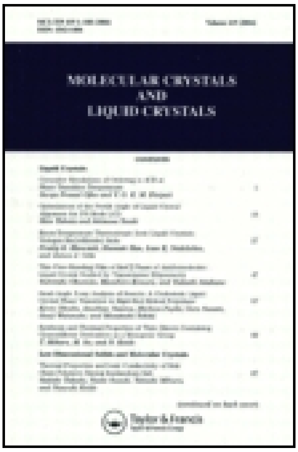

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Development of Environmental Monitoring Sensor Using Quartz Crystal Micro-Balance

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DEVELOPMENT OF ENVIRONMENTAL MONITORING SENSOR USING QUARTZ CRYSTAL MICRO-BALANCE

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Abstract A quartz crystal microbalance (QCM) sensor system for the detection of odorants, especially environmental pollutant, was constructed by depositing various phospholipids, activated carbon and lead-base inorganic pigment on the surface of the QCM. The identification of odorants is discussed in terms of comparison of their normalized patterns of resonant frequency shift and relative response intensities calculated from the response curve.

INTRODUCTION

Odor sensor has wide application area, such as physical and chemical analysis by gas phase detection as well as food quality control, control of fermentation process and environmental measurement and control. Especially, according to the increased interest on environmental problems, study in the field of environmental measurement and control has been actively conducted.

In 1959, Sauerbrey[1] found that quartz crystal can be used as a sensitive sensor by showing the relationship between frequency variation of quartz crystal and mass amount deposited on the crystal. And following King's suggestion[2] that selective film coated on quartz crystal is applicable to the analysis of organic gas, studies on the gas sensor using quartz crystal have been carried out by Guilbault[3,4] and Chang et al.[5,6] Recently, for the development of general purpose odor sensor imitated from olfactory mechanism, multi-channel sensor system in array arrangement of several sensors and analyzing technology of its response pattern were proposed by Ema et al.[7]

Though olfactory mechanism is not elucidated distinctly, Kurihara's proposition[8,9] that no specific receptor exists in olfactory cells and phospholipid and protein in the olfactory cells randomly adsorb odorant and give some response pattern to brain for recognition, is widely accepted. According to the proposition, Chang et al.[5,6] studied the recognition of odorants using quartz crystal, and found that the identification of odorant is available by analyzing the response pattern and it is essential to improve the response sensitivity.

In this study, a six-channel sensor system with various lipids, activated carbon and lead-base inorganic pigment coated on quartz crystal was composed to develop general purpose odor sensor having highly sensitive recognition ability. The sensitivity improvement with activated carbon and selective determination of sulfur compounds using lead-base inorganic pigment were investigated.

PRINCIPLE OF QUARTZ CRYSTAL

When radio frequency (RF) voltage is applied to electrodes attached on both sides of piezoelectric element in the direction of thickness, RF voltage is converted into bulk acoustic wave. Also, if gas is adsorbed on the surface of the quartz crystal, resonant frequency of the bulk acoustic wave varies.

The relationship between the adsorbent mass variation and resonant frequency variation was obtained by Sauerbrey[1]. The sensitivity of QCM is directly pro-portional to the square of resonant frequency and mass variation, and inversely proportional to surface area.

EXPERIMENTAL

Material

Cholesterol, lecithin extracted from soybean, lecithin from egg, activated carbon, lead-base inorganic pigment and alkyd resin were used as sensitive film material. Odorants are propanol, hexane, geosmin, borneol, trimethyl amine and hydrogen sulfide.

Experimental Procedure

Home made six-channel quartz crystal system is demonstrated in Figure 1. The system consists of six quartz crystal and six oscillation circuit and one of the six signals is selected by a personal computer for the measurement of frequency and response analysis. The quartz crystal of this study is 9 MHz AT-cut crystal and electrode diameter is 5 mm. A brief schematic of experimental setup is shown in Figure 2. The setup is composed of thermostat cell, quartz crystal, micro-syringe, frequency counter and personal computer.

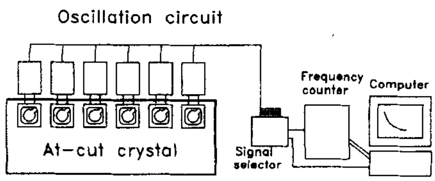

Figure 1 Schematic diagram of oscillation system.

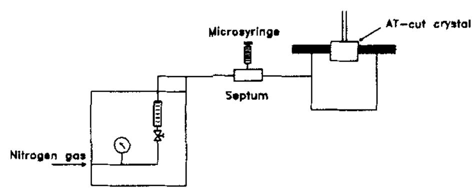

Figure 2 Schematic diagram of experimental apparatus.

Quartz crystal coated with natural lipid is installed in the thermostat cell and nitrogen is fed until resonant frequency is stabilized. After the frequency maintains steady state, odorant is momentarily introduced with micro-syringe and frequency variation is continuously measured with personal computer. Gas concentration is adjusted by odorant amount. Natural lipid is dissolved in chloroform (5 mg/ml), coated on both sides of crystal and dried. The amount of coated lipid is adjusted by measuring frequency variation while the stability of crystal frequency is maintained.

Lead-base inorganic pigment is coated on the crystal for the measurement of sulfur compound. Hydrogen sulfide is generated by dropping sodium sulfide solution in acidic solution contained in sample holder and mixed with nitrogen.

RESULTS AND DISCUSSION

The response of lecithin and activated carbon coated quartz crystal to propanol is given in Figure 3. As applied amount of propanol increases, frequency variation is proportionally raised. Curve (1) is the response of both lecithin and activated carbon coated crystal and (2) is of lecithin only coated crystal. Activated carbon added case shows much better response owing to the increase of effective surface area by adding activated carbon.

For the investigation of sulfide measurement, response curves of resin only coated, inorganic pigment only coated and both resin and pigment coated cases are compared in Figure 4. Resin coated case of curve (1) shows a sudden increase of frequency variation when hydrogen sulfide is applied and the frequency variation is drastically reduced in a couple of minutes to become the initial frequency after 10 minutes. Inorganic pigment is coated in case (2). The frequency is elevated for 2 - 3 minutes and sustained after about 5 minutes because of reaction between sulfide and pigment. In case (3) of resin and pigment coated crystal, the frequency is raised continuously and slowly reduced. Also, after 5 minutes it maintains at a steady frequency. The difference in peak frequency variation is caused by selective reaction between pigment and sulfide. The increased adsorption surface of pigment and resin coated case raises peak frequency variation. Therefore, pigment coated crystal can be employed in the selective analysis of sulfide gas.

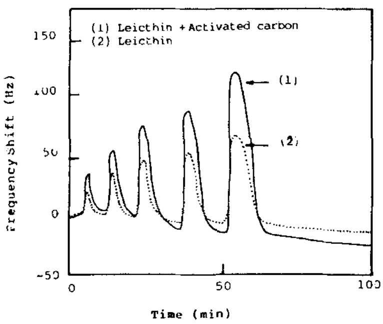

Figure 3 Typical response of AT-cut crystal exposed to consecutive pulse of propanol.

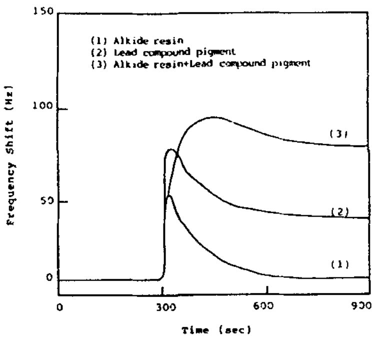

Figure 4 Typical response of lead-base pigment coated AT-crystal exposed to hydrogen sulfide

The frequency variations of lecithin and activated carbon coated crystal for the various concentrations of hexane, geosmin, borneol and trimethyl amine are demonstrated in Figure 5. In this case, the variation is proportional to the concentration of odorant. Also, frequency variation increase is observed for borneol and trimethyl amine and decrease is for hexane and geosmin. It indicates that adsorption of odorant varies not only mass but characteristic of lipid film. In other words, a certain organic gas makes the contact between crystal surface and lipid film loose and the frequency variation is lowered. The same result was observed by Gregory[10]. The response pattern for various odorants based on frequency variation is given in Figure 6 as a bar graph where each odorant shows different pattern. It implies that the pattern can be used for odorant identification.

As a desorption parameter in odorant analysis, the relative response strength calulated from response curve area can also be utilized in the response pattern analysis in which the response pattern is specific and distinct for each odorant. As a con sequence, in the identification of odorant with momentarily varying concentration, the comparison of frequency variation and relative response strength gives an easy identification of odorant species.

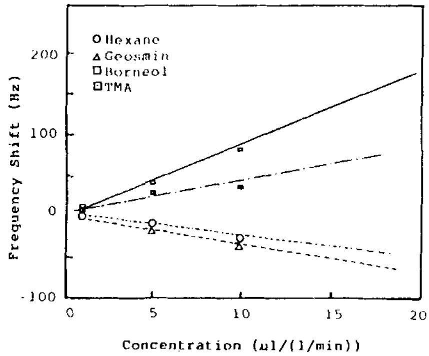

Figure 5 Correlation between odorant concentration and frequency shift for lecithin and activated carbon coated AT-cut resonator.

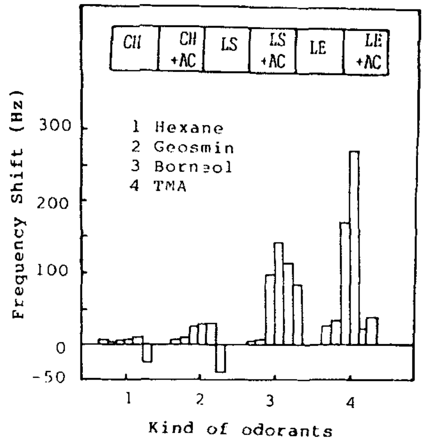

Figure 6 Response patterns of resonant frequency shift.

CONCLUSION

When both lipid and activated carbon are coated on the surface of quartz crystal, activated carbon increases the effective surface area of film and the adsorption of odorant is improved to result in high frequency variation. Simultaneous measurement of frequency variation and relative response strength improves the identification ability for odorant in rapid concentration change system. And it is found that the steady state frequency variation of lead-base inorganic pigment coated film is sustained after contacting sulfide owing to the reaction between pigment and sulfide. As a result, the pigment coated sensor can be used in the selective measurement of sulfide.

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