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인공신경망을 이용한 수정진동자 유기용매 인식시스템의 개발
The development of AT-Cut Quartz Organic Vapor Recognizing System Using Artificial Neural Network

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<요 약>
8개의 수정진동자 위에 서로 다른 종류의 Lipid를 코팅하여서 만든 센서 배열을 가지고 유기용매를 인식할 수 있는 System을 구성한다. 유기용매 인식센서에 대한 수학적 모델을 사용하여 여러 가지 유기용매에 대한 센서의 응답으로부터 센서 표면과 유기용매 간의 물질 전달속도 패턴과 친화력 패턴을 얻어 유기용매 종류를 인식하였다. 패턴인식은 인공신경망을 이용하였으며 인공신경망의 연결강도 수정은 Levenberg-Marquardt 알고리즘을 사용하였다. 신경망의 출력은 4개로 하였고, 디지털 신호인 0과 1의 조합으로 유기용매 종류를 구분하였다. 이 시스템을 이용하여 9개의 유기용매 Acetone, Benzene, Chloroform, Carbon-tetrachloride, Ethylacetate, Buthylacetate, Cyclohexane, Dichloromethane, 1,1,2,2,Tetrachloroethane, 2,2,4Trimethylpentane을 구분하여 인식할 수 있었다.

Keywords : Odorant Sensor, Smell Sensor, AT-Cut Quartz Crystal, Neural Network, Recognition, Organic Solvent Recognition

1. Introduction

Since the first report[1], the use of piezoelectric quartz crystals for the detection of gaseous compounds has become increasingly popular.[2,3,4,5,6,7] These devices are often called quartz crystal microbalances (QCMds). Usually, the quartz crystals are sandwiched between two electrodes, which are then coated with a substrate capable of adsorbing the compounds to be measured.

The response of the devices is based on the decrease in the resonant frequency of the crystal as the mass of the device increases, according to the equation derived by sauerbrey.[8]

The adsorbents most frequently used are lipids.[9,10,11,12]

Many identifications of chemical vapor sensors are depending on steady state values of response. But dynamic response (or transient response) is also important to study sensing phenomena.

Fig.1 shows the different shape of response, but the steady state values of these responses are same.

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Therefore it need identification method to distinguish this kind of reponses.

In this aspect, a mathematical model of dynamic behavior was built and examined by experimental data.

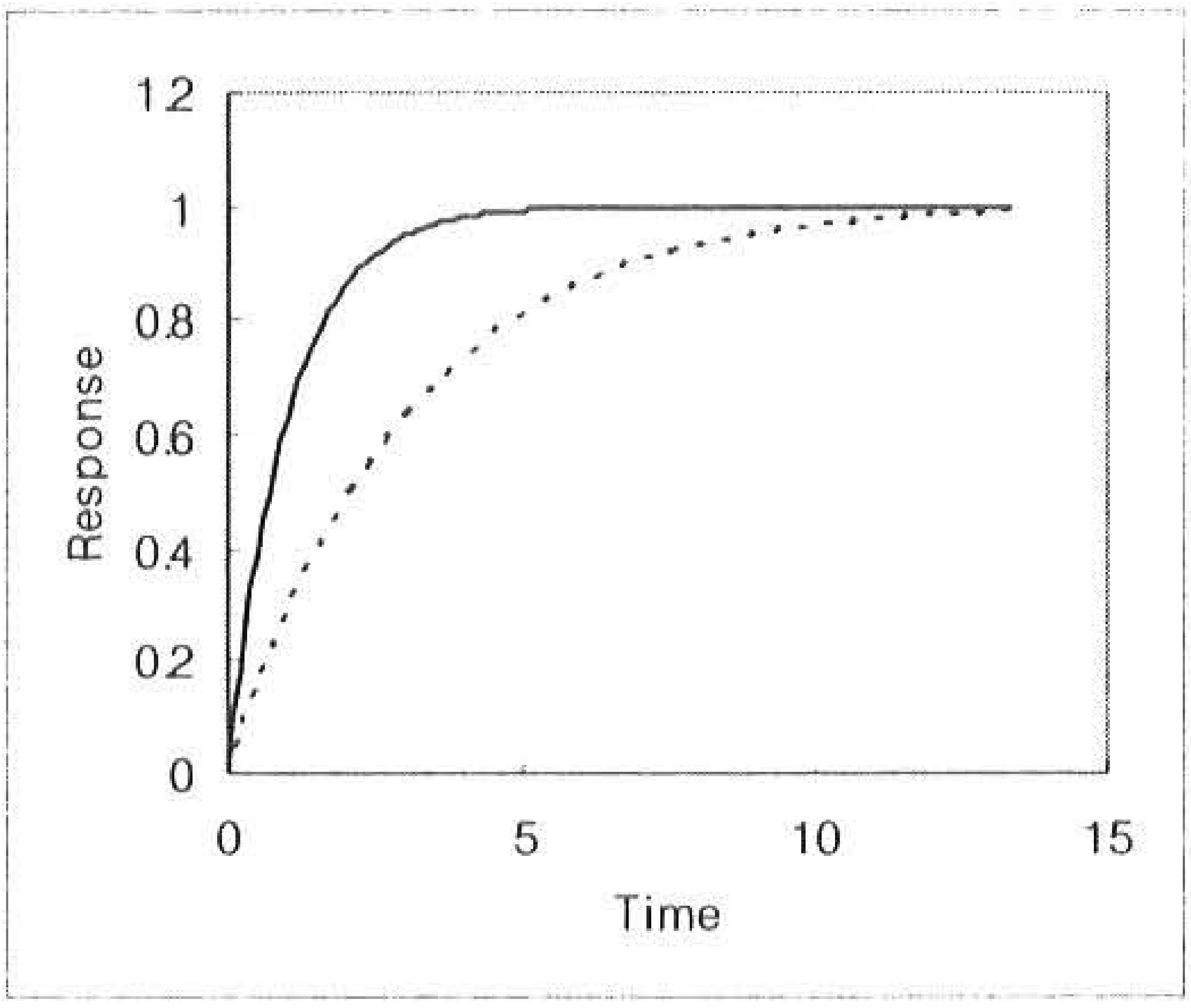
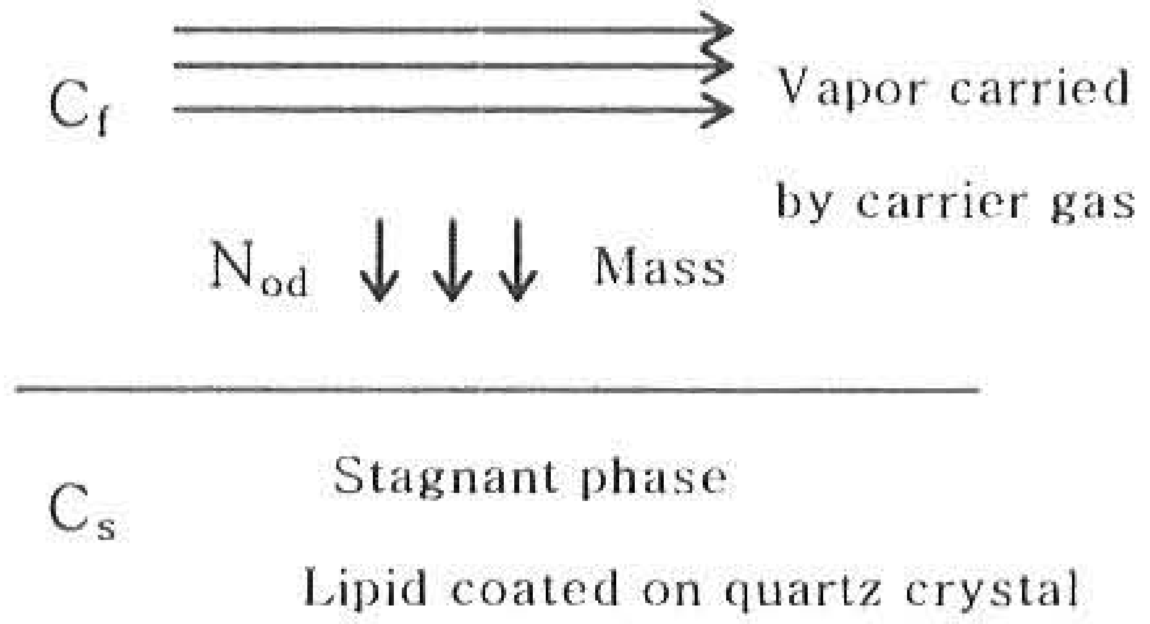


Fig.1The importance of dynamic response.

Mathematical Model

The schematic of the sensing part of a lipid coated AT-cut quartz crystal vapor sensor is shown in Fig.2. In this figure, C_f is concentration of moving phase, C_s is concentration of stagnant phase and N_{od} is total mass flux into stagnant phase. Stagnant phase is lipid which is coated on AT-cut quartz crystal.



Fig,2 Schematic diagram of sensing part

There are some assumptions to build the mathematical model as follows;

Assumption ; C_f is constant and its dependency of mass transfer is small, and mass transfer phenomena is described as lumped parameter system as eq.(1). The change of, mass of stagnant phase(m_s), can be negligible.

$$N_{od} = D_{od}(C_f - C_f^*) \quad (1)$$

where D_{od} is effective mass transfer coefficient and C_f^* is equilibrium concentration for C_s.

The material balance can be described as eq.(2).

$$m_s\frac{dC_s}{dt} = N_{od} = D_{od}(C_f - C_f^*) \quad (2)$$

The equilibrium relationship between C_f^* and C_s follows Henry's law

$$C_f^* = kC_s \quad (3)$$

where k is Henry's constant.

Rearranging the above equations, eq. (4) can be drived.

$$\tau\frac{dC_s}{dt} + C_s = K_1C_f \quad (4)$$

where $\tau = \frac{m_s}{D_{od}k}$ and $K_1 = \frac{1}{k}$

This is the model equation of first order system. In this model equation, the parameter τ is time constant and K_1 is steady state gain.

The solution of eq.(4) for step change with the magnitude of A in C_f is

$$C_s(t) = K_2(1 - e^{-t/\tau}) \quad (5)$$

where $K_2=K_1A$.

The relationship between frequency change of AT-cut quartz resonator and adsorbed mass was reported as eq.(6)

$$\Delta F = k_3m, \quad m = k_4C_s \quad (6)$$

where ΔF is frequency change and m is adsorbed amount.

Rearranging eq.(5) and (6), the response of lipid coated AT-cut quartz resonator for step change in input concentration is

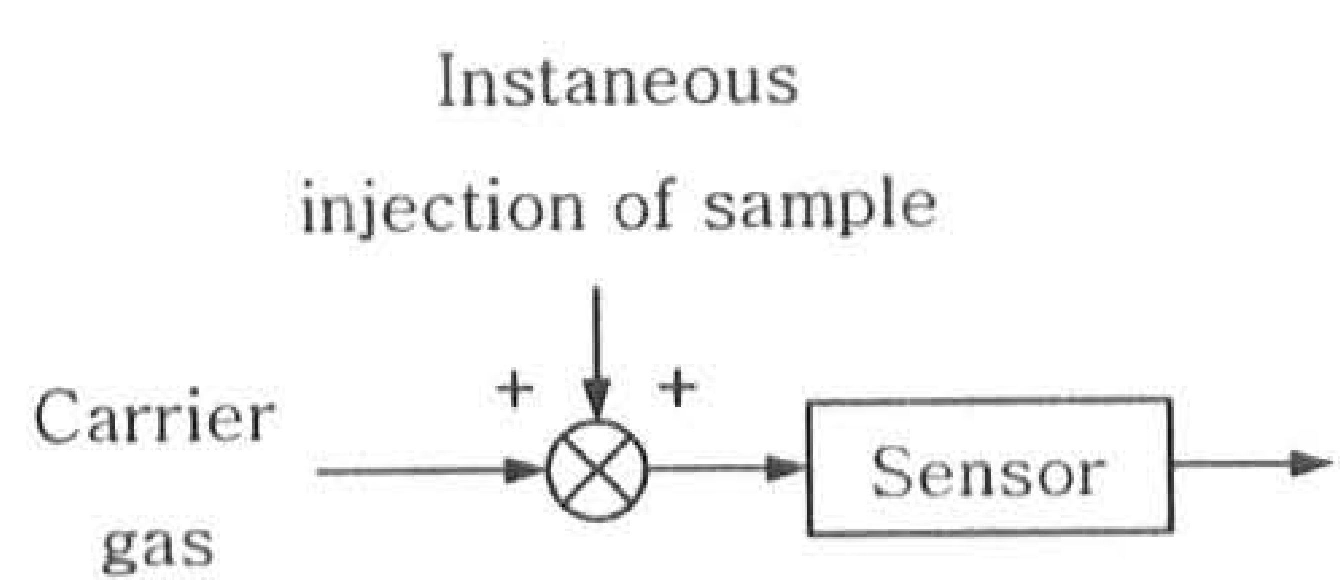
$$\Delta F = K(1 - e^{-t/\tau}) \tag{7}$$

whre $K = K_2 k_3 k_4$

This model equation has two parameters, K and τ. K is steady state value which includes affinity of adsorption and τ is time constant which includes mass transfer coefficient term.

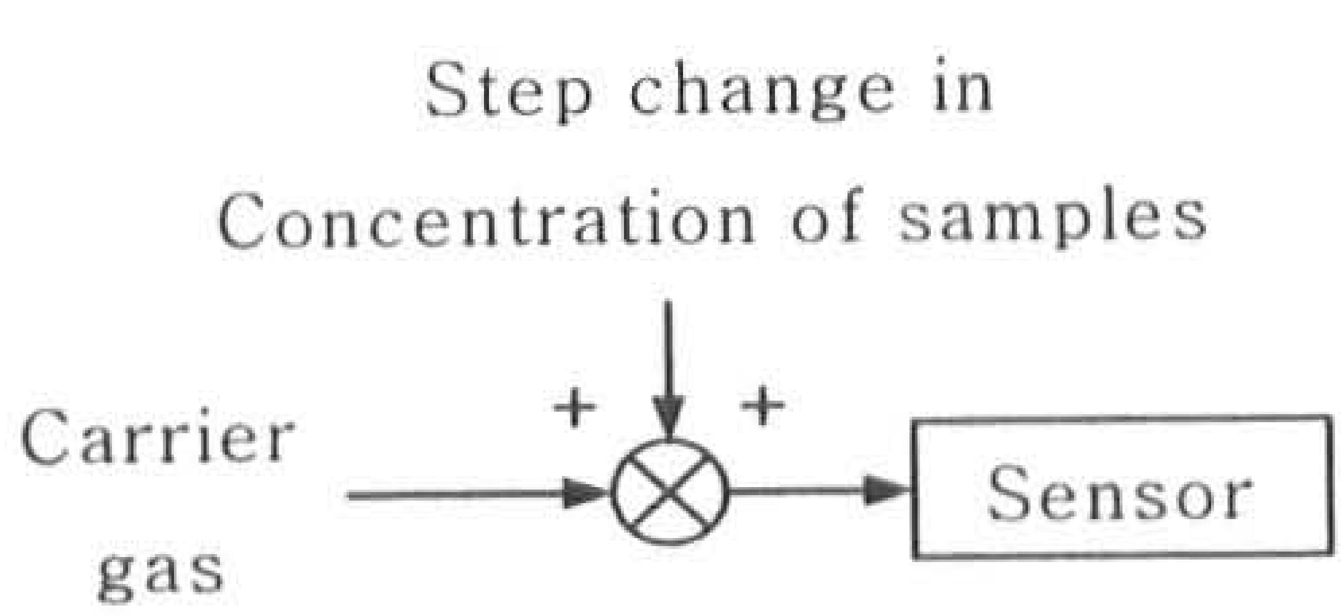
Sampling Method

Two types of flow system can be applied



(a) Injection method

to the vapor sensor as shown in Fig. 3 .



(b) Step change method

Fig. 3. Two kinds of methods to examine a flow type sensor

It is easy to analyze the experimental result by the step response, but it is difficult to get good reproducible response because of disturbance of a noise from surrounding and operation. Integration of the impulse response obtained by instantaneous injection of sample becomes good step response that can be obtained by injection method.

The injection method was modified to increase the sensitivity of sensor. In this modified injection method as shown in Fig.4, water vapor was fed continuously to activate the adsorbent coated sensor surface, then sensitivity of the sensor was increased.

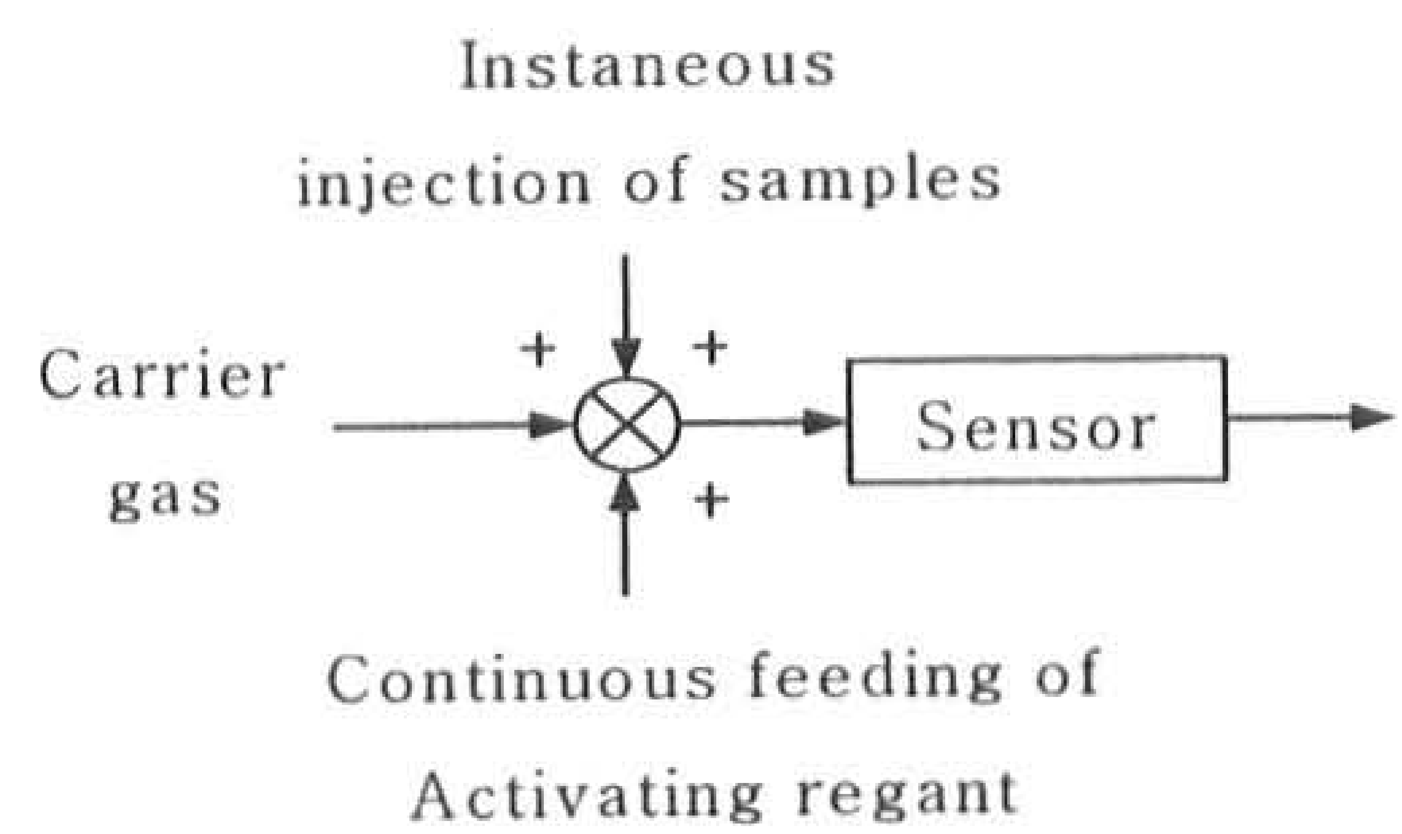


Fig.4 Modified injection method

2. Experimental

Materials

Phosphatidylcholine (PC1, Dicaproyl, Synth -etic), Phosphatidylcholine (PC2, Dioleoyl, Sy -nthetic), Lipid A (LA, from Escherichia Col -i), Phosphatidylserine (PS, L-Serine, Dipalm -itoyl), Phosphatidylinisitol (PI, from bovime liver), Phosphatidylcholine (PC3, type III-B, from Bovine brain), Phosphatidylcholine (PC -4, Dipalmitoyl, Synthetic), and Phosphatidyl -glycerol (PG, from egg york lecithin) were used as coating lipids of sensors.

Acetone(ACE), Benzene(BEN), Chloroform (CHL), Carbontetrachloride (CTC), Ethylacet -ate(EAC), Buthylacetate (BAT), Cyclohex -ane(CHX), Dichloromethane (DCM), 1,1,2,2 -tetrachloroethane(TCE), 2,2,4 Trimethyl -pentane(TEP) were used as recognized organic vapor. These lipids were obtained from Sigma Co., and organic solvents were obtained from Fluka Co.

Apparatus

A schematic diagram of experimental system is shown in Fig.5. Water vapor, generated (2 mg/min) in the gas permeater, was carried into measuring chamber by carrier gas and activated lipid coated sensor surface. Nitrogen was used as carrier gas and its flow rate (1 l/min) was controlled by the rota meter. Sample was injected into temperature controlled (200℃) sample injector and its concentration can be controlled by carrier gas flow rate and injection amount.

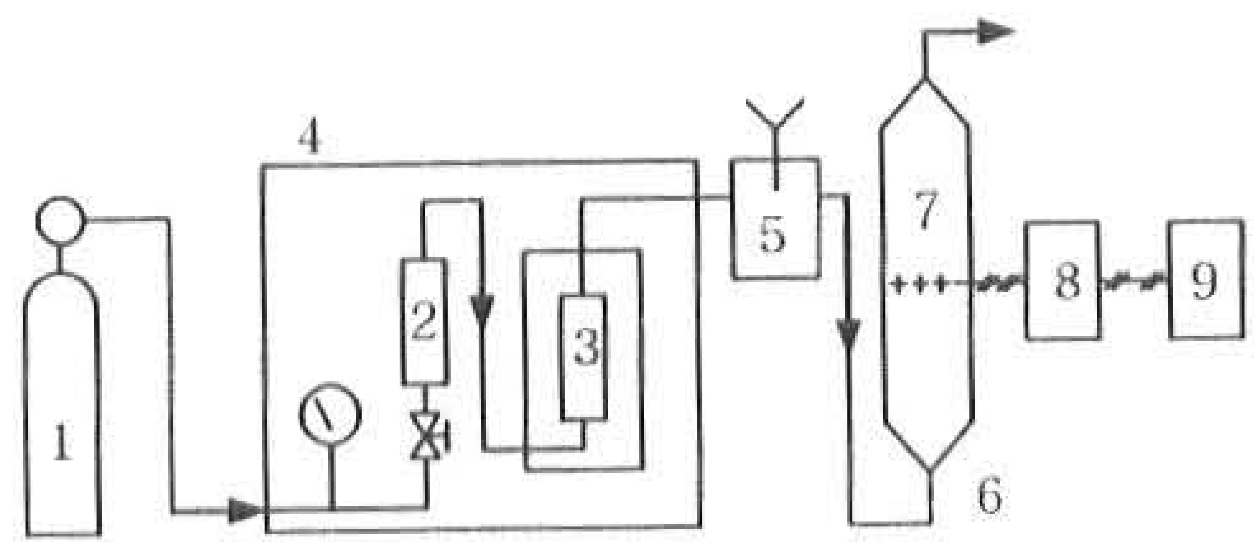


Fig.5 Schematic diagram of experimental system : (1)N2 bomb, (2)Rota meter, (3)Vapor generator, (4)Gas permeater, (5)Sample Injector, (6)Measuring chamber, (7)Sensorarray,(8)Frequencycounter,(9)Computer.

3.Result and Discussion

Fig.6 shows typical responses of the sensor array shown in Fig.5 for the injection of commercial whisky. This response can be considered a impulse response.

Fig.7 shows step responses which are obtained by integration of the impulse response shown in Fig.6.

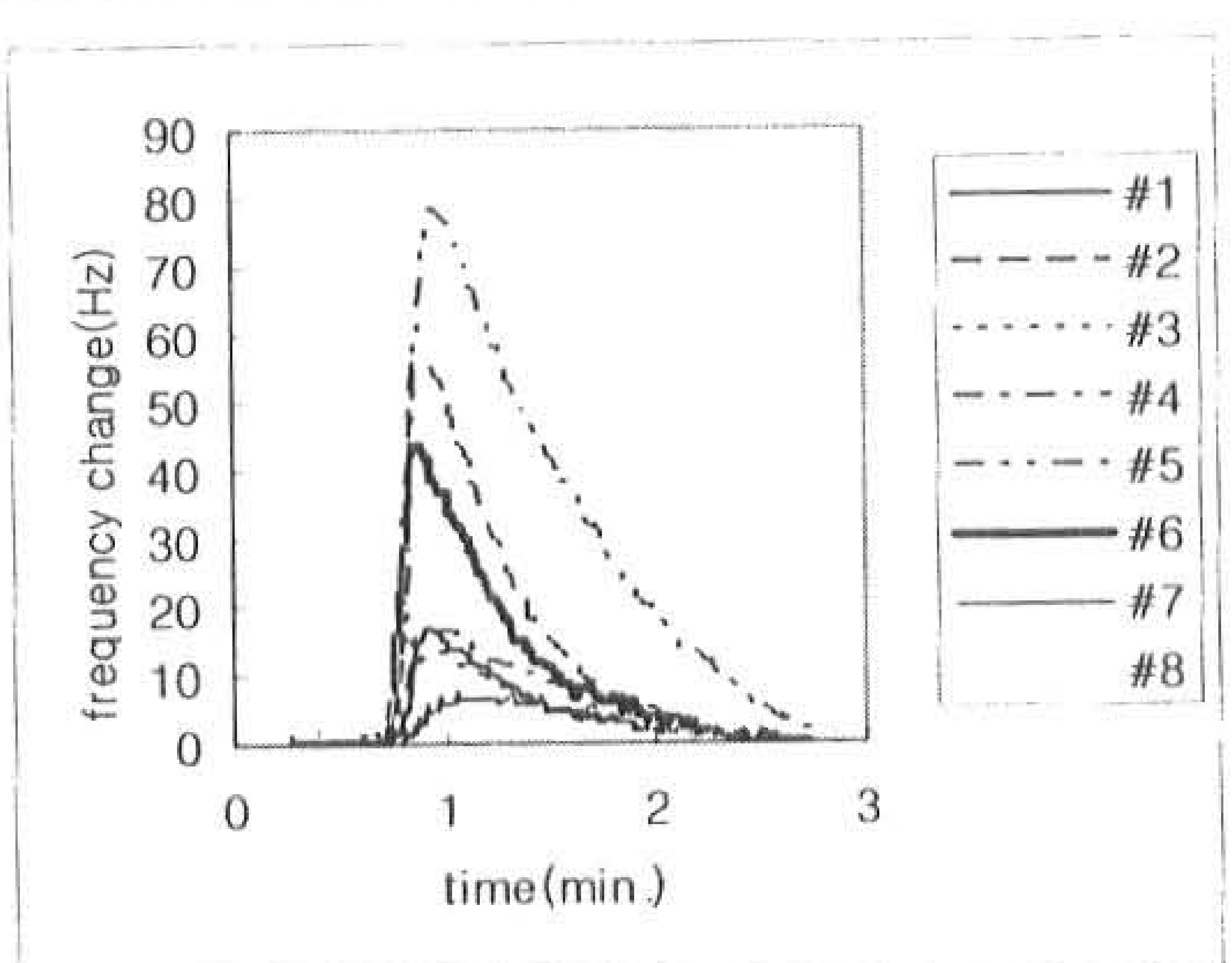


Fig.6.Theresponsesofthesensorarray for 2 μℓ injection of Benzene

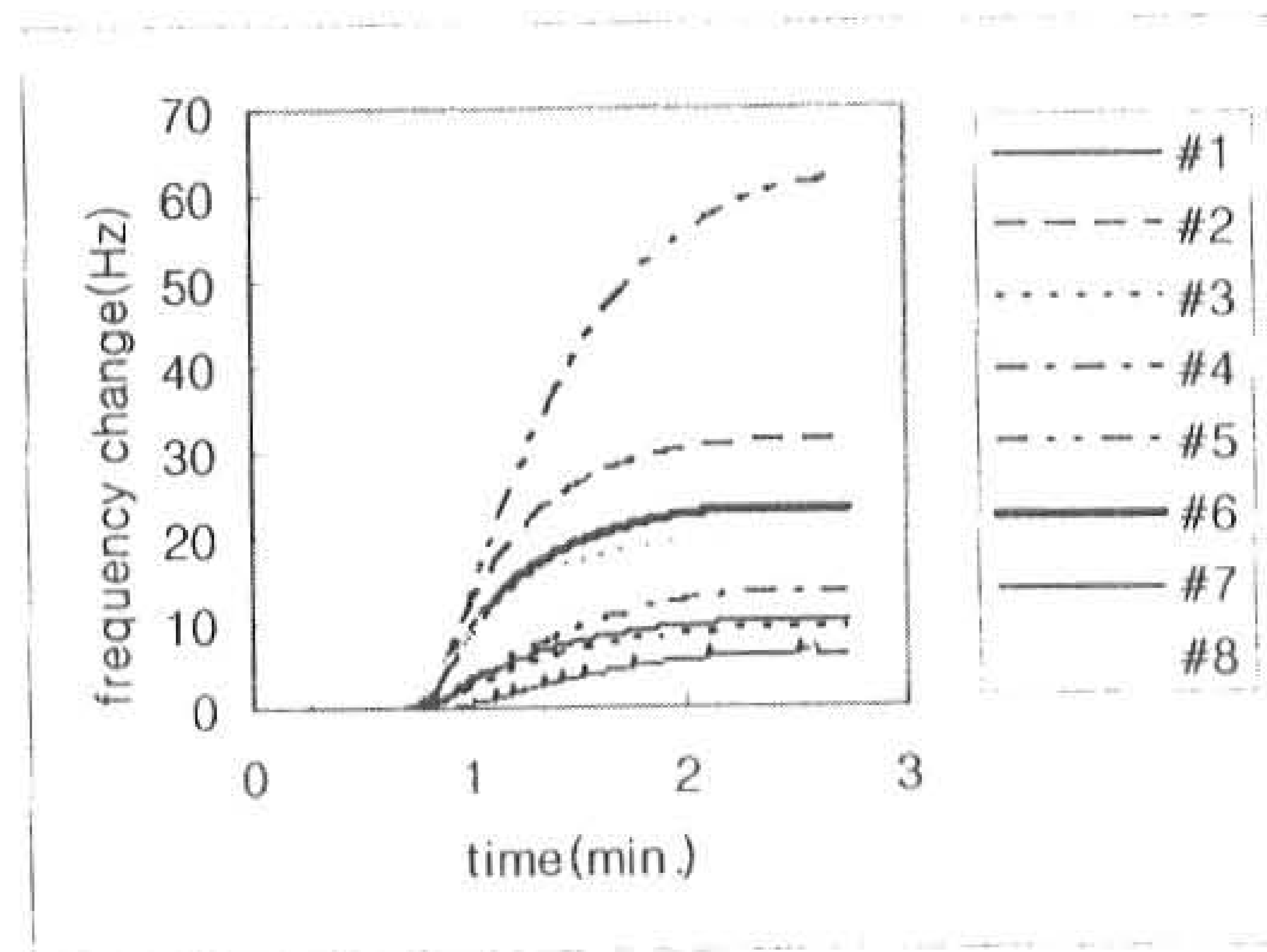


Fig.7. The step response of the sensor array obtained by integrationofimpulseresponseofFig.6.

These responses can be considered to be pseudo first order responses,

$$\Delta F = K(1 - e^{-t/\tau}) \qquad (7)$$

Where ΔF is the response of step change in input concentration, k is the steady state value for step change in input concentration of the sample, t is time and τ is time constant which includes mass transfer rate term. In this model equation, there are two parameters k and τwhich can be used for pattern analysis.

Fig.8 shows the pattern analysis by steady state value for organic solvent. As shown in the figure, pattern can not be distinguished, thus pattern analysis by steady state value is failed.

This results show the adsorbed amounts of various organic solvent on the sensor surface are nearly the same became the frequency shift of the quartz crystal depends on the mass adsorbed on the surface. Of course, since the odorants content in the whisky is very small comparing to the alcohol, odorant effort will be negligible to the overall adsorption on the sensor surface.

Fig.9. shows the pattern analysis by time constant value which was obtained by regression of step response with eq.(2). It shows different patterns for different organic solvent. The cause of difference can be considered that the mass transfer rate of adsorption is different.

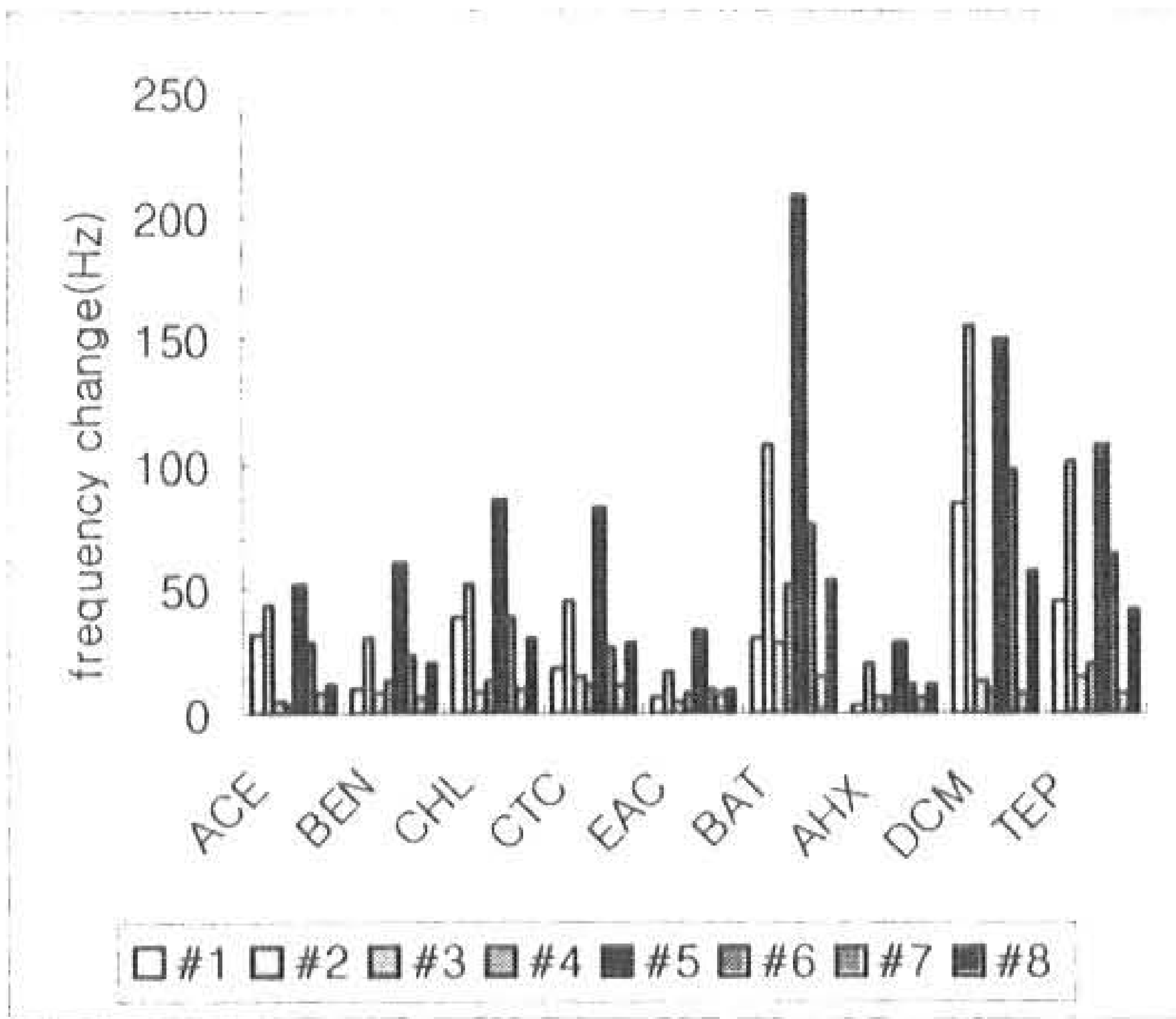


Fig.8. Pattern analysis by steady state value for organic solvent

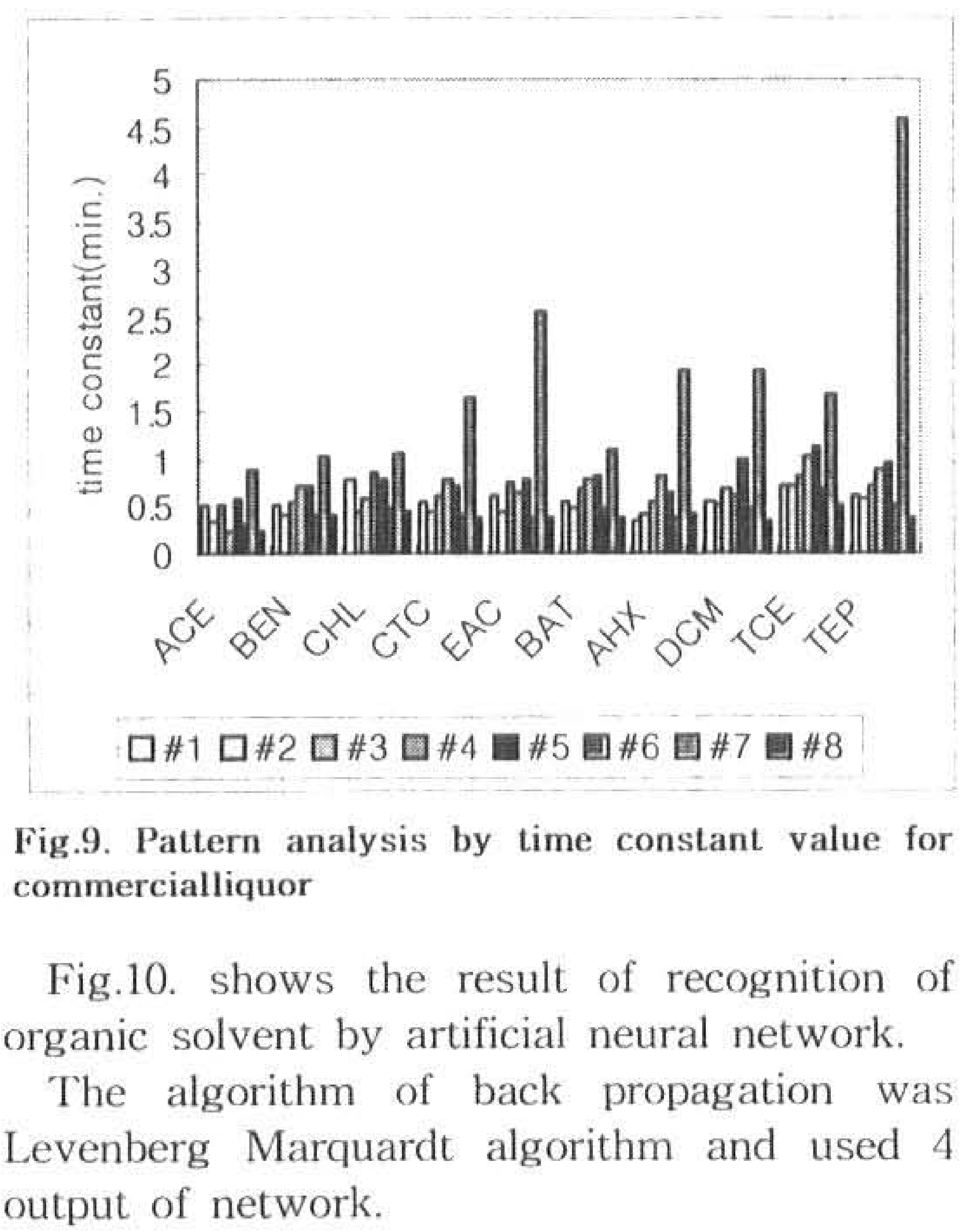


Fig.9. Pattern analysis by time constant value for commercialliquor

Fig.10. shows the result of recognition of organic solvent by artificial neural network.

The algorithm of back propagation was Levenberg Marquardt algorithm and used 4 output of network.

4.Conclusion

AT-cut crystal vapor sensor can be described by the first order model equation. Using this model equation, the odorant of organic solvent can be recognized by artificial neural network pattern analysis using Levenberg Marquardt algorithm.

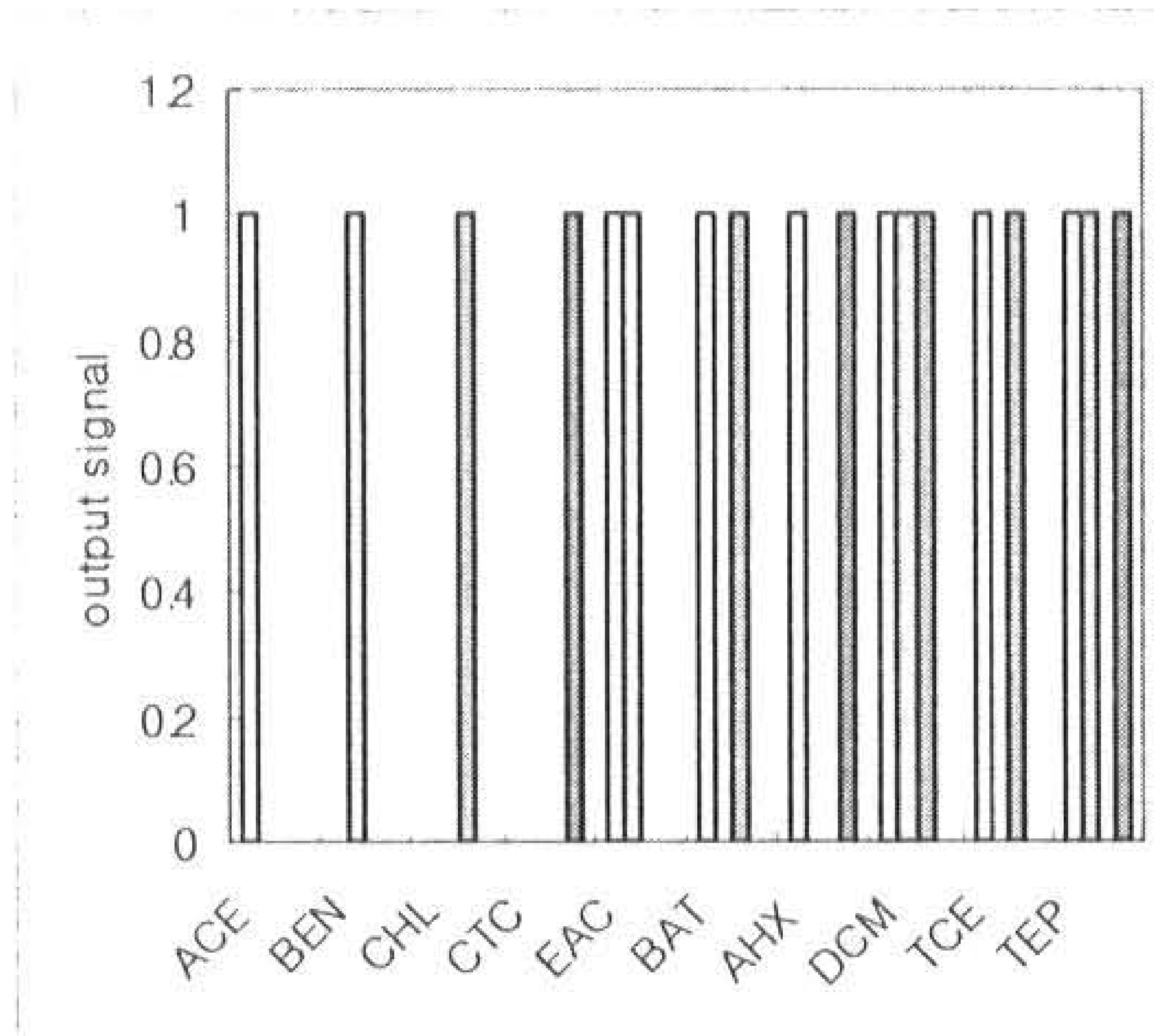


Fig.10. The output signal of neural network for recognitionoforganicsolvent

Nomenclature

C_f : Concentration of fluid phase [mole/cm^3]
C_s : Concentration of stagnant phase [mole/g]
N_{od} : Mass flux [mole/min]
D_{od} : Effective mass transfer coefficient [cm^3/min]
C_f^* : Equilibrium concentration for C_S [mole/cm^3]
m_s : Mass of stagnant phase [g]
k : Henry's constant [g/cm^3]
τ : Time constant [min]
K_1 : Steady state gain [cm^3/g]
A : Magnitude of step change [mole/cm^3]
K_2 : K_1A [mole/g]
ΔF : Frequency [Hz]
m : Absorbed amount [K_g]
k_3 : $\Delta F/m$ [Hz/g]
k_4 : m/C_s [g^2/mole]
K : $K_2k_3k_4$ [Hz]
t : Time [min]

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