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Quartz crystal microbalance sensor array for the detection of volatile organic compounds

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ABSTRACT

A sensor array system consisting of five quartz crystal microbalance (QCM) sensors (four for measuring and one for reference) and an artificial neural network (ANN) method is presented for on-line detection of volatile organic compounds. Three ionic liquids, 1-butyl-3-methylimidazolium chloride (C_4mimCl), 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6), 1-dedocyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4mimNTf_2$), and silicone oil II, which is widely used as gas chromatographic stationary phase, have been selected as sensitive coatings on the quartz surface allowing the sensor array effective to identify chemical vapors, such as toluene, ethanol, acetone and dichloromethane. The success rate for the qualitative recognition reached 100%. Quantitative analysis has also been investigated, within the concentration range of 0.6–6.1 mg/L for toluene, 0.9–7.5 mg/L for ethanol, 2.8–117 mg/L for dichloromethane, and 0.7–38 mg/L for acetone, with a prediction error lower than 8%.

1. Introduction

The detection of volatile organic compounds (VOCs) in environmental protection, health care and food industry has been a challenging task facing analytical workers for decades. Common methods for analyzing VOCs are gas chromatography (GC), mass spectrometry (MS), and fourier transform infrared (FTIR) spectrometry. Although these methods are accurate and reliable, most of them are off-line analyses which are often coupled with solid adsorbent tubes for grabbing samples, and they either need expensive instrumentations or are time-consuming [1,2]. Recently, development of sensors for on-line and *in situ* detection of VOCs has received great attention. As is known, the sensitivity and selectivity of most sensors, such as piezoelectric sensors and metal-oxide gas sensors, depend greatly on the nature of the sensitive layers. However, producing special coatings sensitive to a special analyte, namely, the strict 'lock-and-key' design criterion of traditional sensing devices, is almost unrealizable. Actually, sensors with diverse selectivities, coupled with chemometrics method, are often utilized as a sensor array for on-line VOCs analysis, with higher identification than a single sensor [3–5]. Among all kinds of sensors, quartz crystal microbalance (QCM) sensor has attracted our attention for its low cost, compact volume, easy portability and high sensitivity. Meanwhile, QCM sensors present preponderance over metal-oxide semiconductor sensors in lower operating temperatures [3,6,7]. QCM is extensively employed in gas analysis since it was first introduced by King in 1964 [8], which is based on the frequency decrease upon mass-increase resulting from adsorption of chemical vapors on the sensor surface. The variation of frequency can be calculated using the Sauerbrey equation [9]

$$\Delta f = -2.26 \times 10^{-6} f_0^2 \frac{\Delta M_s}{A} \tag{1}$$

where Δf is the frequency shift (Hz) when the sensor is exposed to chemical vapors, f_0 is the intrinsic frequency of the piezoelectric crystal (Hz), $\Delta M_s/A$ is the mass-increase per unit of area (g/cm^2). Various coating materials for QCM sensor arrays have been reported for recognition of VOCs. Pengchao Si [10] used the principle components analysis (PCA) and an array of eight QCM sensors, each coated with a different conducting polymer, to identify organic vapors, such as toluene, 1-ocatanol, acetate acid, acetone, acetonitrile, ethanol etc. Gyorgy Barko et al. [11] used a QCM array modified by different gas chromatographic stationary phases to detect VOCs assisted by artificial neural network (ANN) analysis. A sensor system with four piezoelectric detectors has been developed by Ying et al. [12] for the analysis of chemical agents. Munoz et al. [13] has built an odor recognition device using QCM coated with lipids and stationary phase materials of GC for identification of orange and melon flavors.

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In this work, an array of five QCMs, each of the four measuring QCM coated with a different material and a blank QCM for reference, was used as a sensor system to measure organic compounds. The sensitive coatings included three ionic liquids and a GC stationary phase. Ionic liquids (ILs) are a class of compounds containing organic cations and various anions, which are liquid at ambient temperatures. The unique properties of ILs, such as negligible vapor pressure and high thermal and chemical stability in air, make them well suited for coatings of sensors and detectors [14–17]. Studies on ILs as QCM coatings revealed that ionic liquids composed of different cations and anion had different sensivities and selectivities towards analytes [18,19]. So we studied the identification property of the sensor array by using an ANN qualitative recognition method for the detection of four typical VOCs of toluene, acetone, ethanol and dichloromethane. Quantitative analyses were carried out by calibration curve-fitting after identification.

2. Experimental

2.1. Reagents and materials

Toluene, dichloromethane, ethanol, acetone and chloroform were all analytical grade, and they were used as received without further purification.

Ionic liquids 1-butyl-3-methylimidazolium chloride (C_4mimCl), 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6) and 1-dedocyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C_4mimNTf_2) were used as QCM sensors' coating materials due to their high sensitivity and selectivity towards VOCs [19], which were prepared according to procedures reported in other literatures [20–22]. Silicone oil II, a widely used gas chromatographic stationary phase (Shanghai Reagent Co., Shanghai, China), was also used as the array's coating material.

2.2. Apparatus

The apparatus consisted of five AT-cut piezoelectric quartz crystals (No. 707 factory, Beijing, China) with a fundamental frequency of 10 MHz. They had a 9 mm outer diameter with gold-plated electrodes of 5 mm diameter on both sides. The experimental set-up of the array system was shown in Fig. 1. Each of the four quartz crystals was coated with a different sorbent layer as working sensors, and a fifth blank quartz crystal was used for reference to eliminate the inferences of temperature and pressure. These crystals were located in the same measuring chamber, with a volume of about 5 mL, and each of them was driven by an independent oscillator circuit so that they worked independently, without mutual interferences. Both of the oscillator circuit and frequency acquisition system were home-built. The resonant frequency of each crystal was recorded every 5 s through the data acquisition system and the data were transferred to a computer via RS232 interface. In this work, the actual frequency and beat frequency of each quartz crystal were recorded in the measurement. The beat frequency is defined as the difference in frequency between the measuring crystal and the reference crystal. In this QCM array system, the beat frequency between each measuring crystal and reference crystal was not achieved by a frequency mixer, but through software approach, namely, by subtracting the frequency of reference from that of corresponding measuring crystal. The beat frequency was saved for later data processing.

2.3. Crystal film preparation and experiment procedures

The coating films on quartz crystals were obtained by dip-coating technique. The adsorbent materials were dissolved in chloroform with concentrations of about 10 mg/mL. Dipping the quartz crystal in the coating solution for a certain time, thin film was obtained when the solvent evaporated. Excess coating materials on the edge of the quartz wafer outside the gold electrodes were wiped off by using a chloroform-soaked filter paper. An appropriated film thickness could be obtained by controlling the coating time.

Before each measurement, the array system was purged with pure N_2 until frequency equilibrium was established. Various concentrations of analytes were introduced into the measuring chamber, and each sensor responded in its characteristic way. After adsorption equilibrium was established, the analyte was wiped off by N_2, which made the frequency of each sensor back to the initial baseline, and the sensor system was ready for the next measurement. The measured analytes were obtained through the gas generation and dilution system which has been described in our previous work [19]. 136 samples of four analytes within the range from 2% to 100% of the saturated analyte vapors generated with the system were measured with the sensor array system. The saturated vapor concentrations of the four organic vapors generated in our experiment are 38.76 mg/L for acetone, 116.50 mg/L for dichloromethane, 7.29 mg/L for ethanol and 6.07 mg/L for toluene. They were divided into two groups: 120 samples for the training set, other 16 samples for the testing set. All measurements were carried out at room temperature with a gas flow rate of 30–90 mL/min.

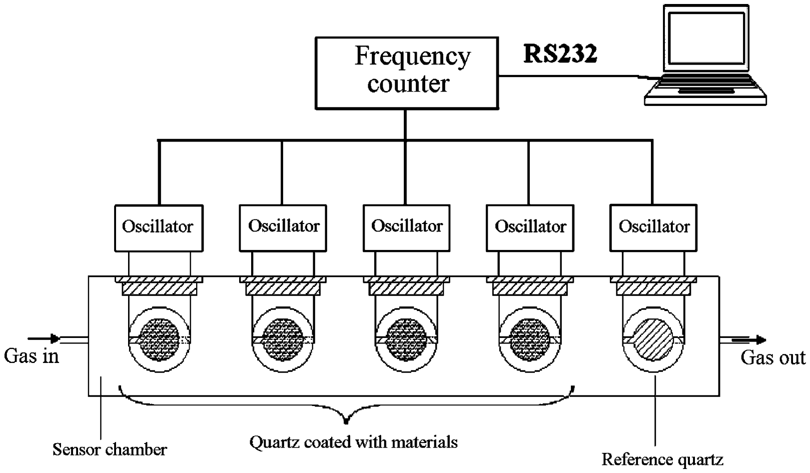

Fig. 1. Schematic diagram of the sensor array system.

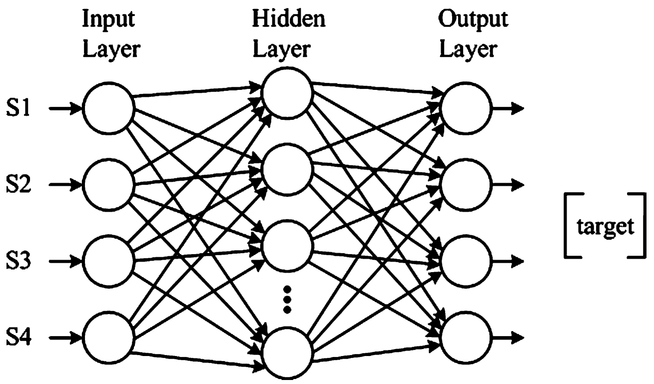

Fig. 2. Topological structure of three-layer back-propagation neural network.

2.4. Artificial neural network

Artificial neural networks (ANNs) are widely used for the identification of analytes measured through sensor array system. In this work, a simple feed forward networks using back propagation learning algorithm was used to handle the frequency signals of the QCM sensor array [11], which were composed of three layers: input layer, hidden layer and output layer. The topological structure of the ANN was shown in Fig. 2. The first (input) layer consisted of four neurons, which was equal to the number of chemical sensors. The number of output neurons was tied to the number of analytes and the number of hidden neurons was generally estimated empirically and was decided through the experiment. In this work, the number of neurons in the input, hidden and output layers were 4, 6 and 4, respectively. The ANN was implemented using software developed in the MATLAB 7.0 environment.

3. Results and discussion

3.1. Optimization of film thickness on quartz crystal

Film thickness on the surface of quartz crystal has an important effect on the sensor performance. The optimum amount of IL coated on the QCM surface was investigated. Fig. 3 shows the frequency change as a function of coated C_4mimCl mass when exposed to 1000 ppm ethanol vapor. Negative frequency change means that adsorption of organic vapors caused a frequency decrease in the QCM sensor. The response of C_4mimCl coated QCM showed an increase with an increase in coated mass below 8.5 μg (corresponding to film thickness of 200 nm, the density of C_4mimCl is 1.08 g/mL [23]). However, the response declined sharply when the thickness was more than 229 nm (corresponding to 9.7 μg C_4mimCl). Frequency response of QCM even increased, instead of decreasing, on exposure to ethanol vapor when the coated mass exceeded 10.5 μg (shown in Fig. 3). This phenomenon is likely due to the two opposite effects on the frequency shifts of an IL coated QCM sensor on exposure to gases, namely, the mass-increase in the IL film resulting in a decrease in the frequency and the viscosity decrease resulting in an increase in the QCM frequency [15,17]. When the film was thin enough (<200 nm for C_4mimCl), the viscosity effect could be ignored, and the Sauerbrey equation (Eq. (1)) worked well [24]. When the coated IL film was specially thicker (>10.5 μg for C_4mimC), the viscosity decrease was the main factor that influenced the QCM performance, which has been utilized as the sensing mechanism for vapor sensing of QCM/IL sensor by Liang et al. [15]. So, the mass of film coatings within the range of 3.5–7.0 μg was used in the following study.

3.2. Characteristic of the QCM sensor array

The oscillating frequency of the piezoelectric crystal is temperature dependent because the material properties of the substrate are temperature dependent [25,26]. When the piezoelectric crystal is coated with sensitive material to make a sensor, the temperature dependence becomes more complicated. However, the temperature effect can be partly eliminated by using an identical piezoelectric crystal to generate a reference frequency. Besides the temperature effect, the buoyancy effect [27], resulted from a change in gas density due to introducing analyte vapor, could also be corrected by the use of reference crystal. Fig. 4 shows the beat frequency responses of the array system to 5.51 mg/L toluene vapor. Excellent reversibility for adsorption of gas in the coated materials and rapid response was observed in the sensorgram of Fig. 4, which conformed that the array system could be easily regenerated and could be used for continuous measurement. Rapid response attributed to the higher diffusion rate of gas molecules in relatively low viscosity of ionic liquids and silicone oil than the diffusion rate of gas molecules in solid coating materials [28,29]. Besides, due to the negligible vapor pressure of ILs, there was no coating loss when the array was used for measurement, which ensured the stability of the system. Due to the high stability of the sensor coatings, and the excellent reversibility of the sensor system, the sensor array could have a long life-time theoretically. Frequency changes, calculated from the frequency difference between gas exposure and purging shown in Fig. 4, were used as eigenvalues for data process, e.g. 89,

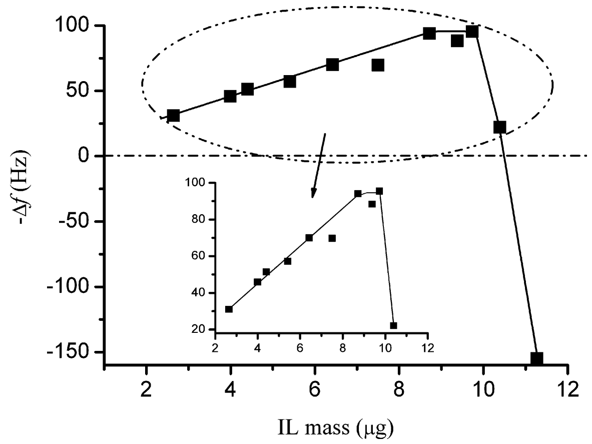

Fig. 3. Frequency change of QCM sensor versus different mass of C_4mimCl on exposure to 1000 ppm ethanol.

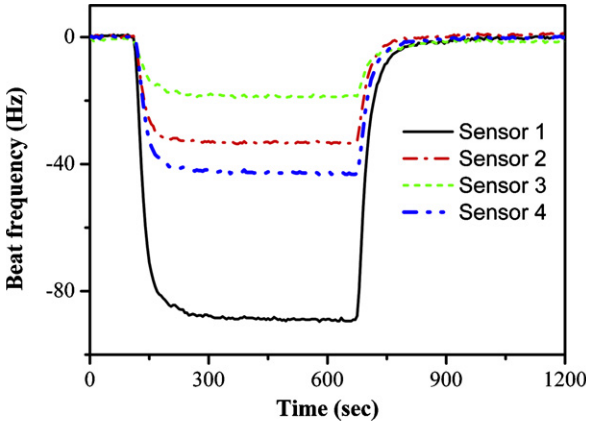

Fig. 4. Sensor array response towards 5.51 mg/L toluene vapor. Sensor coating materials: sensor 1, C_{12}mimNTf$_2$; sensor 2, C_4mimPF$_6$; sensor 3, C_4mimCl; sensor 4, silicone oil II.

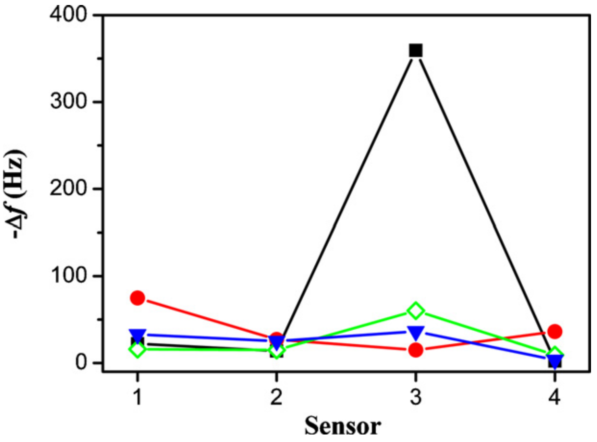

Fig. 5. Sensor array response patterns for (■) ethanol (6.6 mg/L); (●), toluene (4.8 mg/L); (◊), dichloromethane (17.5 mg/L); and (▼), acetone (7.8 mg/L). Sensor coating materials: 1, C_{12}mimNTf$_2$; 2, C_4mimPF$_6$; 3, C_4mimCl; 4, silicone oil II.

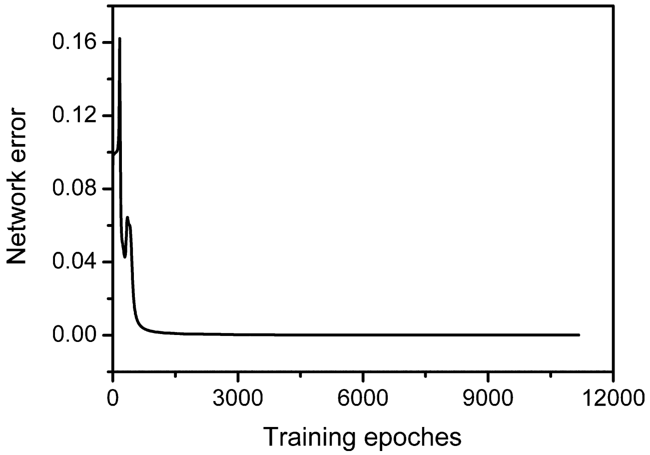

Fig. 6. Convergence curve of the three-layer back-propagation networks.

33, 18 and 43 Hz for each sensor of the array towards 5.51 mg/L toluene.

3.3. *Qualitative analysis of the sensor array system*

Fig. 5 shows the sensor array response to various VOCs. It is clear that each QCM sensor coated with a different coating in the array had quite different response intensities towards the same analyte, e.g. when 4.8 mg/L toluene was measured, signal intensity for each sensor of the array decreased in the sequence of sensor 1 > sensor 4 > sensor 2 > sensor 3; while the array showed quite different response pattern towards other analytes (such as ethanol: sensor 3 > sensor 1 > sensor 2 > sensor 4). On the other hand, the same sensor presented different sensitivities to different VOCs, e.g. response sensitivity decreased in order of ethanol > dichloromethane > acetone > toluene on sensor 3 coated with C_4mimCl, which has been reported in our previous work [19]. Due to the different response patterns of sensor array system, the analyte can be identified through pattern recognition algorithms.

In the pattern recognition process, the level of inputs to the ANN should be arranged between 0 and 1 [30]. As is shown in Figs. 4 and 5, frequency shift outputs of the QCM array were in the range from a few to several hundred Hertz. So the values of these outputs must be normalized for the ANN training and testing process. A normalization process for each sensor response was performed according to Eq. (2):

$$X_{ij} = \frac{\Delta f_{ij}}{\left[\sum_i (\Delta f_{ij})^2\right]^{1/2}} \tag{2}$$

where X_{ij} is the normalized value of sensor j for sample i; Δf_{ij} is the frequency change of sensor j for sample i. The normalized array outputs, $X_{ij} = \{X_{i1}, X_{i2}, X_{i3}, \ldots, X_{ij}\}$, were used as inputs of the ANN recognition system. For training the network, the learning process was repeated until the network error reached 0.0001 with 6 neurons in the hidden layer, and the convergence curve was shown in Fig. 6.

After training the network with 120 samples in the training set, 30 samples in each category, the prediction results for the 16 testing samples, 4 samples in each category, of the ANN were listed in Table 1. It can be seen that outputs generated during testing were typically above 0.9, which is the output element value customarily adopted to show the presence of an analyte, compared with the ideal output value of 1.0; and other output elements were below 0.1, compared with an ideal output value of 0 to show the absence of an analyte. Excellent identification was seen, with the largest output error less than 0.02. These results show that the network discriminates well between these chemical species. In addition, the

Table 1
Prediction results of artificial neural networks.

Sample No.	Output 1		Output 2		Output 3		Output 4		Predicted	Actual
	Actual	Target	Actual	Target	Actual	Target	Actual	Target	gas	gas
1	0.9968	1	0.0000	0	0.0000	0	0.0039	0	T	T
2	0.9968	1	0.0000	0	0.0000	0	0.0040	0	T	T
3	0.9967	1	0.0000	0	0.0000	0	0.0042	0	T	T
4	0.9965	1	0.0000	0	0.0000	0	0.0044	0	T	T
5	0.0000	0	0.9891	1	0.0108	0	0.0001	0	E	E
6	0.0000	0	0.9890	1	0.0108	0	0.0001	0	E	E
7	0.0000	0	0.9898	1	0.0099	0	0.0001	0	E	E
8	0.0000	0	0.9904	1	0.0093	0	0.0001	0	E	E
9	0.0000	0	0.0055	0	0.9874	1	0.0102	0	D	D
10	0.0000	0	0.0093	0	0.9874	1	0.0068	0	D	D
11	0.0000	0	0.0107	0	0.9871	1	0.0061	0	D	D
12	0.0000	0	0.0117	0	0.9868	1	0.0057	0	D	D
13	0.0082	0	0.0000	0	0.0030	0	0.9925	1	A	A
14	0.0071	0	0.0000	0	0.0035	0	0.9931	1	A	A
15	0.0032	0	0.0000	0	0.0090	0	0.9933	1	A	A
16	0.0039	0	0.0000	0	0.0069	0	0.9933	1	A	A

Note: T, toluene; E, ethanol; D, dichloromethane; and A, acetone.

Table 2
Fitting equations of each QCM sensor in the array towards toluene vapor.

	Fitting equation	Correlation coefficient, R^2
Sensor 1	$\Delta f(\mathrm{Hz}) = 15.78C(\mathrm{g/m^3}) - 2.78$	0.996
Sensor 2	$\Delta f(\mathrm{Hz}) = 5.92C(\mathrm{g/m^3}) - 0.73$	0.995
Sensor 3	$\Delta f(\mathrm{Hz}) = 3.22C(\mathrm{g/m^3}) - 0.18$	0.990
Sensor 4	$\Delta f(\mathrm{Hz}) = 7.69C(\mathrm{g/m^3}) - 1.51$	0.996

Table 3
Results of quantity analysis for the testing samples.

No.	Sample	Actual concentration (C_r, mg/L)	Predicted concentration (C_t, mg/L)	Error (%)[a]
1	Toluene	5.20	5.30	1.9
2	Toluene	3.96	3.91	−1.3
3	Toluene	2.76	2.70	−2.2
4	Toluene	0.91	0.97	6.6
5	Ethanol	6.56	6.55	−0.2
6	Ethanol	4.37	4.42	1.1
7	Ethanol	2.93	2.99	2.0
8	Ethanol	1.46	1.43	−2.1
9	Dichloromethane	98.52	96.50	−2.1
10	Dichloromethane	23.30	23.25	−0.2
11	Dichloromethane	5.83	5.77	−1.0
12	Dichloromethane	34.95	36.06	3.2
13	Acetone	32.99	32.92	−0.2
14	Acetone	19.38	18.99	−2.0
15	Acetone	5.81	5.80	−0.2
16	Acetone	1.94	2.10	8.2

[a] Error was calculated by $\% = \frac{C_t - C_r}{C_r} \times 100$

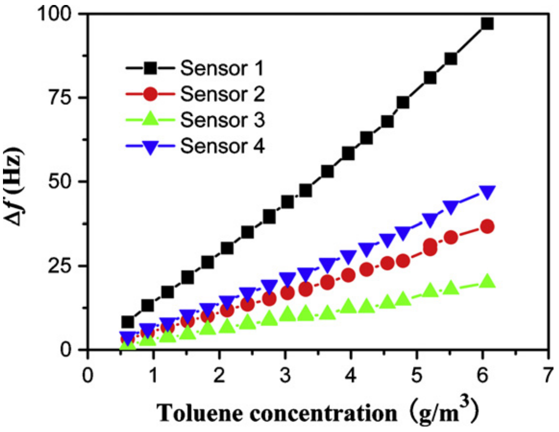

Fig. 7. Response characteristics of the array system towards various concentrations of toluene vapor. Sensor coating materials: sensor 1, C_{12}mimNTf$_2$; sensor 2, C_4mimPF$_6$; sensor 3, C_4mimCl; sensor 4, silicone oil II.

recognition process was very fast, within a second, and the training process took only 2 min.

3.4. Quantitative analysis of the sensor array system

Generally, QCM sensors respond linearly to the concentrations of analytes [18,19,31]. When an analyte has been identified by the neural network, the quantity analysis of chemicals can be carried out through the calibration curves of sensors responses versus chemical concentrations. In this work, all sensors responded proportionally to chemicals within the measured concentration ranges. They were 0.6–6.1 mg/L for toluene, 0.9–7.5 mg/L for ethanol, 2.8–117 mg/L for dichloromethane, and 0.7–38 mg/L for acetone. Fig. 7 shows the calibration curves of the QCM sensor array to different concentrations of toluene vapor for representative. The fitting equations towards toluene for each sensor in the array system are listed Table 2, with the correlation coefficient of $R^2 > 0.99$. Based on the four calibration curves (or parts of them), the concentration of samples in the testing group can be obtained by averaging the concentration values calculated from the fitting equations, which are shown in Table 3, together with all other testing samples. It showed that analytes could be quantified precisely, with the prediction errors lower than 8%. So, when an analyte was identified, its concentration could be estimated with the calibration curve-fitting method.

4. Conclusions

Ionic liquids, due to their unique properties of negligible vapor pressure, tunable selectivity, and high stability, are being widely used as sensitive coatings for chemical sensors. An array of quartz crystal microbalance, each quartz coated with a different ionic liquid or gas chromatographic stationary phase, was presented as a suitable sensor for identifying selected compounds of organic vapors, with rapid response speed. This paper presented that an array of quartz crystal microbalances plus a three-layer neural network was very effective to identify organic vapors. Results showed that it could recognize selected compounds correctly, i.e. the success rate of the system in identifying compounds was 100%. Once an analyte has been identified, quantitative analysis can be carried out due to the linear response characteristic of QCM sensors, with a prediction error lower than 8%.

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