# Development of volatile-organic-compound gas sensor using wireless and electrodeless quartz crystal resonator

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## 1. Introduction

Detection of volatile organic compounds (VOCs) has attracted global attention because of its significance in environmental protection, human health management, food quality control, and industrial process monitoring. VOCs are emitted from various sources, such as industrial processes, research, medical treatments, and daily-life activities. For instance, toluene and xylene volatilize from paints and adhesives in industrial processes. Ethanol and methanol are utilized for disinfection and cleaning in laboratories and medical settings. These VOCs have the potential to cause several health problems based on exposure time and concentration[1]. Additionally, in the context of food quality, various VOCs such as alcohols and esters are released during spoilage[2,3]. Detecting and assessing these gas concentration enable us to monitor food quality. Furthermore, the breath of diabetes and lung cancer patients contains acetone[4] and toluene[5], respectively with other various VOCs. The detection of VOCs in exhaled breath enables early disease diagnosis. Hence, VOC detection is important for various field, demanding real-time monitoring and highly sensitive VOC gas sensors.

In this study, we employ a wireless and electrodeless quartz crystal microbalance (QCM) to a VOC sensor. QCMs are widely used in gas sensing[6,7] due to their excellent characteristics such as high sensitivity, low operating temperature, low power consumption, and low cost. Particularly the wireless and electrodeless QCM (WE-QCM) developed by Ogi *et al.*[8,9] achieves much higher mass sensitivity than conventional QCM because of no heavy-metal electrodes on the QCM surfaces. Here, we investigate the effects of surface condition of WE-QCM, VOC gas type, and its concentration.

## 2. Experiment

We use a 26-μm thick AT-cut quartz resonator, whose fundamental resonance frequency is 64.5 MHz. To detect VOC gas, we form sensitive membrane on the QCM surface. The sensitive membranes can be designed using materials like polydimethylsiloxane, which exhibits high affinity towards non-polar molecules, or polyaniline[10], used for detecting alcohols. When VOC gas molecules are adsorbed onto the sensitive membrane, affecting the resonance frequency and $Q$ value. We deposited 5-nm Cr and 8-nm Au on one side by the radio frequency magnetron sputtering method at room temperature. After deposition, those QCMs are first cleaned with a piranha solution (98% $H_2SO_4$: 30% $H_2O_2$= 7:3) and then rinsed with ultrapure water. To form PEG5000 membrane, we inject 10 mM PEG5000 in absolute ethanol and incubate around 16 h at 4℃.

**Figure 1** shows the flow and measuring system, where QCM is sandwiched between two

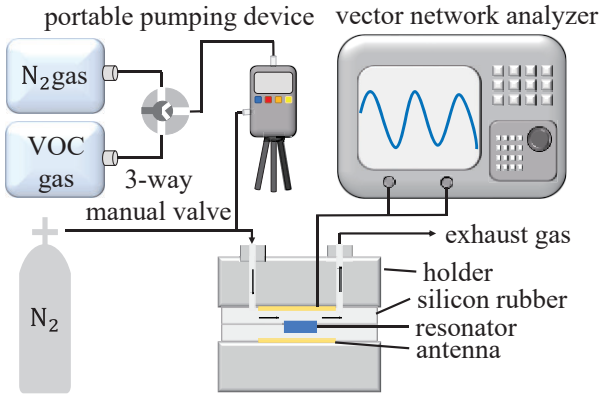


Fig. 1 Schematic diagram of VOC detection experimental system.

silicone rubbers and placed between two antennas in our sensor cell. Resonance frequency changes of the QCM are measured by a vector network analyzer. We prepare several concentration and type VOC gases by injecting VOC solution into a gas bag filled with nitrogen to achieve the desired concentration. We set the flow rates of 99.9999% nitrogen carrier gas and injection gas as 50 mL/min.

## 3. Result and Discussion

**Figure 2** shows the resonance frequency change of the QCM with PEG coating. We inject nitrogen, ethanol, N-methyl-2-pyrrolidone (NMP), and isoamyl acetate around 100 s, leading to an abrupt resonance frequency decrease. Subsequently, different resonance frequency changes trend are

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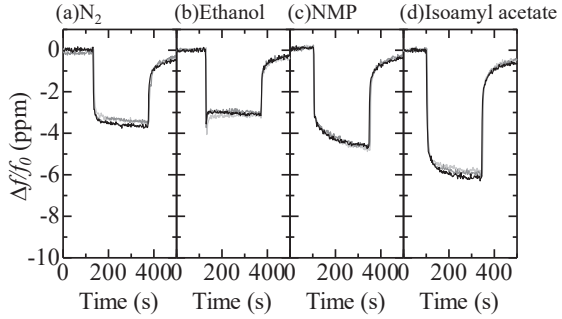


Fig. 2 Typical time-resonance frequency change when (a)nitrogen, (b)2000 ppm ethanol, (c)2000 ppm NMP, and (d)2000 ppm isoamyl acetate injection through a QCM formed with PEG5000 coating.

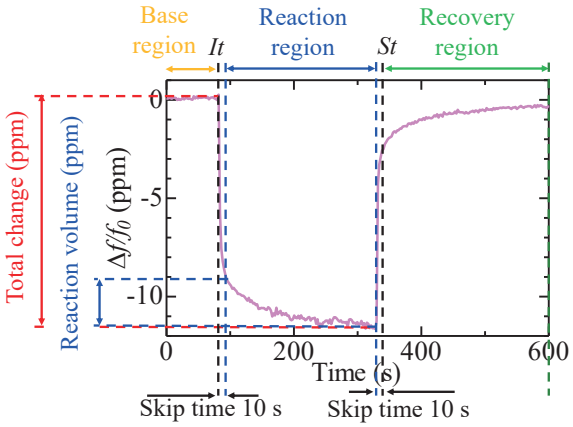


Fig. 3 Fitting method for time-resonance frequency changes due to gas injections.

observed depending on the gas type and concentration, and upon the end of gas injection, the resonance frequency recovered back to the baseline. The frequency changes by these gas injections are analyzed in three segments as shown in **Fig. 3**. A 10 s period after gas injections time (*It*) and a 10 s period after gas injection stop time (*St*) are excluded from the analysis because the effect of pressure changes by gas flow rate changes is more significant than the effect of gas adsorption in this time region. Firstly, we fit the base region and the obtained baseline slope is removed from the entire analysis range, where base region is fitted with a linear function again. Next, we fit reaction region, where the resonance frequency changes by gas adsorption, with Eq. 1.

$$y = A_{ad}e^{I_{ad}It} + C_{ad} \quad (1)$$

Subsequently, we fit Recovery Region, where the resonance frequency changes by gas desorption with Eq. 2.

$$y = A_{des}e^{I_{des}It} + C_{des} \quad (2)$$

$A_{ad}$ and $A_{des}$ are exponential amplitude, $I_{ad}$ and $I_{des}$ are exponential index, and $C_{ad}$ and $C_{des}$ are arbitrary constants. Using these parameters obtained from the analysis, they are plotted onto a two-dimensional plot.

As a result of the above analysis, we can distinguish gas species and evaluate the concentration. Particularly, isoamyl acetate and NMP show clearly different trends compared to the other gas species, making their discrimination easily. We aim to combine multiple VOC QCM gas sensors with different sensitive membranes to achieve the identification of a wider range of gas types.

## 4. Conclusion

In the WE-QCM coated with PEG5000 coating, successful discrimination of VOC gases and concentration identification is achieved for isoamyl acetate and NMP at 100 ppm. We are trying to detect and distinguish much lower concentration gases by optimizing the thickness and type of a sensing membrane. Additionally, when detecting the target VOC gases, it is generally required to detect them from complex gas mixtures, necessitating gas selectivity of the sensing membrane. Therefore, our goal is to achieve high sensitivity detection of various VOC gases by forming multiple types of sensing membranes on each QCM.

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