

Application of modified quartz crystal sensors: Detection of isobutyl alcohol, ethyl acetate and ethylene

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Abstract: Aroma volatilization is one of the very important attributes of agricultural products during ripening. Ingredients of aroma compounds experience changes over products' different ripening stages. This paper aimed to develop a detection system based on modified quartz crystal sensors to detect volatile organic compounds (VOCs). By drop-coating on sensors' surface, four sensors were made using quartz crystal resonators coated with four different absorbable materials: ethyl cellulose, cellulose acetate, 1,2-dioleoyl-sn-glycero-3-[phosphor-L-serine], and galactosyl ceramide. With the diversely coated sensors, three VOCs: isobutyl alcohol, ethyl acetate and ethylene were detected at ppm level. To investigate the structure influence of the coated sensing films on VOCs absorption, the topography of films was imaged in 3D using atomic force microscopy (AFM) in tap mode for qualitative analysis of gas absorption. The selectivity and sensitivity were investigated when sensors were exposed to VOCs with increasing concentrations. The results showed that the frequency shift of sensors was linear to the concentrations of all three VOCs in the range of 5–25 ppm. With values reaching over 4.5 Hz/ppm, the sensitivity of cellulose acetate coated sensor to three VOCs was similar, higher than that of sensors with other coatings. The high sensitivity of the cellulose acetate coated sensor might be due to the film's rough surface and porous structure. The results may help further research on detection of fruits' organic volatiles during the ripening stage.

Keywords: quartz crystal sensor, atomic force microscopy, detection, selectivity, sensitivity, volatile organic compounds

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1 Introduction

The piezoelectric quartz crystal resonator as one of the electronic oscillator devices is widely used in circuits. The important features of quartz crystal oscillator include high mass sensitivity and high frequency stability. The adhesive mass change on electrode surfaces of the quartz

crystal unit will lead to noticeable frequency change of the oscillator^[1]. It can be used to detect micro mass on the nanogram level in the detection field, called quartz crystal microbalance (QCM). The quartz crystal can detect gas change when its surface is coated with a film constructed by a polar or porous substance^[2]. In the detection process, the gas molecule is absorbed or diffused to the sensing film due to the polarity and the porous structure of the film. The adsorption or diffusion results in mass change of the quartz crystal resonator. This in turn causes the change in resonance frequency of the oscillator installed above the quartz crystal resonator.

Aroma is one of the important attributes of fruits, the ingredients of which vary according to ripening stages and product quality^[3-6]. It is a nondestructive technology to determinate the quality and the ripening stage of fruits through aroma analysis^[7,8]. The QCM modified with selective films is one of promising sensors for recognition of ripening stages or quality for fruits.

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The aroma of fruits includes thousands of volatile organic compounds (VOCs). For different fruits, the components of aroma are different. Moreover, the components are related to ripening stages^[9-11]. It has been a difficult task over the last decade to automatically detect the ripening stage of fruits by a non-destruction method, especially through detecting fruit's VOCs^[7]. VOCs detection is also very important in other fields, such as food quality control, environment monitoring, and chemical agent detection^[12,13].

Many methods have been developed to detect fruit VOCs, such as the Fourier transform infrared (FTIR) spectrometry, gas chromatography (GC), mass spectrometry (MS) and chromatography-olfactometry (GC-O)^[4, 11, 14], which are accurate and reliable, but the analysis is time consuming and costly. Quartz crystal microbalance (QCM) sensor was thought to be a promising method to detect VOCs because of its high sensitivity, portability, compactness, time efficiency, and convenience at room temperature and atmospheric pressure^[13]. As a mass-sensitive sensor, QCM is based on the Sauerbrey equation (1):

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (1)$$

In this equation, Δf is the frequency shift (Hz); f_0 is the resonance frequency of the AT-cut quartz crystal (Hz); Δm is the mass change (g); A is the electrode area of the quartz crystal resonator (cm^2); ρ_q is the density of quartz (2.65 g/cm^3), and μ_q is the shear modulus ($2.95 \times 10^{11} \text{ dyn/cm}^2$). This equation has been used to detect micromass, such as VOCs. Since the response of bare QCM sensor to VOCs is nonselective, organic and organometallic coatings are used on QCM devices to provide chemical selectivity. Different coatings have varied abilities to adsorb vapor molecules of gas phase, which is related to the polarity and microstructure of coating materials and ingredients of VOCs. QCMs have been widely used in many fields, Ying et al. analyzed four chemical reagents: dimethyl methyl phosphonate (DMMP), N, N-dimethylacetamide (DMA), 1, 5-dichloropentane (DCP), and dichloroethane (DCE) by using polymer coated sensor array. The result showed that the sensor array is highly selective and sensitive to

them^[13]. Edmonds et al. used coated QCM sensors to detect organic gaseous pollutants chloroform and toluene, and the result was in agreement with expectations^[12]. The QCM system also was explored in the food industry, Escuderos et al. coated the QCM system with chromatographic adsorbents to detect olive oil volatile compounds^[15]. Mirmohseni et al. applied polymer-coated QCM to detect benzene, toluene, ethylbenzene, and xylenes at the ppm level^[16]. In the fruit industry, fruits' flavor and flavor components were studied using lipids or stationary phase materials for gas chromatography coated QCM sensors^[17]. Also QCM sensors modified with nano-materials were used to detect fruit diseases by analysis of volatile organic compounds^[18].

The application of QCM detectors for gas phase has been studied and explored for years, but there are few literatures about using QCM to detect the ripening stages of fruits, possibly because of the complexity of fruit aroma. To explore the feasibility of using QCM sensors to determine the ripening stages of fruits, it is necessary to investigate the relationships of the responses of QCM sensors to major fruit VOCs. Since every component of fruit aroma has its special contribution to the overall aroma, to select materials of sensing film, it is important to investigate the responses of QCM sensors to some frequently present VOCs of fruit aroma. Isobutyl alcohol, ethyl acetate and ethylene are three components present in many fruits' aroma. Targeting the three compounds, the paper investigated the response, sensitivity and selectivity of QCM sensors coated with four materials: 1,2-dioleoyl-sn-glycero-3-[phosphor-L-serine] (DOPS), galactosylceramide (GC), ethyl cellulose (EC), and cellulose acetate (CA).

2 Materials and methods

2.1 Sensors preparation

Quartz crystal resonators (9 MHz AT-cut) with gold electrodes (radius: 8 mm, thickness: 0.185 mm, diameter of electrode: 5 mm) were purchased from Nihon Dempa Kogyo Co. Ltd (Tokyo, Japan), which were cleaned by ethanol and ultrapure water sequentially in ultrasonic bath for 15 min, then placed in an oven to dry at 60°C for 1 h.

The sensing film materials: 1,2-dioleoyl-sn-glycero-3-[phosphor-L-serine] (DOPS), galactosylceramide (cerebroside, GC), ethyl cellulose (EC) and cellulose acetate (CA) were dissolved into solvents before coating. Among them, GC and DOPS were dissolved in chloroform (CHL), EC and CA dissolved into THF. All solutions were prepared at 5 mg/mL. All solvents and solutes were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Sensing films were formed using the drop coating method by depositing 5 μ L the above solutions onto the surface of both gold electrodes of every resonator using a 20 μ L-microsyringe, followed by drying the modified quartz crystals resonators in an oven at 60°C for 1 h to evaporate the solvent thoroughly. The sensors were constructed after repeating the depositing procedure 3 times.

2.2 AFM imaging

In order to understand the influence of the surface topography of sensing films on absorption and diffusion of VOCs, a multimode atomic force microscopy (AFM) (NanoScope V, Veeco Inc, USA) was used to acquire the surface topography of the prepared sensing films at a nanometer scale. The imaging process was carried out in the tap mode.

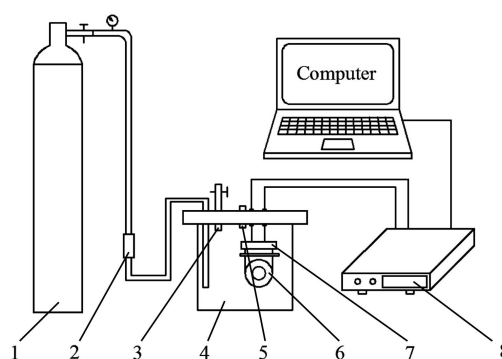
2.3 Experimental setup and test description

The experiment setup was shown in Figure 1, which was built to investigate the responses of coated QCM sensors activated by target samples. The oscillator circuit purchased from Tama Device Co., Ltd. (Kanagawa, Japan) was fixed on the cover of a sealed measurement Teflon chamber with 250 mL volume. The N₂ gas purchased from Taiyo Nippon Sanso Corporation as a carrier gas was circulated into the measurement chamber through a hose to desorb VOCs previously absorbed by QCM sensors after the frequency shift was measured.

Standard target gases ethylene, isobutyl alcohol, and ethyl acted were used to activate the sensors. Isobutyl alcohol (ISO-C₄H₉OH) 100 ppm using nitrogen as the base gas was purchased from Takachiho Chemical Industrial Co. Ltd. (Tokyo, Japan). Ethyl acetate (CH₃COOC₂H₅) 100 ppm based by nitrogen gas was purchased from Taiyo Nippon Sanso Corporation, and

ethylene (C₂H₄) 100 ppm based by nitrogen was purchased from Sumitomo Seika Chemicals Co. Ltd. (Tokyo, Japan). A 60 mL syringe was used to inject samples.

Every experiment, a target gas was injected into the measurement chamber through injection inlet by syringe. The process of injection was presented as follows. At the beginning, the valves of the N₂ bottle and the exhaust hose were switched on to flush the measurement chamber with N₂ at a flow rate of 70 mL/min through adjusting the gas flow meter. When the QCM reached equilibrium, the valve of the N₂ bottle was switched off to stop N₂ from entering. Through penetrating the tip of syringe into the measurement chamber from the injection inlet, the sample gas was quickly injected into the bottom of the chamber at once. To obtain the following concentration levels of 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm in the measurement chamber, the volumes of 100 ppm sample gas needed to inject were 7.5, 15, 22.5, 30, 37.5, 45 mL, respectively. After one concentration level injection was completed, the valve of the exhaust hose was switched off, and data were recorded about 200 s. Then the valves of the N₂ bottle and the exhaust hose were switched on. The sample gas in the chamber was exhausted from the exhaust hose in Figure 1 until the resonance frequency counter (SC-7205 Universal Counter, Iwatsu Test Instruments Corporation, Tokyo, Japan) reached balance. The frequency change of the oscillator was saved once every second into a personal computer, which was controlled by LabVIEW software. All experiments were performed in a thermostatic room (22 \pm 2°C) and repeated 3 times.



1. N₂ bottle 2. Gas flow meter 3. Exhaust hose 4. Measurement chamber 5. Injection inlet 6. Quartz crystal resonator 7. Oscillator 8. Frequency counter

Figure 1 Schematic diagram of experimental setup

2.4 Sensitivity experiment

To explore the sensitivity of sensors coated with the above four sensitive materials versus different gas samples, all 3 target gases were detected by the experimental setup. The frequency shift was monitored on-line through the procedure of measurement. At the beginning of the experiment, the measurement chamber was cleaned thoroughly by N_2 at a flow rate of 70 mL/min to make the resonator reach equilibrium. Then N_2 was switched off and the frequency began to be recorded by LabVIEW software. At this time, the first sample injection towards a concentration of 5 ppm was conducted. Few seconds later when the frequency reached the peak, recording maintained about 100 s when the frequency reduced gradually after the first peak appeared. Before the second injection, the sensor was desorbed by circulating N_2 into the measurement chamber to flush the film again until the frequency reached equilibrium. In following injections, concentration added at each time. The samples were arranged at concentration gradients of 5, 10, 15, 20, and 25 ppm.

3 Results and discussion

3.1 Surface topography of sensing film

3D images of the four representative sensing films' surface at a micrometer scale are displayed in Figure 2. They clearly revealed that the topography of CA and EC coated films were porous, and rougher than that of the DOPS and GC coated films. The porous structure was beneficial to gas molecules diffusion. Those topography differences of different coated films were considered to be caused by molecular structure of film materials. The molecules of DOPS and GC showed strong polarity, and had hydrophilic heads and hydrophobic tails. Under the polar solvent condition, with solvent volatilization, DOPS and GC formed self-assembled membrane on the gold electrodes surface. Molecular arrangement was more orderly, which resulted in smoother films. However, EC and CA were not amphiphilic molecules. After dissolved in polar solvent, films formed with quick solvent volatilization with molecular arrangement being relatively disordered and structure being porous.

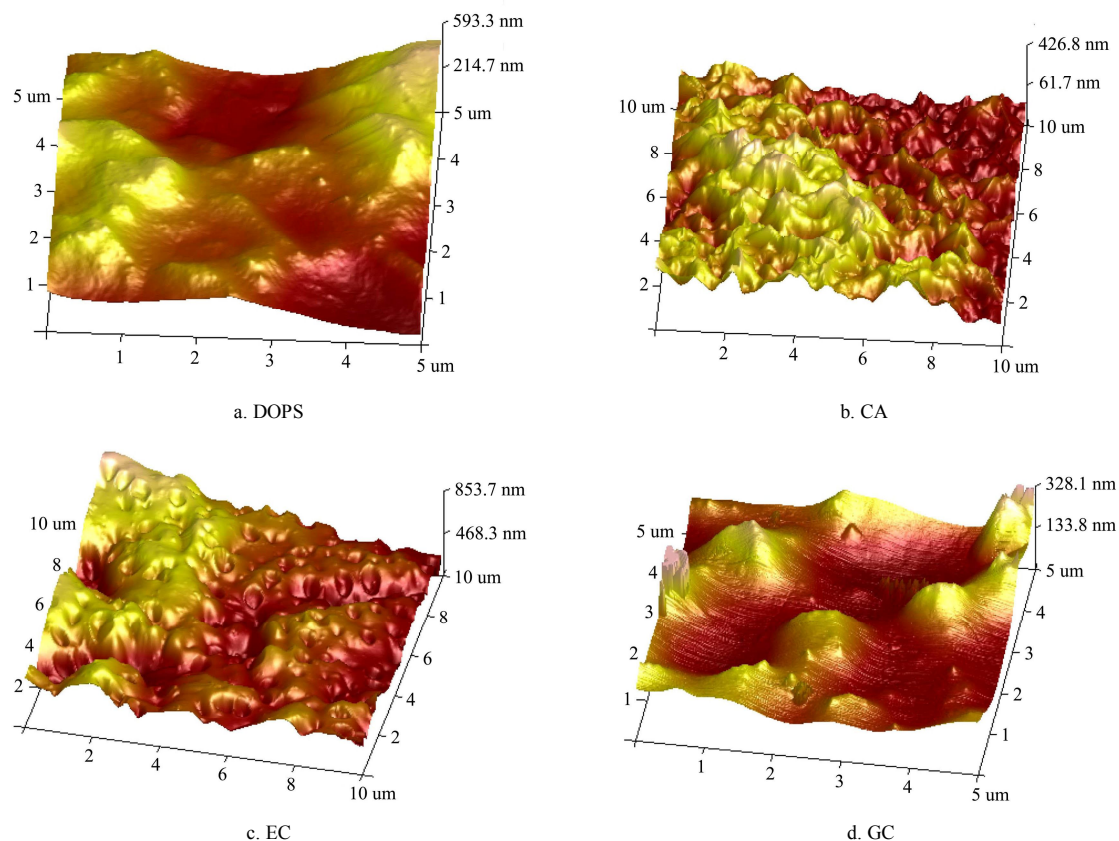


Figure 2 3D AFM images of sensors' film surfaces

3.2 Sensors responses to VOCs

Figure 3 shows the response frequency shifts of

sensors coated with DOPS, GC, EC, and EA exposed to isobutyl alcohol, ethyl acetate and ethylene vapor at

concentrations of 5, 10, 15, 20 and 25 ppm, respectively.

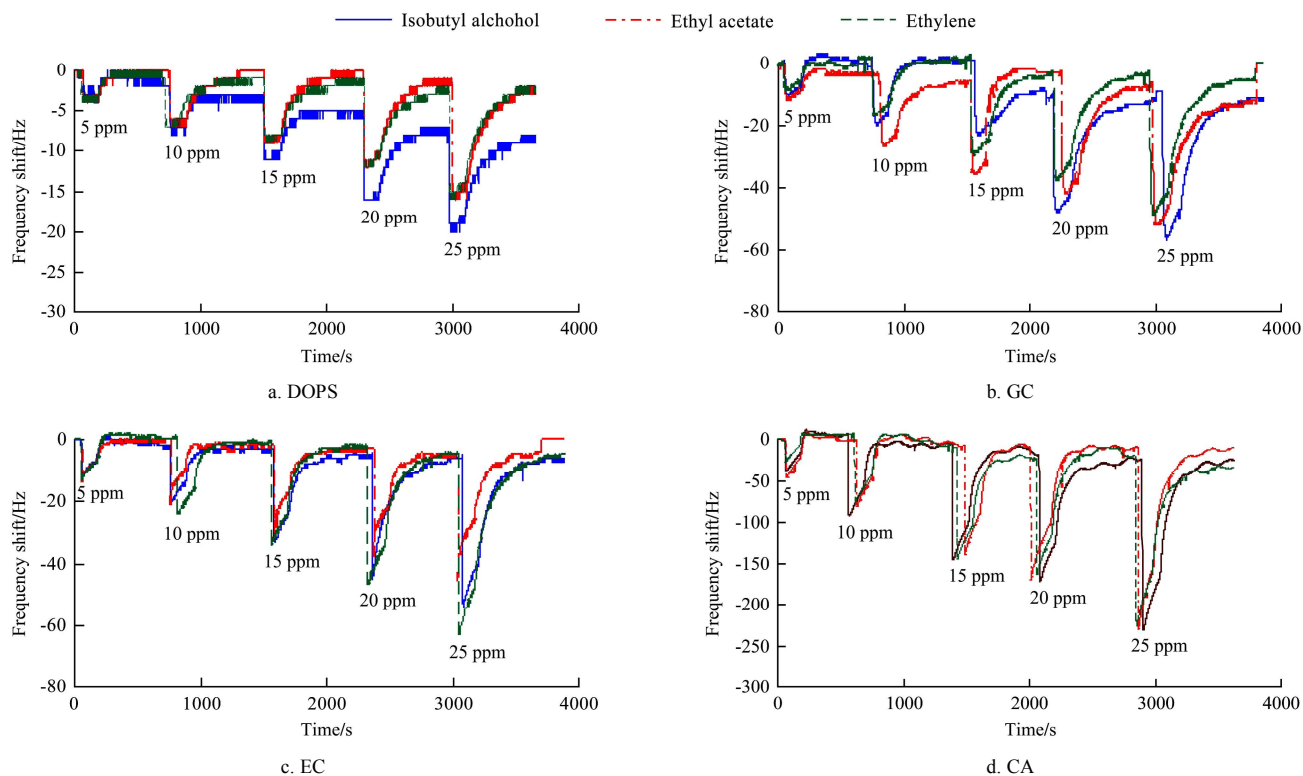


Figure 3 QCM sensors' responses to isobutyl alcohol, ethyl acetate, and ethylene at 5 concentration levels

After each injection the frequency reached peak in a short time and reduced gradually, which agreed with Mirmohseni and Hassanzadeh's research^[12,16]. Figure 3 clearly shows that with sample concentration increased, the frequency change increased. It indicated that all sensors responded fast, and had good reversibility to gas samples except for one pair: the DOPS coated sensor to isobutyl alcohol.

The CA coated sensor was significantly sensitive in responses to all VOCs, and its selectivity was not obvious. This phenomenon was due to the roughness and the porous structure of the film as such topography could contain more gas molecules. The selectivity of the DOPS coated sensor exposed to ethyl acetate and ethylene was the same. While for the DOPS coated sensor exposed to isobutyl alcohol, however, desorption of isobutyl alcohol was not complete due to the strong polarity of both DOPS and isobutyl alcohol (Figure 3a). In the concentration range of 5-25 ppm, the selectivity of GC to three VOCs was not obvious (Figure 3b). The sensitivity of EC coated sensor exposed to ethylene was the greatest, less to isobutyl, and the least to ethyl acetate (Figure 3c). The responses of the QCM sensor coated

with CA to three varieties of VOCs were rapid and reversible, which indicated that physisorption occurred during the measurement, and the frequency change trend versus concentration was almost in complete sync (Figure 3d).

It can be observed clearly from Figure 3 that the frequency shift couldn't return to 0 when flushing the measurement chamber, which showed that the oscillator didn't return to the initial frequency, and sensor drift occurred as the sample gas failed to desorb completely. The sensor drift of DOPS coated sensor to isobutyl alcohol was very obvious, since the drift increased over increasing concentration.

3.3 Linear correlation analysis

Figure 4 shows responses of modified QCM sensors to VOCs by plotting frequency shifts peak versus concentrations of every aroma compound vapor, and all linear regression equations are listed. In each graph the equations from top to bottom are for isobutyl alcohol, ethyl acetate, and ethylene, respectively. Their slopes and R^2 are also exhibited in graphs. The slopes indicate the sensitivity of sensors to VOCs^[12]. It was shown in the concentration range 5-25 ppm that the CA coated

QCM sensor was more sensitive than others as the value of sensitivity was over 4.5 Hz/ppm, and the R^2 readily exceeded 0.98. Compared with CA, DOPS coated

sensor was not sensitive to these VOCs as all the sensitivity values were below 0.5 Hz/ppm.

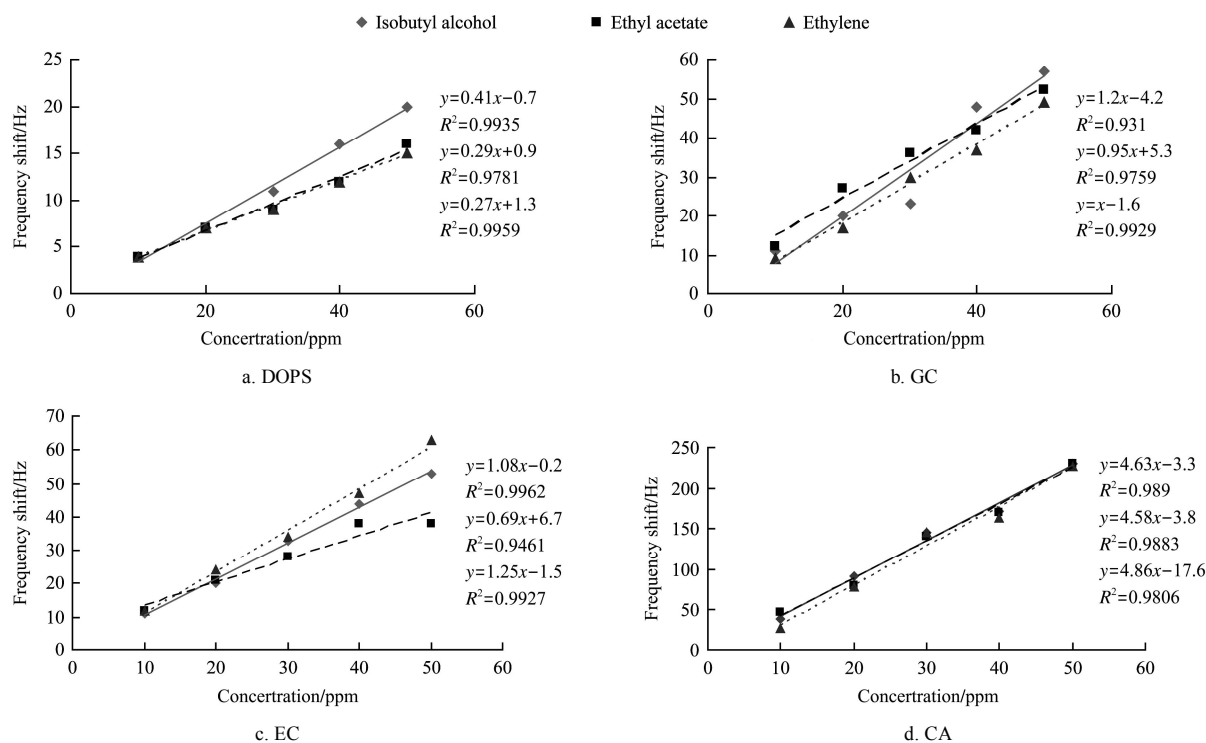


Figure 4 Sensitivity graphs of modified QCM sensors on VOCs

4 Conclusions

A gas detection system was established using modified quartz crystal sensors. To make effective sensors for fruit aroma ingredients, four coating materials: galactosylceramide (cerebroside, GC), 1,2-dioleoyl-sn-glycero-3-[phosphor-L-serine] (DOPS), ethyl cellulose (EC) and cellulose acetate (CA) were separately tested as coating materials on quartz crystal resonators. All four materials were sensitive to three major fruit aroma compounds: isobutyl alcohol, ethyl acetate, and ethylene on ppm level. Frequency shifts of four QCM sensors to isobutyl alcohol, ethyl acetate and ethylene were linearly correlated in ranges of 5-25 ppm. Results showed that the sensor coated with CA was clearly sensitive to three VOCs with sensitivity value over 4.5 Hz/ppm, which could be owing to the rough and porous structure of the CA coated film. Moreover, EC coated sensor was more sensitive to ethylene than to others. The overall sensitivity of the DOPS coated sensor to three VOCs was lower than the other sensors. Specifically, the sensor was more sensitive to isobutyl alcohol than to ethyl acetate and ethylene. For future application of this

system in the fruit industry, the detection of fruits' ripening stage was under experiment.

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