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Chemically Coated Quartz Crystal Sensors for Fragrance Recognition

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Abstract— Detection and identification of fragrances or odorous compounds that can readily evaporate at room temperature, has gained considerable attention. An array of quartz crystal sensors coated with different chemical materials was employed in the present study to detect the fragrances. Due to the differing vapor-chemical material partitioning coefficients, the sensor array produces a fingerprint of normalized frequency shifts for each fragrance. Principle Component Analysis method was used to visualize the classification of each fragrance in two-dimensional space. Back propagation neural network was used to distinguish the species of fragrances implemented in the personal computer. All-digital interface was implemented on the Field Programmable Gate Array. The results showed that the sensor array could produce a specific response pattern for each fragrance and the neural network can be taught to recognize seven fragrances of perfume and four fragrances of tea leafs.

Index Terms— fragrance, neural network, normalized frequency shift, principle component analysis, quartz crystal sensor, recognition

1 Introduction

Fragrance-the state or quality of having a pleasant odor-is used not only in perfumes but in a wide range of consumer products from household cleaners and soaps to food and beverage industries. Perfumes originally were made of natural materials, whereas the modern perfumery industry makes extensive use of synthetic chemicals. Nowadays, it is estimated that out of the 3000 fragrance ingredients available to the perfumers, fewer than 5% come directly from natural sources [1].

The instrument of Electronic Nose is designed to detect and identify among complex odors using a sensor array. The sensor array consists of a number of non-specific sensors coated with a variety of odor-sensitive materials. An odor stimulus produces a characteristic fingerprint from this sensor array. Patterns or fingerprints from known odors are used to construct a database of a pattern recognition system so that unknown odors can be classified. A major problem in odorous vapor identification is the substantial similarity of patterns obtained for different vapors. This phenomenon is attributed to low selectivity of the sensing system [2].

Quartz crystal, composed of Silicon and Oxygen (SiO_2), exhibits piezoelectric properties. It generates an electrical potential when a pressure is applied on the surfaces of the quartz crystal. Inversely, when an electrical potential is applied to the surfaces of a quartz crystal, mechanical deformation or vibration is generated. These vibrations occur at a frequency determined by the physical dimension of the piece of quartz crystal. Piezoelectric quartz crystal is a material with very sensitive response for the changes in mass. Its sensing mechanism is based on the shift in the quartz crystal resonant frequency due to the adsorption of gas molecules onto the crystal's surface. For sensing applications, a sensitive sensing film is cast on the surface of the quartz crystals. The absorption rate is affected by the size and polarity of both the vapor and the sensing film [2]. 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, expressed by the Sauerbrey equation:

$$\Delta f = -\left(\frac{2f^2}{\rho v A}\right)\Delta M \qquad (1)$$

where ρ is density of the crystal and v is acoustic speed in crystal.

It is well known that the use of a gas sensor array together with pattern recognition analysis offers advantages in the identification of samples, because of the low selectivity of a sensor array. Principal Component Analysis (PCA), a well-known technology of statistics, is useful in selecting the classic independents of all materials. The method can distinguish the different species by taking a view of the profile discrimination with the responses of several channels in a plot [3], [4], [5], [6], [7]. PCA contains an orthogonalization procedure such as singular-value decomposition that decomposes the primary data matrix by projecting the multi-dimensional dataset onto new coordinate base formed by the orthogonal directions with data maximum variance. The data matrix consists of a number of experiments, each consisting of a number of variables. The eigenvectors of the data matrix are called principal components and they are uncorrelated among them. The magnitude of each eigenvector is expressed by its own eigen value, which gives a measure of the variance related to that principal component. The variance is related to the quantity of information which is supplied by the component. By elimination of the less important eigenvectors, it is possible to achieve fewer vectors without any considerable information loss. During data processing, the results are transformed in a plane or in a space

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of the first two or three eigenvectors. The coordinates of the data in the new base are called their score. The scores plot is usually used for the classification of the data clusters.

Pattern recognition techniques based on artificial neural network approaches were very widely used for gas sensors applications [8],[9],[10],[11],[12]. The multi-layer perceptron architecture is the most widely used for practical applications of neural networks [13]. 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. 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:

$$y_k = \sum_{j=1}^{M} w_{kj} x_j + w_{k0} \tag{2}$$

The basis function can be given by logistic activation function:

$$\Phi_k = \frac{1}{1+e^{-y_k}} \tag{3}$$

The network is able to learn arbitrarily complex non linear regressions by adjusting the weights in the network to minimize the entropy cost function using an appropriate optimization algorithm. Back propagation neural network is the most popular algorithm used in the electronic nose technology [13]. This method is a supervised learning algorithm based on the generalized delta rule, usually using gradient descent for minimizing the total squared output error between the desired and the actual net outputs. The performance of back propagation neural network is dependent on several factors, e.g., the number of hidden layers, learning rate, momentum and training data [14].

In this paper, quantitative and qualitative analysis of the fragrances was done by using quartz crystal microbalance sensor array. PCA was used to visualize the classification of each fragrances detected by the sensor array, while three layer neural network structure with back propagation method was employed in online identification.

2 Method

The materials of the sensors were AT-cut spherical quartz crystals, with a basic resonant frequency of 10 MHz and were provided with gold electrodes on both sides. The crystals were coated with the prepared chemically materials of squalane, apiezone-L, ethyl cellulose, silicone OV-17, silicone OV-25 and polyethylene glycol PEG-1540 using spray method. The sensors were mounted in a sealed test chamber, shown in figure 1.

The fragrance generation system consisted of calibrated mass flow controllers, conventional gas bubblers containing the liquid sample, and a pair of three-way electronic valves. The sample vapor was generated by flowing of 50 mL/min carrier gas of dry nitrogen (N_2), through the bubbler within forty seconds. The electronic valves were controlled by computer to automatically expose the sensor array to various sorts of fragrances. The frequency response was monitored using a multi channel frequency counter interfaced to personal computer via Universal Serial Bus (USB) communication. All-digital interface was implemented on the Field Programmable Gate Array (FPGA) Xilinx XC3S500E Spartan-3E and software Xilinx ISE Webpack 9.2i, shown in figure 2. Real time data were displayed and analyzed to obtain resonant frequency shifts between before and after odor exposure. All experiments were performed at the temperature of 32 °C.

The sensor array was exposed to seven fragrances of perfume liquid, namely apple, frangipani, jasmine, melon, rose, sandalwood, and vanilla and also exposed to four fragrances of Indonesia local tea, namely Balap Sepeda, Gopek, Hijau Daun, and Poci. After fragrance exposure, the sensor array

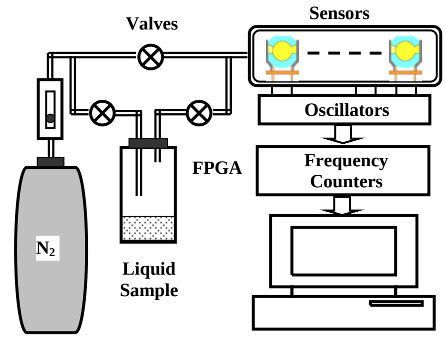

Fig. 1. The experimental setup of fragrance identification system.

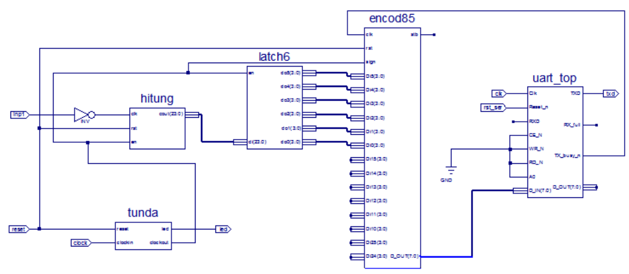

Fig. 2. The digital interface implemented on the FPGA.

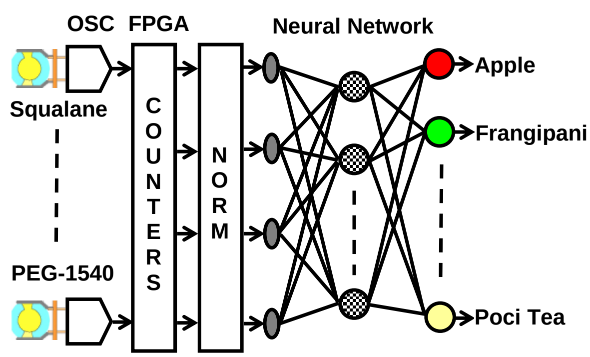

Fig. 3. The sensor array combined with Neural Network pattern recognition.

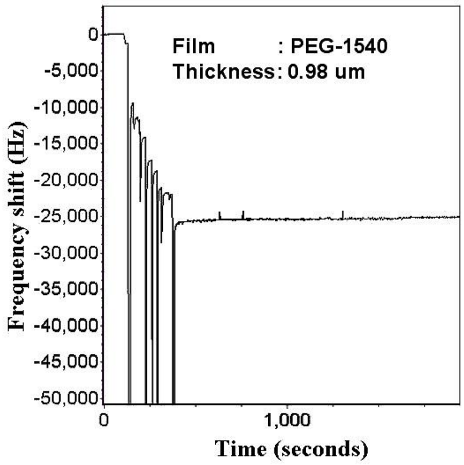

Fig. 4. Typical time response of the sensor resulted from the coating procedure.

was purged with dry N2 to flush the vapor molecules. At each sample, the frequency shifts of each sensor within forty seconds after sample injection were recorded to obtain a six dimensional pattern, representing the exposed fragrance.

The multilayer neural network was applied to the sensor array to recognize fragrances automatically. The number of input nodes was six correspond to the number of sensors, and the number of output neurons was eleven equal to that of the sort of fragrances, shown in figure 3. The number of hidden neurons was twenty to accelerate and improve the convergence in training phase. Both learning rate and moment constant were empirically determined to be 0.01.

3 RESULTS AND DISCUSSION

3.1 Coating thickness

The crystals were washed with chloroform before coating and fundamental frequencies were recorded. The coating materials were prepared in chloroform and then airbrushed onto the crystal surfaces with 1 bar N_2 pressure. The chloroform evaporated and the procedure was repeated several times on each side of the crystal surface until the coating frequency shifts were between 2 to 30 kHz, shown in Fig. 4.

The frequency drop is the response of additional coating

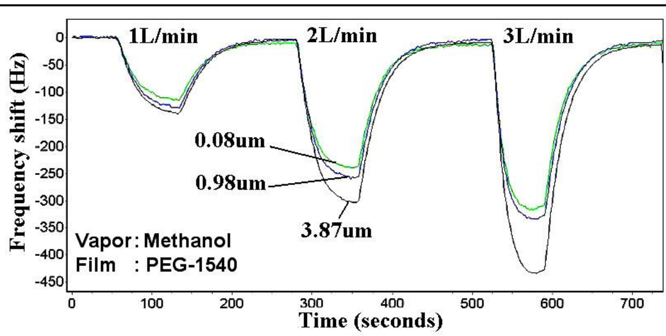

Fig. 5. Influence of the coating thickness on the sensitivity.

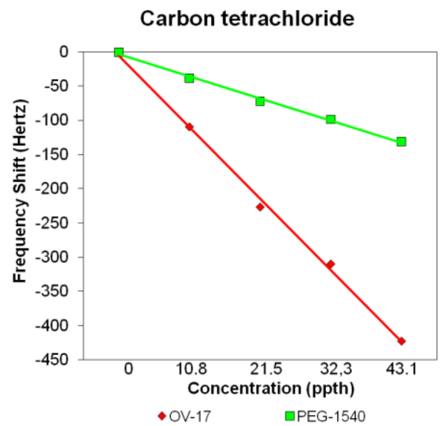

Fig. 6. The sensitivity of the sensor exposed to various concentrations of a sample vapor.

material. The thickness of the coating film (h_{film}) was lated from frequency shift detected after coating application (Δf_{film}), according to:

$$h_{film} = -\frac{\Delta f_{film}\,\rho v}{2 f^2 \rho_{film}} \quad (4)$$

where ρ_{film} is density of the coating film. In the coating procedure, there was a problem with too large amounts of coating material, which caused to the crystal to cease the oscillating mechanism. An array of three crystals having same coating but different thickness was exposed in a solvent vapor carried by N_2. In figure 5 shows that thicker coating lead to higher frequency shift or higher sensitivity. This was emphasized in a previous study by simulating the diffusion and reaction model of analytes in sensor layer [15]. The chemical materials, therefore, were coated onto the crystal surfaces with the similar thickness for further experiments.

3.2 Sensitivity

The crystals coated with different chemical material were flowed by N_2 to obtain its own baseline. After the frequencies became stable, a liquid solvent sample was injected into the sensor chamber. The concentration (C) is obtained from the equation:

$$C = \frac{\rho_s V_s R\,T}{V_{tube}\,M_s\,P} 10^3 \text{ (ppm)} \quad (5)$$

where ρ_s is the density of the sample (g mL^{-1}), V_s is the sample volume (μL), R is ideal gas constant (0,082 L atm $mol^{-1}K^{-1}$), T is the sensor chamber temperature (K), V_{tube} is the chamber volume (L), M_s is the sample molecular weight (g mol^{-1}), and P is the sensor chamber pressure (atm).

Figure 6 shows that each sensor has different frequency shift to a sample vapor and has a linier relationship between frequency shift and vapor concentration, corresponds to the Equation (1). The procedure was repeated for other samples and coating films with various concentrations to each vapor. Effect of vapor concentration to resonant frequency shift of the sensor array under 500 Hz has linear relationship with the mean determination rate R^2 of 0.98.

3.3 Fragrance Recognition

The first experiment was carried out with the sample of perfume fragrances. The baseline value was obtained when the dry N2 gas was flowed into the sensor chamber. During in the sample injection, the frequency is decreasing due to the acoustic losses, shown in figure 7. Since the concentration for an unknown fragrance 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 sensor response with sum of all of the sensor responses. The normalized frequency shifts of the sensor array for each perfume fragrance are shown in figure 8.

The second experiment was carried out with the samples of Indonesia local tea fragrances. The typical response and the normalized frequency shifts of the sensor array to the tea fragrances are shown in figure 9 and figure 10, respectively.

The measurement data are six-dimensional, since six sensors were used. The mapping method is required to find a low dimensional vector that preserves most of the information in the original feature vector. Scattering diagram by PCA with two of the most significant components is shown in figure 11. The eleven clusters formed match with the eleven types of fragrances so that the fragrance were completely separated in the principal component space, with the cumulative sum of the variances:

76.8587
91.0435
97.8779
99.7120
99.9714
100.0000

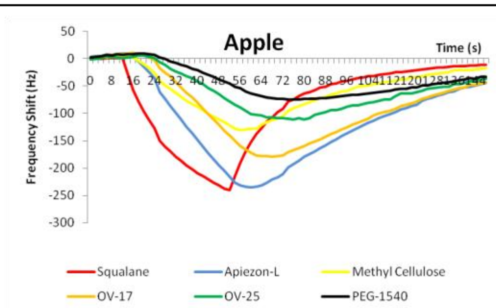

Fig. 7. The time response of the sensor array to perfume fragrance.

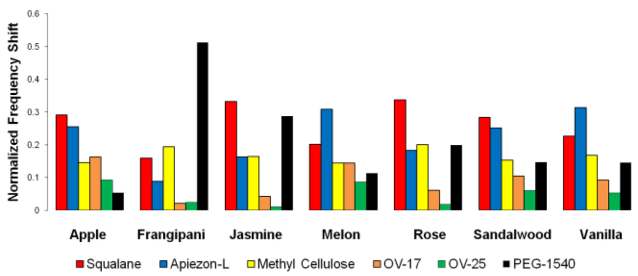

Fig. 8. The signatures of individual perfume fragrance produced by the sensor array.

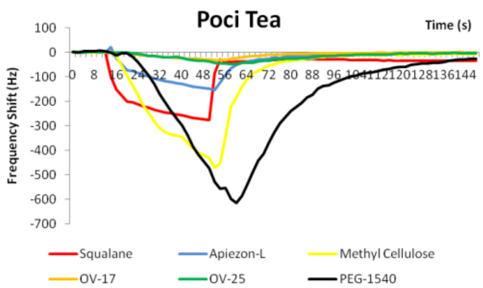

Fig. 9. The time response of the sensor array to tea fragrance

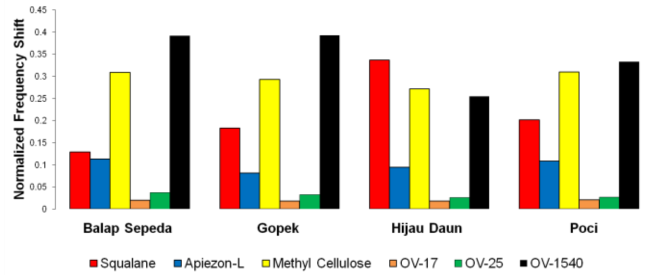

Fig. 10. The signatures of individual tea fragrance produced by the sensor array

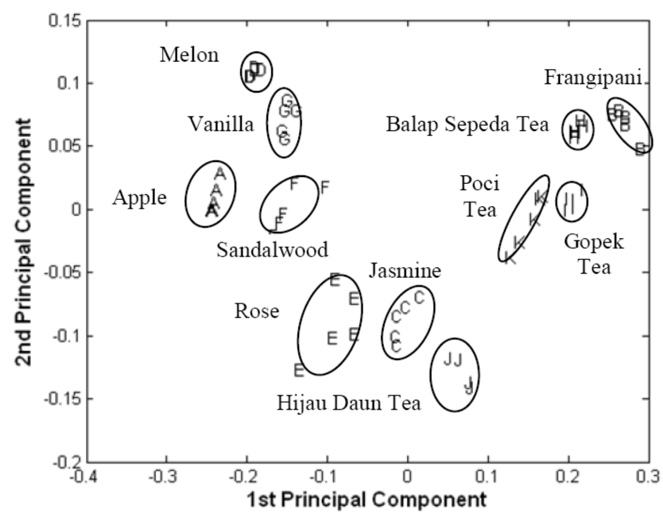

Fig. 11. The scattering diagram of perfume and tea leaf fragrances visualized by PCA

This shows that at least 91 % of the variance is accounted by the first two principal components.

The multilayer neural network was applied to recognize all fragrances automatically. In the training phase, 55 data sets were fed into the neural network. The neural can be taught to discriminate each fragrance with the error rate of 1 % taking 27.390 epochs, shown in figure 12. In the running phase, the others 55 data sets were fed into the neural network. The network can recognize all fragrances tested in the experiment with the identification rate of 93 %. The activation rates of the output neurons were shown in figure 13.

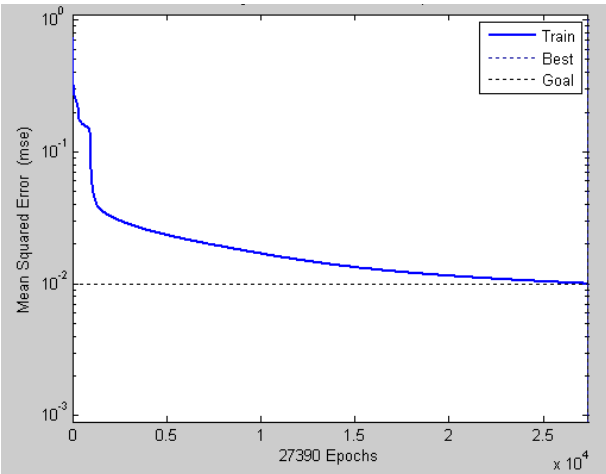

Fig. 12. The error profile of neural network in the training phase

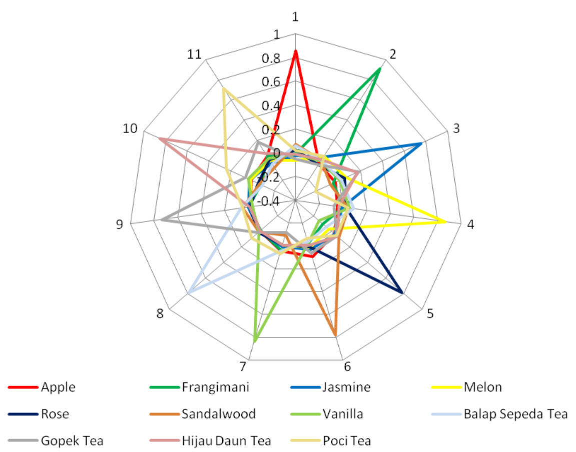

Fig. 13. The response of the neural network to each fragrance in the running phase

4 Conclusion

It has been investigated that the electronic nose comprising six quartz crystal sensors and back propagation neural network was able to distinguish several samples of fragrances. This system has been shown to resolve the fragrances, including fragrances of different classes (i.e. apple, frangipani, jasmine, melon, rose, sandalwood, and vanilla) as well as those within a particular class of Indonesia local tea (i.e. Balap Sepeda, Gopek, Hijau Daun, and Poci). The neural network can be taught to recognize all of the fragrances with the identification rate of 93 %.

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