Electronic Nose using Gas Chromatography Column and Quartz Crystal Microbalance

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Abstrak

Hidung elektronik umumnya terdiri dari sebuah deret sensor kimia yang berbeda karakteristinya seperti quartz crystal microbalance (QCM) yang dikombinasikan dengan algoritma pengenal pola seperti jaringan syaraf tiruan. Karena pemrosesan dilakukan secara paralel, sistim ini memerlukan sejumlah besar sensor dan rangkaian yang dapat menimbulkan permasalahan cakap silang antar kanal. Pada penelitian ini, sebuah sistim pengenal odor yang baru telah dikembangkan yang mengkombinasikan antara metoda gas chromatography (GC) dan hidung elektronik. Sistem ini terdiri dari kolom GC dan sebuah sensor QCM 10-MHz yang menghasilkan pola yang khas untuk setiap odor dalam ranah waktu. Beberapa odor senyawa organik digunakan untuk mengevaluasi selektivitas sistem tersebut. Metoda analisa komponen utama digunakan untuk visualisasi taraf klasifikasi setiap odor pada ruang dua dimensi. Sistem ini dapat membedakan pelarut organik termasuk senyawa yang berbeda kelas (senyawa aromatik terhadap alkohol), begitu pula senyawa dalam kelas yang sama (methanol terhadap etanol) dan juga bahan bakar (premium terhadap pertamax). Jaringan syaraf tiruan dapat dilatih untuk mengenali jenis odor yang diujikan dalam eksperimen ini dengan taraf identifikasi 85%. Untuk itu sistem ini dapat menggantikan hidung manusia, terutama untuk evaluasi odor yang beracun.

Kata kunci: jaringan syaraf tiruan, kolom GC, pergeseran frekuensi resonansi, sensor QCM

Abstract

The conventional electronic nose usually consists of an array of dissimilar chemical sensors such as quartz crystal microbalance (QCM) combined with pattern recognition algorithm such as Neural network. Because of parallel processing, the system needs a huge number of sensors and circuits which may emerge complexity and inter-channel crosstalk problems. In this research, a new type of odor identification which combines between gas chromatography (GC) and electronic nose methods has been developed. The system consists of a GC column and a 10-MHz quartz crystal microbalance sensor producing a unique pattern for an odor in time domain. This method offers advantages of substantially reduced size, interferences and power consumption in comparison to existing odor identification system. Several odors of organic compounds were introduced to evaluate the selectivity of the system. Principle component analysis method was used to visualize the classification of each odor in two-dimensional space. This system could resolve common organic solvents, including molecules of different classes (aromatic from alcohols) as well as those within a particular class (methanol from ethanol) and also fuels (premium from pertamax). The neural network can be taught to recognize the odors tested in the experiment with identification rate of 85 %. It is therefore the system may take the place of human nose, especially for poisonous odor evaluations.

Keywords: GC column, neural network, QCM sensor, resonant frequency shift

1. Introduction

Odor is elicited by chemicals in a gas phase which are detected via olfaction producing recognizable smells. Odor is considered an important environmental pollution issue in every country. Inorganic and organic chemical plants as well as refineries are examples of the main industrial odor sources. In the field of agriculture and biological processes, waste-water treatment plants, feed processing plants, meat rendering plants and composting facilities are regarded as odor sources in the environment. Odor is one or more volatile molecules having a molecular weight of about between 30 and 300 g/mole in air [1]

Gas chromatography (GC) is an analytical technique for separating compounds based primarily on their volatilities. This method provides both qualitative and quantitative information

for individual compounds present in a sample. Compounds move through a GC column as gases, either because the compounds are normally gases or they can be heated and vaporized into a gaseous state. The compounds partition between a stationary phase, which can be either solid or liquid, and a mobile phase (gas). The differential partitioning into the stationary phase allows the compounds to be separated in time and space. The Flame Ionization Detector (FID) is a mass sensitive detector, the output of which is directly proportional to the ratio of the compound's carbon mass to the total compound mass. In the case of odor emissions analysis, the flame temperature was maintained at 225 ℃. Gas pressure values were 400 hPa for air and 700 hPa for hydrogen. Thus, the sample is destroyed in the flame [2].

An alternative approach to chemical sensing is closer conceptually to a design widely proposed for the mammalian sense of olfaction called Electronic Nose. An array of different sensors (such as Quartz Crystal Microbalance or QCM array) is used to respond to a number of different chemical odors in room temperature [3], [4], [5]. The sample is not destroyed in the sensor chamber. Although in this design, identification of an odor cannot be accomplished from the response of a single sensor element, a distinct pattern of responses produced over the collection of sensors in the array could provide a fingerprint that would allow classification and identification of the odor by pattern recognition algorithm (such as Neural Network) [6], [7], [8], [9]. Because of parallel processing, the system needs a huge number of sensors and circuits which may emerge complexity and inter-channel crosstalk problems [10].

A new type of odor identification which combines between GC and Electronic Nose methods is reported here. The system consists of two parts: one section uses nitrogen gas, GC column and QCM sensor, and the other section uses Neural Network pattern recognition methods. Each odor presented to the sensing system will produce a signature or "fingerprints". Presenting many different odors to the sensor yields a database of fingerprints, which the pattern recognition system uses to recognize automatically each odor.

The GC column is the heart of the system. It consists of a stationary phase which greatly influences the separation of the compounds. The structure of the stationary phase affects the amount of time the compounds take to move through the column. Typical stationary phases are large molecular weight polysiloxane, polyethylene glycol, or polyester polymers [11]. The compounds pass through a column with different velocities and thus individual chemicals exit the column at specific times, as shown in Figure 1.
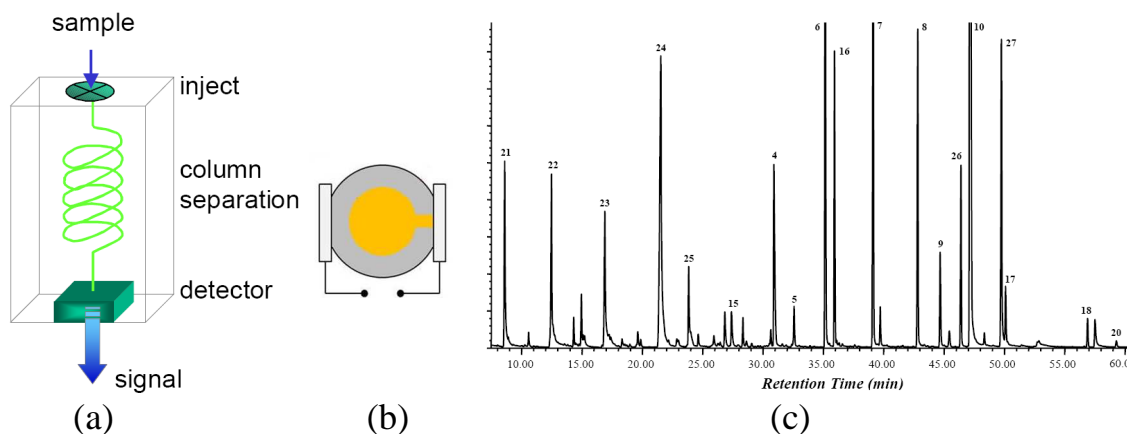

Figure 1. (a) GC column (b) QCM sensor and (c) chromatogram of the sample.

As the samples exit the column, they are detected and quantified by a solid state detector of QCM. The material has long been used in electronic equipment for frequency controlling. When an oscillating potential is applied at a frequency near the resonant frequency of a piezoelectric crystal, a stable oscillating circuit is formed. Adding mass to the surface of acoustic resonator changes its resonant frequencies [12]. The shift in resonant frequency (Δf) is

proportional to the original resonant frequency of crystal (f) squared and the change in mass (ΔM) on the crystal surface [13], expressed by

$$\Delta f = -\left(\frac{2f^2}{\rho_{SiO_2} vA} \right) \Delta M \tag{1}$$

where ρ_{SiO2} is density of the crystal and v is acoustic speed in crystal.

2. Research Method

Figure 2 depicts a schematic of the experimental setup. The odor generation system consisted of a gas stream module and a three-way valve. The gas stream module included a reference module, dry ultra high purity nitrogen (99.999%) flowing at 50 mL/min that served to establish the baseline response and the odor carrier. The sample was transferred into a packed column with 3.2 mm inner diameter and 1.6 m length. The column contains 60/80 mesh Shincarbona support material coated with 5 % Thermon-3000. The column temperature was maintained at 40°C. A 10 MHz-QCM sensor was installed in a 0.3 mL sensor chamber and connected to 5V-CMOS oscillator circuit. The resonant frequency shift of the sensor was monitored before and following exposure to the odors. Every 2 seconds, the frequency response was measured using a 24-bit frequency counter implemented in FPGA Spartan-3E and Xilinx ISE 9.1i software. The 200 points of the frequency shifts are sent to a personal computer via USB communication.
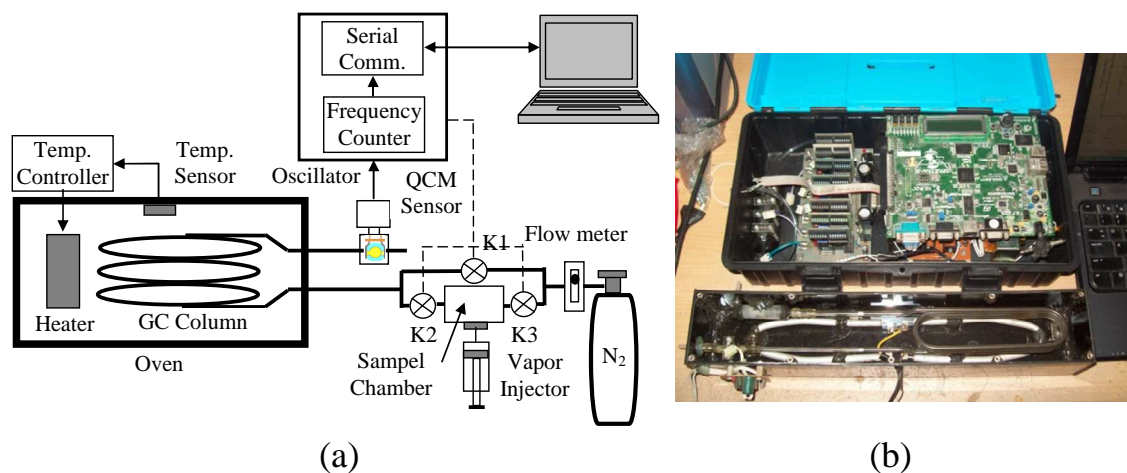

(a)   (b)

Figure 2. (a) Block Diagram and (b) Photo setup of the apparatus used for the experiments.

An organic compound of n-hexane with different sample volume of odor was injected to evaluate its sensitivity. Several compounds with various physical and chemical properties are introduced to evaluate its selectivity. The samples were organic solvents (such as benzene, n-hexane, ethanol, methanol, ethyl acetate, acetone, and acetonitrile), fuels (such as premium, pertamax, pertamax plus, spiritus burner, butane and octane booster), fragrances (such as rose, and melon), insecticides and fresh air.

The measurement data are two hundred-dimensional, since two hundred points in time domain are used as an odor signature. The mapping method is required to find a low dimensional vector *z* that preserves most of the information in the original feature vector *x*. In the case of dimensionality reduction techniques belonging to the linear transformation family, the mapping is given by

$$z = T\,x \tag{2}$$

Principal Components Analysis (PCA) is a linear transformation that preserves as much data variance as possible. PCA chooses T that minimizes the mean squared distance between original data and those reconstructed from reduced data. It is shown that:

$$T = U\Lambda^{-1/2} \tag{3}$$

where U and Λ are, respectively, the eigenvectors matrix and the diagonal eigen values matrix of the data covariance matrix [14]. PCA was very widely used for gas sensors applications, especially in electronic nose system [15], [16], [17], [18], [19].

The multi-layer perceptron is probably the most widely used architecture for practical applications of Neural Networks. In most cases, the network consists of two layers of adaptive weights with full connectivity between inputs and hidden units, and between hidden units and outputs. The network is able to learn arbitrarily complex non linear regressions by adjusting the weights w in the network using an appropriate optimization algorithm. One way to generalize the linear discriminant function, so as to permit a much larger range of possible decision boundaries, is to transform the input vector x using a set of predefined nonlinear basis function Φ and represent the output as a linear combination of this function:

$$y_k = \sum_{j=1}^{M} w_{kj} x_j + wb_k \tag{4}$$

The basis function can be given by logistic activation function:

$$\Phi_k = \frac{1}{1 + e^{-y_k}} \tag{5}$$

The network is trained to minimize the entropy cost function. The parameters are learnt from data using generally a gradient descent technique known as a back-propagation of errors [10]. The three-layer neural network was applied to the system to recognize odors automatically using back propagation algorithm trained by gradient descent method with adaptive learning rate, shown in Figure 3. The number of input nodes was two hundred corresponds to the number of points of the retention time, and the number of output neurons was sixteen equal to that of the sort of odors. The number of hidden neurons was a hundred to accelerate and improve the convergence in training phase.
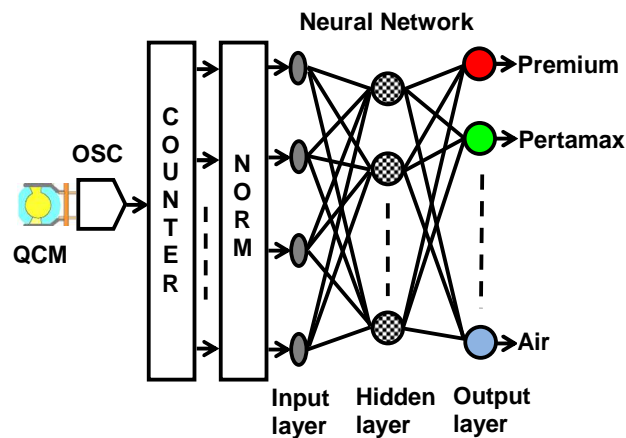

Figure 3. The electronic signal conditioning combined with Neural Network pattern recognition.

3. Results and Discussion

Figure 4(a) shows a typical response to an odor with different concentration. The area of sensor response is proportional to the odor concentration. Figure 4(b) shows a response to mixture odors. Due to their different polarities, each odor has different retention time. Since the concentration for an unknown odor is also unknown, the identification must be based on signature patterns, and not on the concentration dependent amplitudes. Therefore the concentration information was removed by normalizing each pattern by dividing of each maximum peak of the sensor response, shown in Figure 5. The radar patterns of 5 mL volume of each odor are shown in Figure 6.
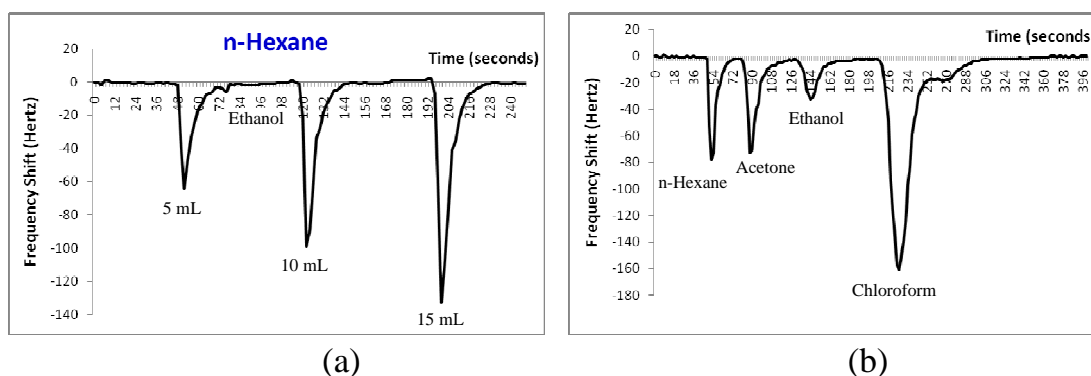

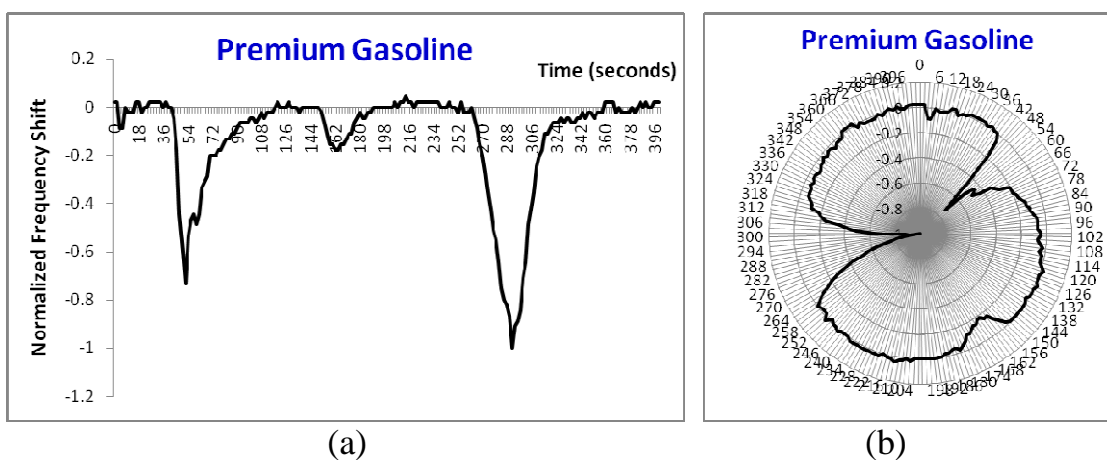Figure 4. Typical time responses for (a) different concentration and (b) mixture vodor.

Figure 5. The concentration information (a) Normalized and (b) polar patterns.

Scattering diagram by PCA with two of the most significant components is shown in Figure 7. The diagram shows that the aromatic hydrocarbon (such as benzene) and alcohol (such as ethanol and methanol) are well separated because of the different class of their polarities (benzene and ethanol are polar and non-polar, respectively). It is interesting results that between ethanol and methanol could be separated perfectly although they have similar polarities (the dipole moments of ethanol and methanol are 1.69 and 1.70 Debye, respectively) as well as between Premium and Pertamax gasoline (the octane number of Premium and Pertamax are 88 and 92, respectively). However, the diagram also shows that several odors are not separated perfectly. Both ethanol and spiritus burner have similar class because the spirit fuel is ethanol denatured with $c.5\%$ methanol [20]. Several insecticides have similar responses resulting overlapping classes of each other.
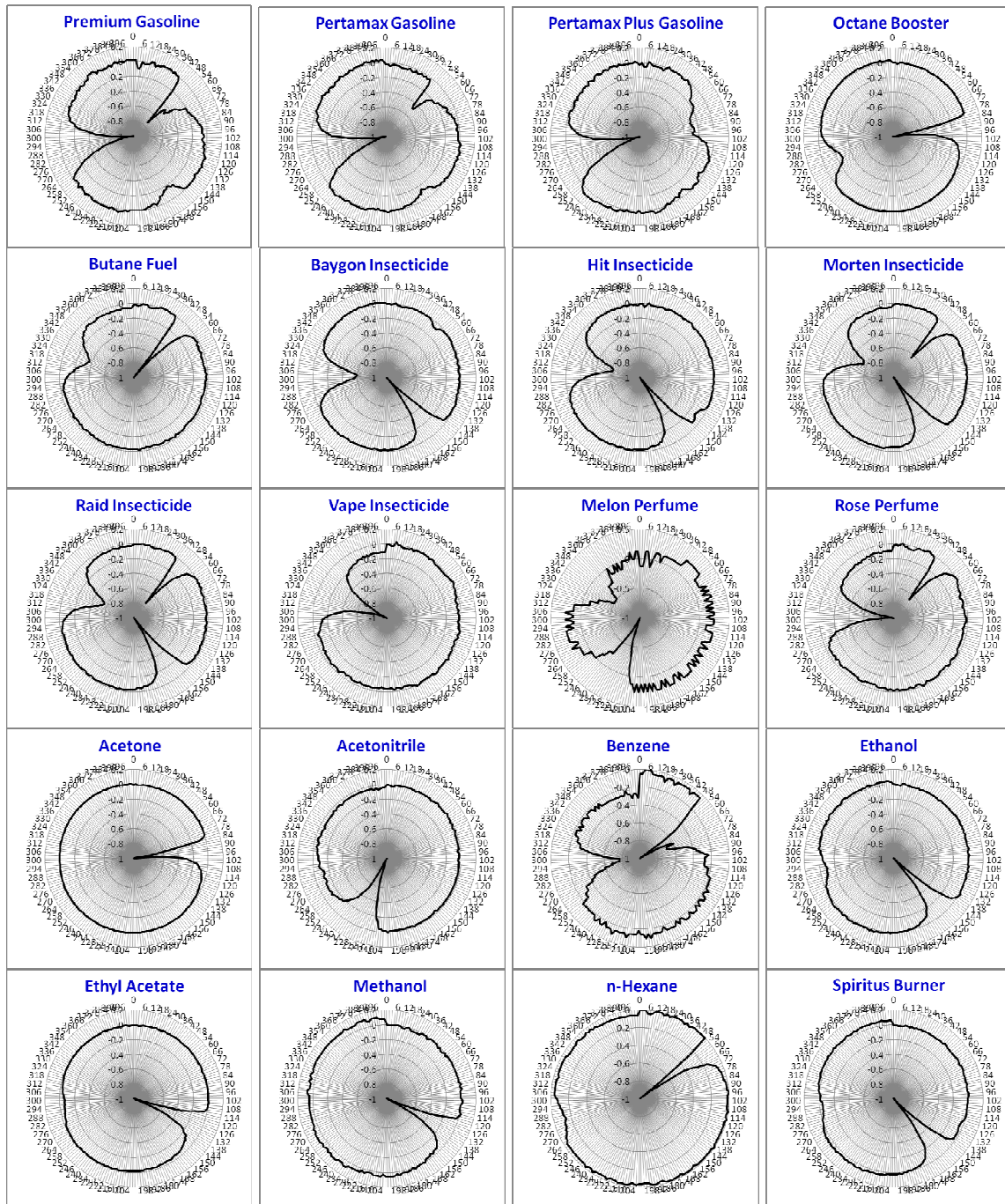
Figure 6. Radar patterns of odors.

The multilayer neural network was applied to the sensor to recognize odors automatically. Both learning rate and moment constant were empirically determined to be 0.01. In the training phase, 80 data sets were input to the Neural Network. The network can be taught to discriminate each odor with the error rate of 1 % taking 24.657 epochs. In the running phase, the others 80 data sets were fed into the Neural Network. The network can recognize all odors tested in the experiment with the identification rate of 85 %, shown in Figure 8.
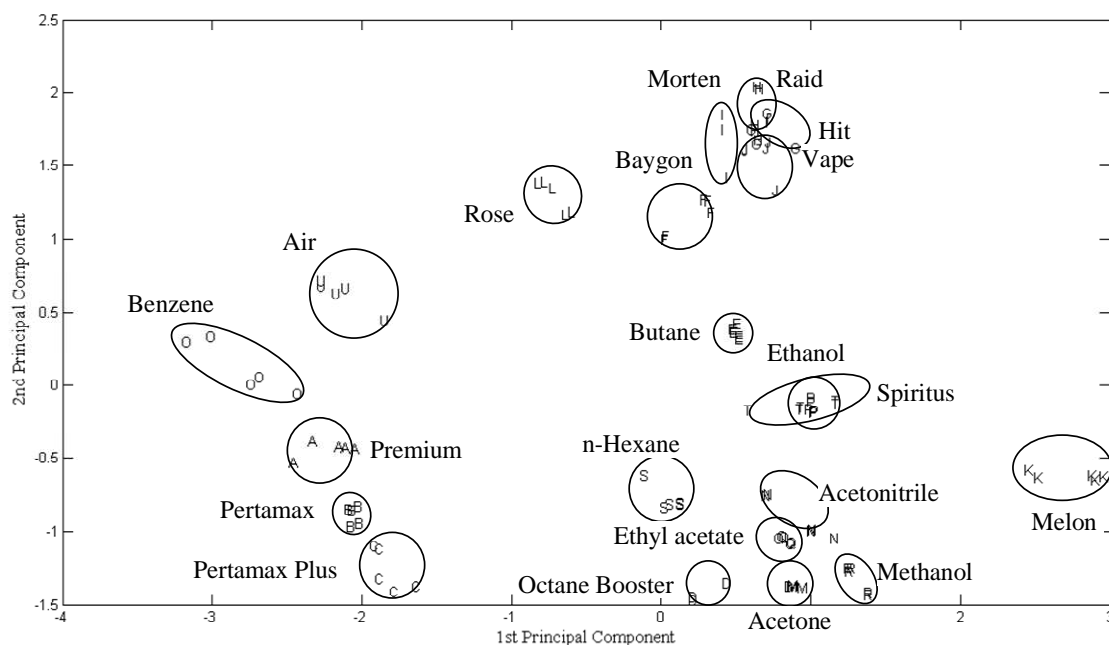
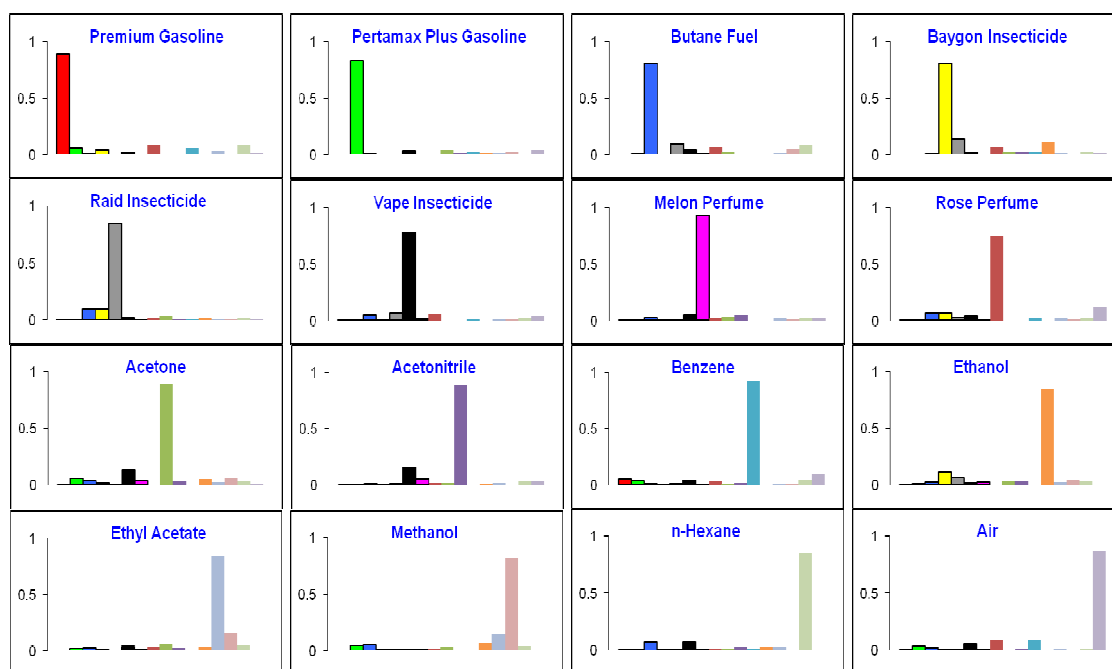Figure 7. The classification of each odor visualized by PCA method.

Figure 8. Responses of the neural network to each odor in the running phase.

4. Conclusion

It has been constructed an Electronic Nose composed of a GC Column, a QCM and a Neural Network pattern recognition. The system produces a unique pattern for an odor in time domain of 400 seconds. Sixteen odors could be classified separately by PCA method. The neural network can be taught to recognize all the odors tested in the experiment using the back propagation algorithm with identification rate of 85 %. For the future works, the time consuming,

however, is need to be reduced with the shorter column without decreasing its selectivity. The proper sensitive chemical material must be coated on the QCM sensor to enhance its sensitivity.

Acknowledgement

References

[1]   Yuwono A, Lammers PS. Odor Pollution in the Environment and the Detection Instrumentation. *CIGR Journal of Scientific Research and Development*. 2004; IV: 1- 33.
[2]   Knothe G, Kenar JA. Determination of the fatty acid profile by 1H-NMR spectroscopy. *Eur. J. Lipid Sci. Technol.* 2004; 106: 88–96.
[3]   Abe T,Higuchi M. A Monolithic QCM Array Designed for Mounting on a Flow Cell. *IEEE Sensors Journal*. 2011; 11(1): 86-90.
[4]   Abe T, Li X. Dual-Channel Quartz-Crystal Microbalance for Sensing Under UV Radiation. *IEEE Sensors Journal*. 2007; 7(3): 321-322.
[5]   Werff MJ, Yuan YJ, Hirst ER, Xu WL, Chen H, Bronlund JE. Quartz Crystal Microbalance Induced Bond Rupture Sensing for Medical Diagnostics. *IEEE Sensors Journal*. 2007; 7(5): 762-769.
[6]   Kumar R, Das RR, Mishra VN, Dwivedi R. A Neuro-Fuzzy Classifier-Cum-Quantifier for Analysis of Alcohols and Alcoholic Beverages Using Responses of Thick-Film Tin Oxide Gas Sensor Array. *IEEE Sensors Journal*. 2010; 10(9): 1461-1468.
[7]   Lozano J, Santos JP, Aleixandre M, Sayago I, Gutiérrez J, Horrillo MC. Identification of Typical Wine Aromas by Means of an Electronic Nose. *IEEE Sensors Journal*. 2006; 6(1): 173-178.
[8]   Hoda S, Zohdy AA, Allen JN, Ewing RL. *Spiking Neural Network E-NOSE Classifier Chip*. Aerospace and Electronics Conference (NAECON), Proceedings of the IEEE. Fairborn, OH. 2010: 374-378.
[9]   Jamal M, Khan MR, Imam SA, Jamal A. *Artificial Neural Network Based E-Nose And Their Analytical Applications In Various Field*. Control Automation Robotics & Vision (ICARCV), Proceedings of the IEEE. Singapore. 2010: 691 – 698.
[10] Manoosingh LL. Design of a Chemical Agent Detector Based on Polymer Coated Surface Acoustic Wave (SAW) Resonator Technology. PhD Thesis. South Florida: University of South Florida; 2004.
[11] Eiceman GA. Gas Chromatography. *Anal. Chem.* 2006; 78: 3985-3996.
[12] Liu N, Yang J, Chen W. Effects of Mass Layer Nonuniformity on a Quartz-Crystal Microbalance. *IEEE Sensors Journal*. 2011; 11(4): 934-938.
[13] Jaruwongrungsee K, Maturos T, Sritongkum P. Analysis of Quartz Crystal Microbalance Sensor Array with Circular Flow Chamber. *International Journal of Applied Biomedical Engineering*. 2009; 2(2): 50-54.
[14] Bermak A, Belhouari SB, Shi M, Martinez D. Pattern Recognition Techniques for Odor Discrimination in Gas Sensor Array. *Encyclopedia of Sensors*. 2006; X: 1-17.
[15] Rivai M. Pengaruh Principle Component Analysis Terhadap Tingkat Identifikasi Neural Network Pada Sistim Sensor Gas. *Telkomnika*. 2007; 5(3): 159-166.
[16] Tran VH, Chan HP, Thurston M, Jackson P, Lewis C, Yates D, Bell G, Thomas PS. Breath Analysis of Lung Cancer Patients Using an Electronic Nose Detection System. *IEEE Sensors Journal*. 2010; 10(9): 1514-1518.
[17] Brezmes J, Fructuoso LL, Llobet E, Vilanova X, Recasens I, Orts J, Saiz G, Correig X. Evaluation of an Electronic Nose to Assess Fruit Ripeness. *IEEE Sensors Journal*. 2005; 5(1): 97-108.
[18] Brezmes J, Cabré P, Rojo S, Llobet E, Vilanova X, Correig X. Discrimination Between Different Samples of Olive Oil Using Variable Selection Techniques and Modified Fuzzy Artmap Neural Networks. *IEEE Sensors Journal*. 2005; 5(3): 463-470.
[19] Kashwan KR, Bhuyan M. *Robust Electronic-Nose System with Temperature and Humidity Drift Compensation for Tea and Spice Flavour Discrimination*. IEEE Conference-Asian Conference on Sensors And International Conference on New Techniques in Pharmaceutical and Biomedical Research. Kuala Lumpur. 2005: 154-158.
[20] Lawecki R. Material Safety Data Sheet Methylated Spirits. New Shouth Wales :Trojan Hospitality PTY Limited. 2004: 1-5.