

Finding the composition of gas mixtures by a phthalocyanine-coated QCM sensor array and an artificial neural network

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Abstract

This paper presents a system, which is made of an array of eight phthalocyanine-coated QCM sensors and an ANN to find the corresponding composition of a gas mixture. The digital data collected from the sensor responses were preprocessed by a sliding window algorithm, and then used to train a three layer ANN to determine the gas compositions. The system is tested with the following gas mixtures: (1) ethanol–acetone, (2) ethanol–trichloroethylene, (3) acetone–trichloroethylene. The success rate of the system in identifying the constituent component amounts is 84.5 and 94.3%. Similarly, overall average prediction error is 10.6%.

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1. Introduction

The analysis of a mixture of gases represents one of the main objectives of current research in the sensor field. The problem can be solved by either adopting highly selective sensors or using an array of sensors, which are scarcely selective, incorporated with a data-analysis technique. An array of quartz crystal microbalances (QCM) also called acoustic sensors are widely used for detecting the change of resonant frequency of each sensor as a function of gases. Over the past 15 years, a lot of important work has been done on developing gas recognition systems from its smell using pattern recognition algorithms, principal component analysis, neural networks and fuzzy logic systems [1,2].

In this work, an array of eight quartz crystal microbalances (QCMs) are used as sensor system to measure the mixed gas attributes. Firstly, signals from the sensor array in response to gas mixtures were preprocessed by a sliding window algorithm to obtain a valid data set. Then, this data is used to train a three layer artificial neural network (ANN), and later any digital data

from sensor array is applied to the ANN to find the corresponding composition of the gas mixture.

During the study, three different gas mixtures were analyzed: (1) ethanol and acetone, (2) ethanol and trichloroethylene, (3) acetone and trichloroethylene. Each experiment includes purging phase and application of gas mixture phase sequentially, which takes about 165 min for measurement of five different gas compositions. The gas compositions were obtained changing one of the constituent gas amount in five times, and holding the other's fixed (See Fig. 1)

2. Experimental

The principal of QCM sensors for smell sensing is based on the changes (called Δf) in the fundamental oscillation frequency to upon absorption of molecules from the gas phase. To a first approximation the frequency change Δf results from the increase in oscillating mass Δm [3]:

$$\Delta f = \frac{C_f f_0^2}{A} \Delta m$$

where, A is the area of sensitive layers, C_f is the mass sensitivity constant of the quartz crystal, f_0 fundamental resonance of the quartz crystals, Δm mass changes.

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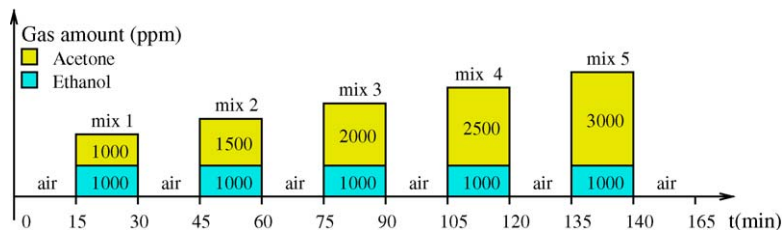


Fig. 1. Obtaining different mixtures by holding the amount of ethanol fixed and changing the amount of acetone. Figure shows experiment 3 in Table 1.

Fig. 2 shows a schematic view of the experimental setup. The piezoelectric crystals used were AT-Cut 10.000 MHz quartz crystal (ICM International Crystal Manufacturers Co., OK, USA) with gold-plated electrodes (diameter $\Phi = 3$ mm) on both sides mounted in a HC6/U holder. The instrumentation utilized consist of a Standard Laboratory Oscillator Circuit (ICM Co., OK, USA), power supply and frequency counter (Keithley programmable counter, model 776). The frequency changes of vibrating crystals were monitored directly by the frequency counter. The sensors and frequency counters are altogether called standard sensor cell (SSC), shown in Fig. 2.

Calibrated Mass Flow Controllers (MFC), (MKS Instruments Inc, USA) were used to control the flow rates of carrier gas and sample gas streams. Sensors were tested by isothermal gas exposure experiments at a constant operating temperature. The gas streams were generated from the cooled bubblers (saturation vapor pressures were calculated using Antoine equation [4,5]) with synthetic air as carrier gas and passed through stainless steel tubing in a water bath to adjust the gas temperature. The gas streams were diluted with pure synthetic air to adjust the desired analyte concentration with computer driven MFCs. Typical experiments consisted of repeated exposure to analyte gas and subsequent purging with pure air to reset the base-line. The sensor data were recorded every 3–4 s at a constant of 200 ml/min.

Table 1 shows compositions of mixtures of ethanol, trichloroethylene and acetone used in this work. Some of the data shown in the Table 1 are used for training the artificial

neural network and the rest is used for the determination of the success rate. Those without the “t” sign were used for training of the network.

The data logger records the frequency differences to 10 MHz of each sensor in the SSC every 3–4 s in the system shown in Fig. 1. This makes a great amount of raw data for each experiment. A computer is used to store this data and process it later as off-line. Fig. 3 shows the sensor-3 response drawn from collected data for acetone–trichloroethylene mixture. Upper ripples of pulse like train in the figure shows the sensor-3 responses for alternative gas compositions; lower ripples show sensor cleaning reactions (called purging phase). The data collection is a continuous process during both measurement and sensor cleaning.

When a gas mixture is introduced to the sensor chamber, each sensor responds in a characteristic way by drifting from its center frequency (10 MHz for our sensors). This drift amount is different for each sensor even in the purging phase, and called as “base line”. Since coated with different compositions, each sensor has a different base line: for example, the sensor-3 has a baseline around 2340 Hz Δf amounts shown in all the figures are distance to the 10 MHz center frequencies of the sensor crystals.

The data shown in Fig. 3 is spiky and includes purging phases, which must be removed to obtain valid data. The spikes are rounded using a sliding window algorithm with a window size of 50. The sliding window is an iterative approach, and holds 50 samples at a time from a sequence of interest. The sequence is made up with sensor data for our experiments.

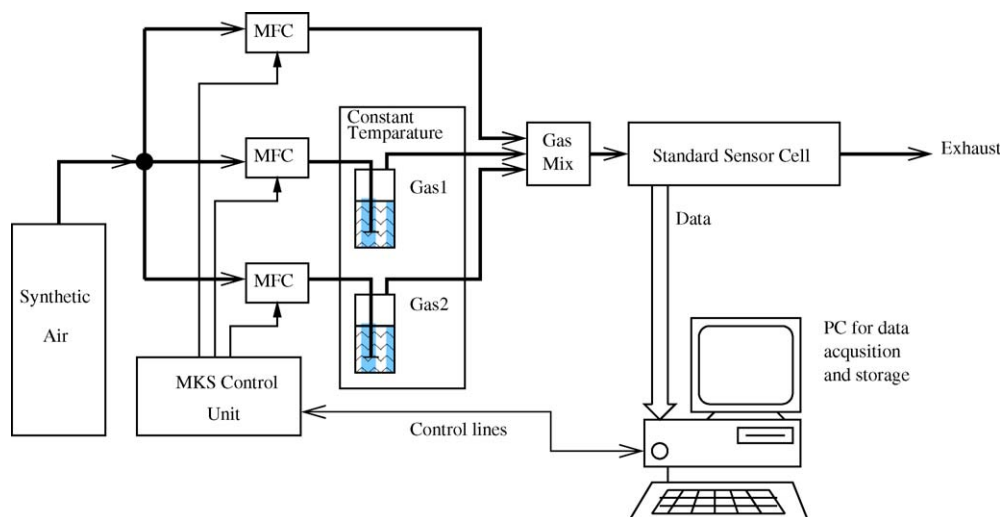


Fig. 2. Schematic view of the experimental setup.

Table 1

Compositions of three different gas combinations: (i) acetone and ethanol, (ii) acetone and trichloroethylene and (iii) ethanol and trichloroethylene

Experiment		Gas composition ((i) acetone (ppm):ethanol (ppm), (ii) acetone (ppm):trichloroethylene (ppm))				
(i)	(ii)					
1	6	250:1000	250:1500	250:2000	250:2500	250:3000
2	7	500:1000 ^f	500:1500	500:2000	500:2500 ^f	500:3000
3	8	1000:1000	1000:1500	1000:2000	1000:2500	1000:3000
4	9	2000:1000 ^f	2000:1500	2000:2000	2000:2500 ^f	2000:3000
5	10	3000:1000	3000:1500	3000:2000	3000:2500	3000:3000
(iii)	Gas composition ((iii) ethanol (ppm):trichloroethylene (ppm))					
11	250:550	250:1650	250:2200	250:2750	250:3300	
12	500:550 ^f	500:1650	500:2200 ^f	500:2750	500:3300	
13	1000:550	1000:1650	1000:2200	1000:2750	1000:3300	
14	2000:550 ^f	2000:1650	2000:2200 ^f	2000:2750	2000:3300	
15	3000:550	3000:1650	3000:2200	3000:2750	3000:3300	

While the window slides from left to the right hand side over the sequence, it calculates the moving average of the samples except purging phases. The Fig. 3(b) shows the filtered sensor responses.

In the next step, the maximum of each pulse like train is calculated and this maximum is assigned as representative for associated mixture. This is because the most real measurement occurs when the sensor is saturated, or putting it another way, actual Δf samples must be taken when the upper curve starts becoming horizontal. Hence, we picked the maximum numbers from filtered graphs as a representative Δf measurement for a composition. The great amount of data is reduced to five for each sensor during one experiment. This calculated maximums are shown with vertical lines in the Fig. 3(b).

Once the representative Δf s are obtained both for each sensor and each gas composition, then a surface is plotted for every sensor; putting ppm amounts of one constituent gas in x-axis, and the other in y-axis, and Δf in z-axis. An example plot is shown in Fig. 4. In fact, these figures contain behavioral information about the sensor responses to decide whether sensor outputs are linear or not, according to constituent gas amounts. It is seen that the surfaces are not linear and cannot be parameterized in any way.

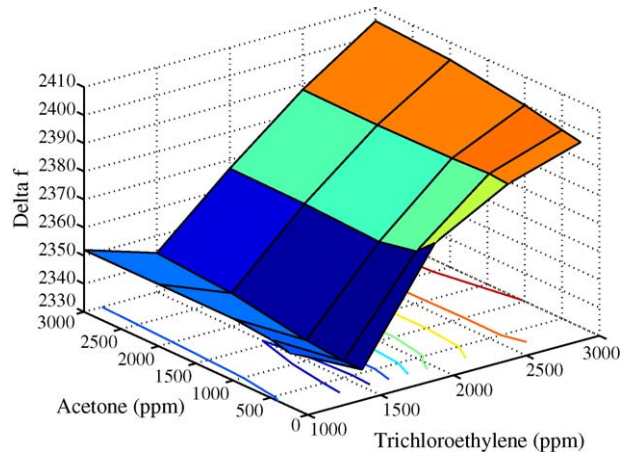


Fig. 4. The sensor-3 output is plotted according to different gas mixtures and different compositions.

3. Results and discussion

Since artificial neural networks are non-parametric methods and do not require linearity of sensor responses, a back propagation neural network was used composed one hidden layer

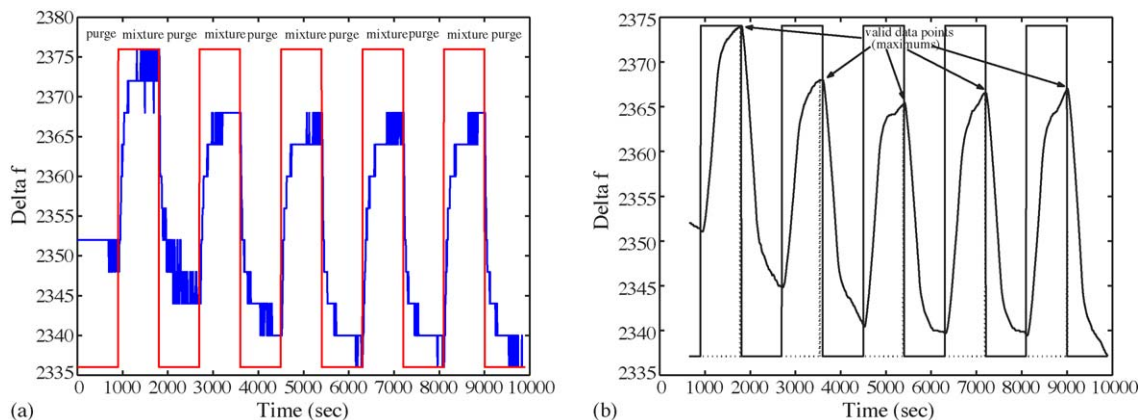


Fig. 3. (a) Sensor-3 responses for variable concentration of acetone and trichloroethylene and (b) the data is processed (filtered) with sliding window algorithm.

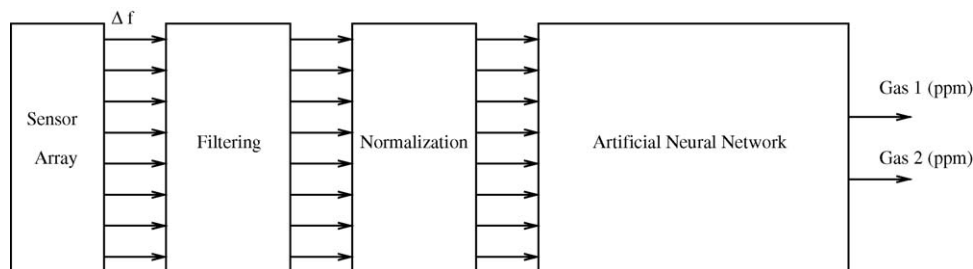


Fig. 5. Data processing system.

Table 2
Test results

Gases in a mixture (ppm)			Predictions (ppm)		Prediction error	
Acetone	Ethanol	Trichloroethylene	Gas 1	Gas 2	Gas 1 (%)	Gas 2 (%)
–	500	550	590.16	562.22	12.4	7.3
500	1000	–	604.80	1037.15	20.1	3.7
500	–	1000	598.60	1021.90	19.7	2.2
–	500	2200	552.72	2219.80	10.5	0.9
500	2500	–	518.26	2555.73	3.6	2.2
500	–	2500	580.06	2623.80	16.0	4.9
–	2000	550	2306.32	596.26	15.3	8.4
2000	1000	–	2676.28	1307.98	33.8	30.8
2000	–	1000	2245.40	1009.16	12.3	0.9
–	2000	2200	2269.60	2213.80	13.5	0.6
2000	2500	–	2410.42	2655.66	20.5	6.2
2000	–	2500	2173.00	2519.40	8.6	0.8

First three columns show the actual amounts; second two columns show the ANN predictions and the last two columns show the prediction errors.

to discriminate between different samples [6,7]. The number of neurons in the input, hidden and the output layers are 8, 30 and 2, respectively [8]. Eight neuron inputs in the first layer are tied to filtered sensor array outputs, and two neurons in the last stage are connected to system output that show gas concentrations. A back propagation neural network is preferred out of many neural network model because it was simple, fast and very good on prediction [9,10,12].

Training of the neural network was performed with 84% of the whole data. The remaining 16% of the data was used for testing the success rate of the system. The selected training data is marked with t shown in Table 1. The recorded Δf values were somewhere in between 2340–2408 Hz, however, the level of the inputs to an ANN should be arranged between 0 and 1. Hence, a normalization process for each sensor response was performed by dividing whole data with the maximum Δf . Then, the normalized values are used to train and test the system. The ANN is implemented using software developed in the MATLAB 6.5 environment (Math Works, USA) [11]. Fig. 5 shows data processing system, which includes normalization and ANN parts used in this work.

We first used “gradient descent with momentum” learning algorithm provided in MATLAB for training the ANN. The training process was completed quickly, however, overall prediction errors were very high: 39.1% for gas 1, 9.1% for gas 2 and 24.1% overall. Then, we tested several other learning algorithms, and the best results were obtained with “basic gradient descent” algorithm. The parameters were 22,000,000 epoch and

a performance goal 10^{-6} . The training process took approximately 2.5 days.

Then, the average prediction errors dropped down to 15.5% for gas 1, 5.7% for gas 2 and 10.6% overall. The test results are shown in Table 2. The average prediction error for gas 1 amount is higher than expected, however, the results could be better if the experiments were done with linear increments in gas amounts. Another way to increase success rate is to use more training data.

However, more training data require more experiment, and as it is mentioned in Section 2, each experiment takes 165 min producing approximately 19,800 integer data with 4 s sampling rate. This amount of data must be filtered and reduced to 40 meaningful data for training the ANN. To increase success rate both linear increment in gas amounts and training the ANN with more data should be experimented and tested in the future.

4. Conclusion

We have demonstrated that finding the compositions of gas mixtures using an array of QCM sensors and ANN is possible. The success rate in identifying the constituent component amounts of the approach 84.5% for gas 1, 94.3% for gas 2. Similarly, average prediction errors are 15.5% for gas 1, 5.7% for gas 2 and 10.6% overall. The sensor array and the method developed to process the sensor data in this work is promising for future experiments.

Although the system developed in this work is applicable only when a gas mixture belongs to the certain specified categories, however, it can be expanded toward a successful identification of gas species and determination of its concentration in a gas mixture by using different kinds of sensor arrays.

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Biographies

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