft Excel 97 (Microsoft, UK) was used for initial data manipulation. Minitab 12.1 (Minitab Inc., USA) was used for Principal Component Analysis.

The PCT was made of stainless steel tube of 4 mm i.d., 45 mm in length. This was wrapped with a length of 32 gauge Nichrome wire. Approximately 20 turns of wire were used for the PCT. The Nichrome wire was connected to an ISO-TECH laboratory DC power supply (supplied by RS Components, Northants, UK) where the voltage was set at full and the Amperes varied until a desired temperature was reached (180°C was the maintained temperature). A fine wire K-type thermocouple (Farnell, West Yorks, UK) was attached to the PCT and the temperature read from a Lutron multimeter (supplied by RS components, Northants, UK).

Porapak S (Waters Assoc., INC, Framingham, MASS., USA) was packed tightly into the PCT as the adsorbent.

The three alcohols, methanol, ethanol, 1-propanol and 1-butanol, and toluene were all >98% pure and used as received (Fisher Chemicals, Loughborough, Leics, UK).

A Hamilton GC syringe (Supplied by Alltech, Lancs, UK) was used to prepare 0.01%–0.05% v/v water and toluene mixtures. All water was double distilled before use.

#### *PZ quartz crystal coating*

The QCM coatings used were OV-1, Carbowax 20M, OV-17, diethylene glycol succinate, Silar 10C and OV-210 (Phase Separations Ltd, Deeside, UK). These were chosen to give a wide range of functional groups and polarities. Coating solutions were prepared by diluting 3 g of GLC stationary phase to 100 g of a volatile solvent, either dichloromethane or an 80:20% v/v solution of toluene and methanol, resulting in a 3% v/v solutions. A 10× dilution was then carried out to give a 0.3% v/v coating solution. The 6 PZQ's to be used were initially cleaned with acetone for 2 h, followed by ethanol for 2 h. They were then rinsed with double distilled water. The crystals were coated with the solution by means of a fine brush. The frequency was monitored by a FLUKE PM6685 Universal Frequency Counter (Fluke UK Ltd, Watford, UK) during the coating process to enable similar frequency shifts for each QCM. The QCMs were immediately placed into the EN chamber and conditioned by passing nitrogen over them for 6 h.

#### *Sampling*

A 250 mL glass bottle with cap valves containing 100 mL of sample was placed in a water bath 27°C and connected as sample bottle in Fig. 1. A PTFE four-way valve allowed the gas streams to be alternated over the sensor array for sampling and purging, whilst the nitrogen flow rate for both was set at 100 mL min<sup>-1</sup>. A PTFE two-way valve in the sample line allowed the sample bottle to be by-passed for PCT cleaning. Sampling times were determined from the breakthrough times of the compounds to be examined. The standard sampling time was 180 s of sample to PCT, the two-way valve would then be turned and breakthrough times for the sample determined. Heating of the PCT with pure samples would take place at the instance of breakthrough detection. The heating of the PCT was stopped when detection readings had fallen to half of their peak response.

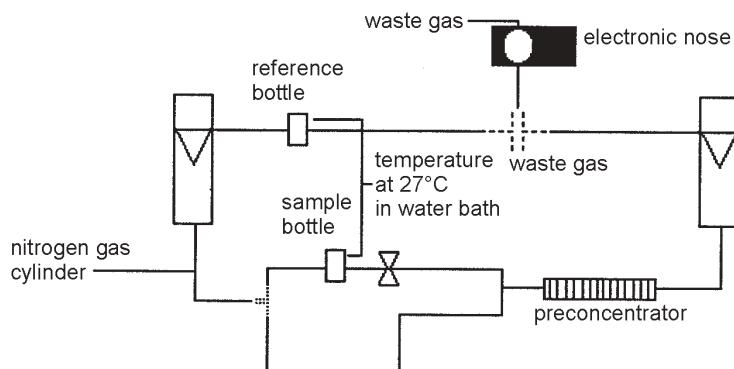


Fig. 1 Schematic of test apparatus

## Data analysis techniques

### Principal component analysis

PCA is a commonly used multivariate technique, which acts unsupervised, i.e. no prior knowledge is assumed of the data. It reduces the dimensionality of the data so that it may be examined in lower dimensional space. This method allows natural clustering of the data to be observed as well as providing an insight into how effective a pattern recognition system may classify the data. PCA works by finding a new set of axis, principal components (PC), which are linear combinations of the original variables.

$$\begin{aligned} Y_1 &= a_{11}X_1 + a_{12}X_2 + \dots + a_{1n}X_n \\ Y_2 &= a_{21}X_1 + a_{22}X_2 + \dots + a_{2n}X_n \end{aligned} \quad (2)$$

where  $Y_x$  – Principal Component  $x$ ,  $X_x$  – Original Variable  $x$ ,  $a_x$  – Coefficient  $x$ .

The coefficients are chosen so that each new variable is uncorrelated with the others. The PCs also are chosen so that they account for variation in the data. The components are calculated so that  $PC_1$  will account for the largest variance,  $PC_2$  the next largest etc. etc. This is where the reduction in the dimensions of the data takes place, as typically the first 3 components will account for 85% or more of the variation in the data.

## Results and discussion

### Effect of humidity on EN readings

The responses of the QCMs can be dependent upon the coatings employed. Figure 2 shows the frequency change of the crystal coated with OV-210. It can be seen that at higher humidity an increased response is obtained. Figure 3 shows the PCA scores plot for all QCMs of the EN to 30 and 50% humidity and gives the same information as Fig. 2, i.e. that for different humidity values different clusters are formed. A widespread cluster representing the 50% humidity readings can be seen on the left side of the plot clearly separated from a widespread cluster on the right side of the plot representing the 30% humidity data.

These results show that water content of samples investigated could play a part in the responses of the EN. Therefore, to stop the nose from acting as a humidity sensor it is important to neutralise the effect of the humidity. A pre-separation, pre-concentration tube (PCT) was chosen for this purpose. The tube functions like a GC capillary tube in that it will allow for separation of components due to their properties, i.e. polarity etc.

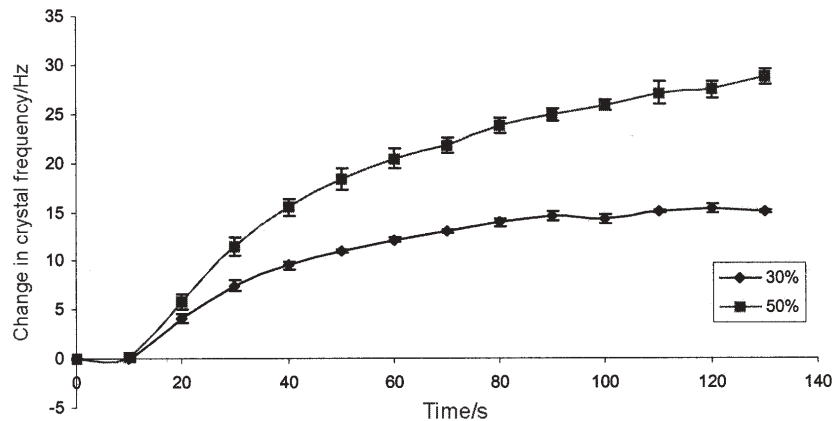


Fig. 2 Effect of humidity on OV-210 coated QCM response

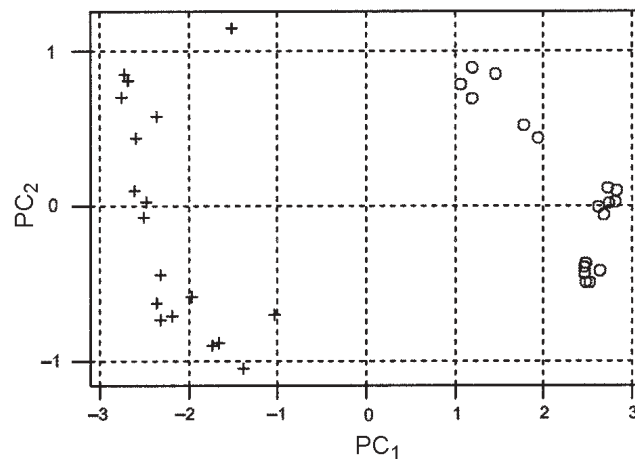


Fig. 3 PCA plot of the effect of humidity on the 6 crystals response.  $\circ$  – 30%;  $+$  – 50%

#### Breakthrough times and flow rates

The PCT tubes breakthrough times were calculated for varying substances at a flow rate of  $100 \text{ mL min}^{-1}$  (Table 1). It can be seen that the polar compounds are not retained, or loosely retained by the Porapak S. Therefore the breakthrough times of the alcohols are too similar for them to be separated. Although Methanol breakthrough

takes place at 200 s, for a sampling time of 180 s, the complete elution of the methanol does not take place until 500 s, therefore making discrimination between mixtures of the alcohols difficult.

Methanol samples were used to investigate the usefulness of pre-concentration. Control samples involved 180 s of exposure to the methanol at a flow rate of 100 mL min<sup>-1</sup>. At breakthrough the PCT was heated and maintained at 180°C until the nose response had dropped to half its peak value. A higher value of QCM response was observed with the heating step, than when carried out without this stage. This is due to a shorter elution time for the methanol with an increased temperature leading to an increase in the amount coming off the tube over a set instance. The effect of temperature with blank samples, i.e. just nitrogen, as well as methanol samples after they have passed through the tube (770 s) has been investigated. It was found that a very small heat and pressure pulse was observed 130 s after heating began, producing a maximum change in frequency of 10 Hz.

Toluene does not breakthrough the PCT until over 1000 s (Table 1) if the tube is at ambient temperature. This therefore means the PCT can be loaded with a large amount of the toluene, i.e. 1000 s of sampling, also that it is possible to separate the toluene from alcohols, or water.

**Table 1** Breakthrough time of various compounds for Porapak S PCT with a flow rate of 100 mL min<sup>-1</sup>

Compound	Breakthrough/s
Methanol	200±30
Water	240±20
1-Butanol	260±10
Toluene	1190±50
Toluene with heating at 770 s	960±50

A heating step at 770 s was also investigated with toluene. 770 s would allow water to leave the PCT (for a 3 min sample exposure time) and permit the desorption of water from the sensor coatings. The heating step resulted in breakthrough being observed at an earlier time (Table 1), 960 s, and of a higher value, as it allows more toluene to come off the Porapak S within a set instance. Due to the success of these tests, different concentrations of toluene in water were investigated. The initial work was carried out with 1% v/v of toluene in water. The response of the EN was found to go beyond the range of the nose for this concentration and so could not be recorded.

#### *Toluene concentrations in water*

The measurable scale of the EN for concentration of toluene was found to be between 0.01 to 0.05% v/v. Figures 4 and 5 show the differences in QCM response for 2 different concentrations of toluene, 0.05 and 0.01% respectively. It is clearly shown that the size of re-

sponse is related to the concentration, i.e. Fig. 4 shows a QCM response to be around 300 Hz, whereas in Fig. 5 the same crystal response is shown to be approx 35 Hz. The first peak observed on both the graphs relates to the water, and this as expected remains relatively constant for each of the different toluene concentrations, giving a peak of around 50 Hz. Interestingly on Fig. 5 the heat and pressure pulse can also be observed at

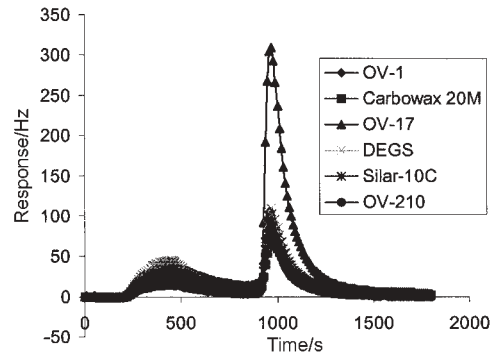


Fig. 4 Response of nose to 0.05% toluene in water v/v using PCT with heating step at 770 s

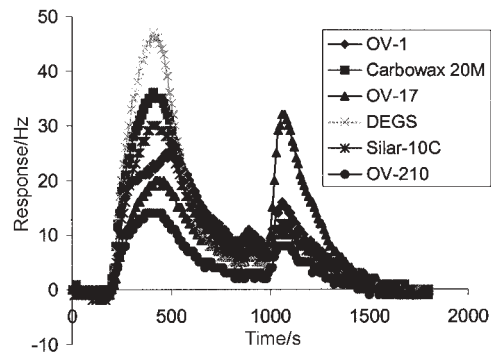


Fig. 5 Response of nose to 0.01% toluene in water v/v using PCT with heating step at 770 s

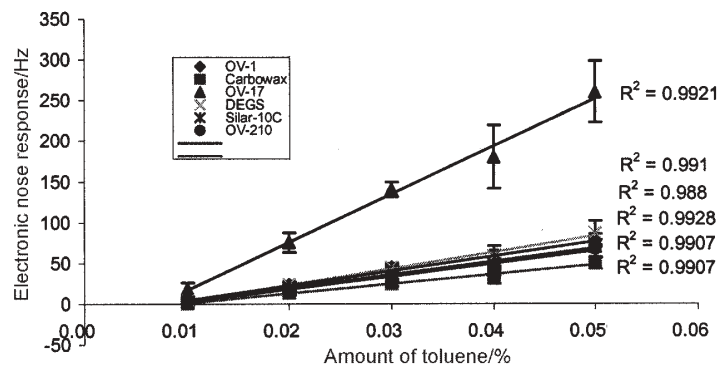


Fig. 6 Calibration curve for all 6 crystals

900 s just before the breakthrough of the toluene at 960 s. This is because the responses are now quite small and thus 10 Hz is a comparable value.

Calibration curves were plotted for toluene concentration against maximum response for each QCM (Fig. 6). It can be seen that only the OV-17 crystal gave a large response to the increase in concentration. However, every crystal did show a linear increase. The error bars represent the standard deviation from the mean of six runs and the relative error is found to be similar for all readings.

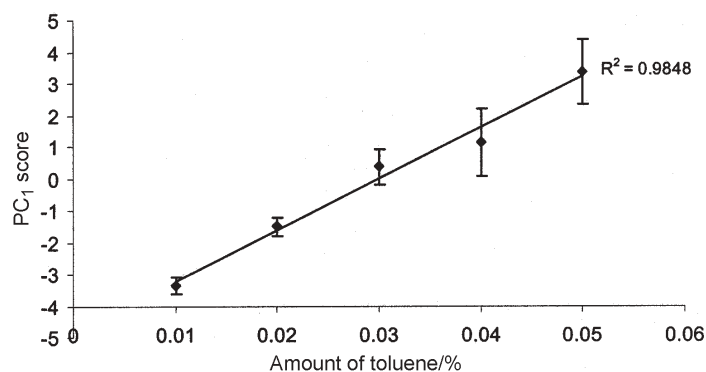


Fig. 7 PC regression of toluene concentration

Principal Component Regression (PCR) (Fig. 7) allows the information to be viewed without the complication of observing 6 separate lines. As with Fig. 6, the variance in the results is found to increase with concentration, although the relative error remains the same. The calibration curve linearly increases with concentration, although its correlation coefficient value (0.9848) is slightly lower than that of the individual lines.

## Conclusions

It has been shown that humidity effects EN responses and therefore water in samples can act as interference during sensing. It has also been revealed that a PCT tube packed with an appropriate stationary phase, can be used to remove, or separate this interference also offering the possibility of pre-concentrating trace amounts of useful analytes to produce a response from the EN. The EN with the addition of a Porapak S PCT was successful in detecting different concentrations of toluene pollution in water. The responses to toluene over the range of 0.01% v/v in water to 0.05% has been shown to be linear in nature and determinable in approximately 20 min of sampling time. Changing the characteristics (length, diameter and packing material) of the PCT could allow for reduction in the total sensing time to less than ten minutes, whilst also increasing the range and limit of detection. Changing of the stationary phase would also allow for different chemicals, such as the alcohols, to be detected by this method.

This form of detection with a quicker sampling time could be valuable for the detection of water pollution. Further work looking at the detection of petrol, diesel,



and waste fuel with the nose system should allow for detection and quantification of contaminants of water rapidly.

\* \* \*

The authors acknowledge ERDF funding under contract 70/41/001 for this project. We also wish to acknowledge support of Kevin Middleton and Jill Legg in the construction of the electronic nose.

## References

- 1 H. Maarse and D. K. Van der Heij (Eds), Trends in Flavour Research, Elsevier Science B. V. (1994) 151.
- 2 Y. G. Martín, J. L. P. Pavón, B. M. Cordero and C. G. Pinto, Anal. Chim. Acta, 384 (1999) 83.
- 3 R. M. Stuetz, S. George, R. A. Fenner and S. J. Hall, J. Chem. Technol. Biotechnol., 74 (1999) 1069.
- 4 Z. Ali, W. T. O'Hare, T. Sarkodie-Gyan and B. J. Theaker, J. Therm. Anal. Cal., 55 (1999) 371.
- 5 E. T. Zellers and M. Han, Anal. Chim. Acta, 68 (1996) 2409.
- 6 F. Welle, A. Mauer, E.-M. Keil and M. Slama, Sens. Acts. B, 69 (2000) 372.
- 7 M. Fang, K. Vetelino, M. Rothery, J. Hines and G. C. Frye, Sens. Acts. B, 56 (1999) 155.
- 8 T. Nakamoto, Y. Isaka, T. Ishige and T. Moriizumi, Sens. Acts. B, 69 (2000) 58.
- 9 W. Muenchmeyer, A. Walte and G. Matz, Sens. Acts. B, 69 (2000) 379.
- 10 Z. Ali, C. L. P. Thomas, J. F. Alder and G. B. Marshall, Analyst, 117 (1992) 899.
- 11 W. A. Groves, E. T. Zellers and G. C. Frye, Anal. Chim. Acta, 371 (1998) 131.
- 12 A. Wheeler and A. J. Robell, J. Catal., 13 (1969) 299.
- 13 E. T. Zellers, M. Morishita and Q.-Y. Cai, Sens. Acts. B, 67 (2000) 244.
- 14 I. Herble, A. Liebming, U. Weimar and W. Göpel, Sens. Acts. B, 68 (2000) 53.