Real-time sensing of roses' aroma using an odor sensor of quartz crystal resonaotors

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Abstract: In order to detect plant aroma in a natural environment, we have investigated roses' aroma using an odor sensor of quartz crystal resonator (QCR). In present work, we describe experimental setup for real-time sensing of roses' aroma and feature extraction of roses' aroma sensed by QCR sensors. This method can distinguish as different aroma as human sense of smell judged for two kinds of roses. We measured one rose's aroma 3 times repeatedly in first day, second day and third day, respectively, and the result shows that rose aroma of first day is different from the ones of the other two days.

References

[1] S. Mitachi, K. Sasaki, M. Kondoh, and I. Sugimoto, "Odor Sensing in Natural Environment Using Quartz Crystal Resonators: Application to Aroma Sensing of Roses Cultivated in an Outside Garden," *Acta Horticulturae*, no. 679, pp. 113–119, 2005.

[2] M. Indou, "Scent and its chemical composition of various rose species and hybrids," *aromatopia*, no. 28, pp. 18–20, 1998.

[3] M. Takano, K. Sasaki, T. Muto, I. Sugimoto, and S. Mitachi, "Aroma Sensing of Roses Using an odor sensor of Quartz Crystal Resonators," *J. Japan Association on Odor Environment*, vol. 36, no. 6, pp. 345–355, 2005.

[4] I. Sugimoto, M. Nakamura, H. Kuwano, and R. Shimada, "Environmental Gas-Sensing Using Plasma-Deposited Organic Films," *Trans. IEE of Japan*, vol. 118-E, no. 2, pp. 86–91, 1998.

[5] I. Sugimoto, M. Seyama, M. Nakamura, N. Kasai, T. Mashiba, and K. Yasuda, "Molecular Structures and Organic Gas Sorption Characteristics of Carbonaceous Films Prepared by Sputtering of Organic Molecules," *Maku (Membrane)*, vol. 30, no. 2, pp. 105–115, 2005.

1 Introduction

In order to detect aroma in natural environment using the odor sensor of quartz crystal resonator (QCR), we have already investigated to find the most suitable desiccant to eliminate moisture influences [1]. It has been also

reported that constituents of rose aroma are different from each other in roses [2]. Then, we have measured 20 kinds of roses to detect and classify aroma of these naturally being cultivated roses in an outside garden using an odor sensor of quartz crystal resonators [3].

A flower of rose was covered by a Tedlar-bag® and we collected rose aroma before sensing. This metod enabled us to detect the aroma of roses cultivated in outside garden, but it needs more than three hours. There was the possibility that surrounding air entered into the bag from a small space. In present work, we introduced the aroma of fresh-cut flower settled in the glass container directly into the sensor. The time between introducing the aroma and obtaining the measurement results was reduced drastically.

We obtained a baseline, where signal is stable, before introducing aroma into the sensor. We extracted the aroma feature from the change before and after aroma introducing. It took more than five minutes from signal changing to signal stabilizing. We tried to shorten the time drastically to decide the feature of the aroma by improving the experimental setup and the data processing method.

In present work, we have measured two kinds of roses' aroma. Authors have different impression for these. One of them is sweet, the other is citrus. These are *Garden-party* and *Royal-highness*, respectively. These roses are cultivated in outside garden in Tokyo University of Technology. A cut rose was measured immediately, after one day and after two days.

2 Experiment

Figure 1 is a photograph of a commercially available odor sensor system and its sensor elements. The system is constituted by a sensor part which is composed by seven QCR sensor elements with organic sensory films [4]. In present work, the sensor consists of carbonaceous films prepared by sputtering of organic molecules. The sensors can detect chemical compounds broadly and have the detection limit at the ppb level [4]. The sputtered films from monomeric biomolecules, such as amino acids and monosaccharides, have small sorption capabilities over wide range of organics gases. On the other hand, EVA (Ethylene vinyl acetate) and PE (Polyethylene) films have large sorption capacities. The combination of dissimilar films, which are highly orthogonal with each other, can offer the discriminative of organic gases. They are capable for classification of functional groups [5]. Many compounds have been identified in rose aromas. The main components of aromas are Citronellol ($C_{10}H_{20}O$), Geraniol ($C_{10}H_{18}O$), Phenethyl alcohol ($C_8H_{10}O$) [2]. It has been reported that the sensors can detect these chemical compounds as different patterns, each other [1].

The resonant frequency changing signals are fed into a personal computer through a serial interface. Multiple sensor modules can be connected together and used at the same time with one personal computer. The circuit board contains an oscillation circuit for each QCR. S1 (D-Phenylalanine), S2 (D-Tyrosine), S3 (DL-Histidine), S4 (D-Glucose), S5 (Adenine), S6 (Polyethylene),

S7 (Polychlorotrifluoroethylene). S8 is the sealed D-Phenylalanine for temperature monitoring. S9 is the standard QCR offering the reference resonance frequency. Other parts are an electric power supply and a data processing PC.

A schematic diagram of the experimental setup is shown in Fig. 1. This setup consists of three glass containers connected with tubes: the first is for odor sensor positioned in, the second is for a fresh cut flower in, and the third is empty and for reference. In present work, there are two gas routes. One is a route to decide the baseline by introducing pure air into the container. Another one is a route to measure rose aroma by pure air introducing to the glass container. We introduced at first pure air to clean the odor sensor and to obtain a baseline. Just before sensing, cut flower is put it in glass container. We turned the valves to introduce a rose aroma into the sensors from the glass container. Both are adjusted in the same flow rate. Each route is switched with the valve.
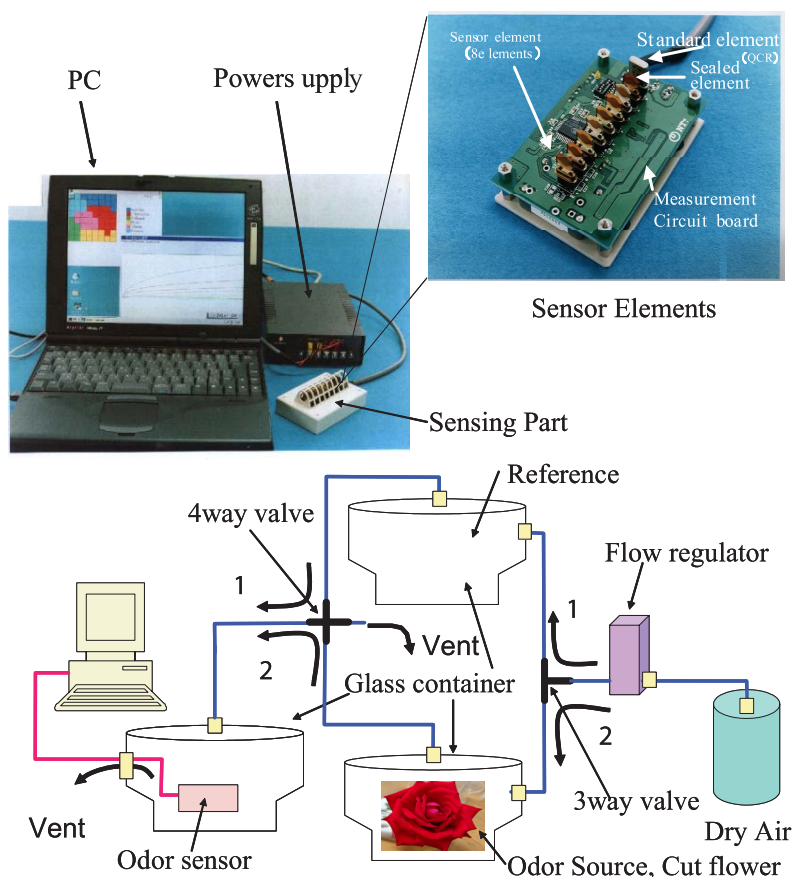

Fig. 1. QCR type odor sensing system and experimental setup for real-time roses' aroma measuring

When rose aroma is introduced into the sensors, frequency shifts are generated by the sensors according to molecular selectivity of the adsorption layers. In present work, the times in which frequency shifts to maximum are

expressed by equation (1), and these times are normalized by equation (2),

$$t_n = \max \Delta f_n, \tag{1}$$

where Δf_n is frequency shift about the elements S_n, n is the number of sensor elements,

$$\frac{t_n}{\sum_{n=1}^{6} t_n}, \tag{2}$$

where t_n is time of maximum frequency shift for the element S_n, and n is the number of each sensor element. This is an equation to exclude strength of the aroma and to characterize constituent of rose aroma proportional to composition ratio.

It has reported that the constituent composition ratio of rose aroma is different in each other rose [2]. This sensor element is a mass-sensitive transducer. Sensor elements with different molecular selectivity are assembled in an array. When the sensor detects an odorous compound, each element generates a different electrical signal pattern, respectively. We distinguish each aroma by the different patterns.

The QCR type sensor system is suitable to detect the rose aroma as the constituent ratio difference in a gas mixture. This system's baseline fluctuation is less than $2\,\mathrm{Hz/min}$ and pure air flow rate was $0.5\,\mathrm{L/min}$. The duration of rose aroma introduction was 1 second. The experiments were done with no desiccant.

3   Results and discussion

Figure 2 indicates a measured example. The time to reach maximum frequency shift is different in each sensor. The reason why we did not use frequency shift but used time delay is that the sensor output makes difference apparently. Concerning S1, S2 and S3 in Fig. 2, the difference of the time delay is more apparent than that of the frequency shift. It is similar in S4 and S5. We investigated two kinds of roses, *Garden-Party* and *Royal-Highness*, and for *pure water* as a reference.

The aroma was introduced to the sensor during only 1 s from 30 s to 31 s. The change occurred after 42 s. The change doesn't occur at the same time as aroma introduced to the sensor. It can be thought that the aroma diffusion throughout the glass container is nesessary for sensors to respond.

Figure 3 shows radar chart patterns of aroma features calculated with equation (2). Each result indicates the mean value of three times measurements. The values of S3, S5 and S6 show that the patterns of *Garden-Party* and the one of *Royal-Highness* are different[1].

Transpiration is the evaporation of water from aerial parts of plants, especially in leaves but also in flower petals. The pattern of *pure-water* is different from the other patterns. This indicated that in addition to the evaporation of water, another gas molecules evaporated from roses appear in the patterns.

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[1]In the feeling by authors' sense of smell, an aroma of *Garden-Party* was sweet and that of *Royal-Highness* was citrus.

The data for *Garden-Party* show the results for measurement of one time a day for three days repeatedly. The data for S1, S2, S3 and S4 show that the pattern of first day is different from those of second day and of third day. It can be thought that the chemical components of rose aroma have been changed by aging.

We tested the error range of the mean delay time for each sensor in an aroma of the *Garden-Party*. If the data are expressed by normal distribution function, 68% of the values are within one standard deviation. In our experiments, there was no overlap between the mean value of the first day and the second day or the third day about this confidence interval. These two mean values are significantly different. Therefore the probability that more than two sensors are in the same time in error is very small.
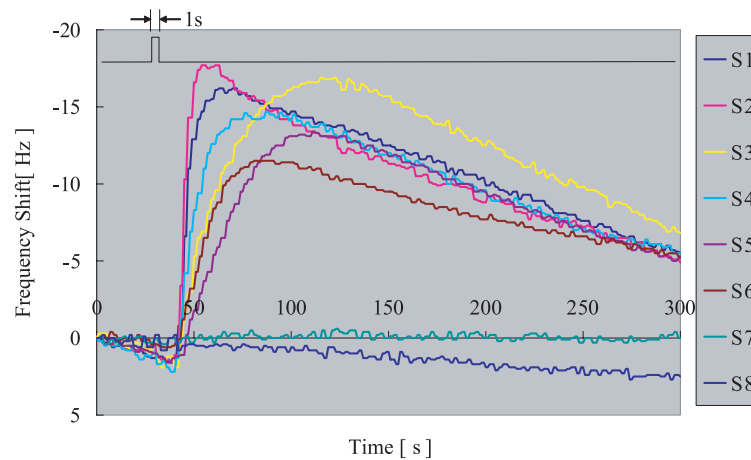
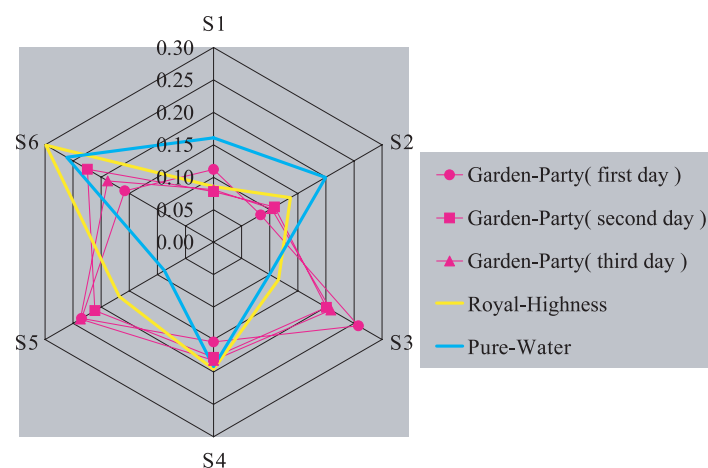**Fig. 2.** Frequency shift of an odor sample

Fig. 3. Radar chart patterns of *Garden-Party, Royal-Highness* and *Pure-water*

4   Conclusion

In present work, an experimental set up, in which the rose aroma can directly be introduced into the sensor, was prepared. The experimental results of radar chart patterns for aroma of *Garden-Party* and *Royal-Highness* indicated that each kind of rose classified into two patterns. We concluded that roses can be distinguished each oher by the system. We need further detail investigation to detect the very slow change by freshness lost etc. Nevertheless, this work will allow us to classify a rose real-timely, when it is applied to synchronize color/shape image processing with the odor sensing. If the odor sensing with this method is repeated, it seems to be useful measurement of aroma change of fresh cut roses.