Odor Sensing in Natural Environment Using Quartz Crystal Resonators: Application to Aroma Sensing of Roses Cultivated in an Outside Garden

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Abstract
In order to detect phytoncide or aroma in a natural environment using an odor sensor of quartz crystal resonator (QCR), the authors investigated the most suitable drying agent to eliminate moisture influences. The odor sensor used is a system of QCRs coated with organic sensory films. It was experimentally found that calcium chloride is the most suitable desiccant for odor sensing to eliminate moisture influences and for use in the natural environment. We then measured 6 kinds of roses; *Love* (red), *Star light* (yellow), *White Christmas* (white), *Snow white* (white), *Catherine Deneuve* (pinky orange), and *First love* (pink), to detect the aroma of these naturally cultivated roses in an outside garden. We have successfully detected the aroma of roses by eliminating moisture influences on the odor sensor by using a calcium chloride desiccant tube. It was found that *White Christmas*, *Star light*, and *Catherine Deneuve* indicate a similar pattern and *Snow white*, *First love*, and *Love* indicate another similar pattern. It was concluded that the odor similarity is not corresponding to the color of roses.

INTRODUCTION
Chemical communication among plants in the natural environment is an interesting phenomenon. In this communication, phytoncide or aroma plays an important role. The concentration of these phytoncides, or aroma compounds, in the natural environment is very low in general. The real time monitoring is important to elucidate the chemical communication in the natural environment. The odor sensor comprised of a quartz crystal resonator (QCR) coated with the sensitive films should meet these requirements. The QCR coated with plasma organic films made up from radio-frequency sputtering has an extremely low detection limit of less than ppb level for organic vapors (Sugimoto et al., 1999). However, the characteristics of these organic sensory films are easily influenced by the moisture of the atmosphere. The most suitable desiccant was investigated to eliminate moisture influences. If the moisture influences on the QCR sensor can be eliminated, it is possible to sense odor in a natural environment as we like. This paper reports the most suitable desiccant for odor sensing to eliminate moisture influences and for use in the natural environment. By using the desiccant, the authors have successfully detected the aroma of 6 kinds of roses which are naturally cultivated in an outside garden. Finally, we compare the patterns among 6 kinds of roses and the representative ingredients of rose aroma, *citronellol*, 2-*phenylethanol*, and *geraniol*, as references.

MATERIALS AND METHODS
Principle and Apparatus
In 1959, Sauerbray found the mass loading effect on quartz crystal resonator (Sauerbrey, 1959), which is expressed by the following relation between the minute mass changes of quartz crystal vibrator and the shift of resonant frequency,
where $df$ is the shift of resonant frequency, $f$ is resonant frequency, $dM$ is mass change of quartz crystal resonator, $v$ is sound wave velocity, $S$ is area of electrode, and $\rho_q$ is the density of quartz crystal. Fig. 1 is the structure of QCR and Fig. 2 shows the setup of odor sensing system used in the series of experiments.

The attached photographs indicate a commercially available odor sensor system and its sensor elements (Fig. 3 and 4). The system is constructed of a sensor part which is composed of seven QCR sensor elements with organic sensory films; #1 (D-Phenylalanine), #2 (D-Tyrosine), #3 (DL-Histidine), #4 (D-Glucose), #5 (Adenine), #6 (Polyethylene), #7 (Polychlorotrifluoroethylene), #8 is the sealed D-Phenylalanine for temperature monitoring, #9 is the standard QCR offering the reference resonance frequency. Other parts include an electric power supply and a data processing PC.

Desiccant Selection

In order to find the best desiccant to eliminate moisture, $\alpha$-pinene was used as a representative example of aroma and tested silicagel, CaCl$_2$, P$_2$O$_5$, and CaO (Mitachi, 2002; Mitachi, 2003). Fig. 5A shows an experimental set up to test desiccant efficiency. By using a three way valve and a four way valve, pure air was first introduced to clean the odor sensor and obtain a base line. Then these valves were turned to introduce $\alpha$-pinene vapor from the bubbler and passed it in purified water in a gas washing bottle when to introduce it with 100% relative humidity air. Seven experimental conditions were tested; (1) Ambient air only, (2) Relative humidity 100% air, (3) Ambient air with desiccant, (4) Relative humidity 100% air with desiccant, (5) Ambient air with sample gas, (6) Ambient air with sample gas and desiccant, (7) Relative humidity 100% air with sample gas and desiccant (Mitachi, 2003).

Rose Aroma Sensing: Fig. 5B shows the set up of rose aroma sensing. A Tedlar-bagTM was used to collect rose aroma. A rose flower was covered by a Tedlar-bagTM in the evening of the day before sensing and collected the next morning. The bag was set up with the system and the aroma in it was measured by the odor sensor (Fig. 5B).

RESULTS

Selection of Desiccant

The 7 step experiment proceeded to select the best desiccant for aroma sensing among silicagel, CaCl$_2$, P$_2$O$_5$, and CaO. The detailed results and discussion are being reported (Mitachi, 2002; Mitachi, 2003). In this paper, the authors reported the important conclusion to apply to the rose aroma sensing. Fig. 6 shows time course of resonant frequency shift (RFS) for ambient air. #1 and #3 elements of the sensors shows large RFSs. Fig. 7a shows time course of RFS for 100% relative humidity air. Several elements including #1 and #3 show large RFSs. Fig. 7b is for ambient air with a desiccant CaCl$_2$. 6 elements show downward shifts, which mean moisture dissolution from the surface of each element. Fig. 8 shows time course of RFS for ambient air mixed with $\alpha$-pinene vapor and for ambient air mixed with $\alpha$-pinene vapor with the desiccant CaCl$_2$. It is clear that elements #2 and #6 show large RFS in both cases with and without the desiccant. On the other hand, the sensory behaviors of #1 and #3 elements changed so much between with and without desiccant. This result indicated that the desiccant of CaCl$_2$ eliminates moisture very well and it does not influence $\alpha$-pinene vapor. This means it is very useful as a desiccant for odor sensor use in the natural environment. As we have already reported, silicagel adsorbed both aroma compounds and moisture, and the results were unstable (Mitachi, 2002). The authors are reporting that P$_2$O$_5$ could not absorb moisture perfectly and reacted with $\alpha$-pinene inducing decoloration. CaO did not adsorb $\alpha$-pinene but could

$$df = \frac{-2f^2dM}{\nu S \rho_q}$$
not absorb moisture perfectly. $CaCl_2$ is the best desiccant for the QCR odor sensor because it does not react with aroma, eliminate moisture effectively and the results were reproducible. These results indicate that we can distinguish an aroma ($\alpha$-pinene) under high humidity and the odor sensing system with the desiccant $CaCl_2$ is very effective.

This system seems to be widely applicable to the sensing of various kinds of aroma under natural environment; in a high humid forest or jungle.

**Application to Aroma Sensing of Roses Cultivated in an Outside Garden**

Based on the above-mentioned result, we tried to detect the aroma of 6 kinds of different colored roses; *Catherine Deneuve* (pinky orange), *Star light* (yellow), *Snow white* (white), *White Christmas* (white), *Love* (red), and *First love* (pink).

These roses were naturally being cultivated in an outside garden on our university campus. Each rose’s flower was covered with a Tedlar-bagTM (Fig. 9). These roses were blooming in June and early July of 2002, which was the rainy season in Japan.

After collecting aroma from the rose inside the bag, we measured using the QCR odor sensor with a desiccant tube of $CaCl_2$ (Fig. 5B). Fig. 10 shows time course of RFS for *Catherine Deneuve*. Six elements from #1 to #6 showed large shifts for the sampled aroma.

**DISCUSSION**

We have just proposed a pattern recognition method of RFS of our odor sensors by using a radar chart [5], in which the RSF for each element was normalized by the RSF of element #1 which usually indicates the maximum RFS. Fig. 11 shows the radar charts using the normalized RFSs for *Catherine Deneuve*. #1, #3, and #4 elements reacted relatively well. Fig. 12 shows the radar chart using the normalized RFSs for *Catherine Deneuve* (pinky orange), *Star light* (yellow), and *White Christmas* (white). These roses showed similar patterns, which #1 and #3 elements react well. *Citronellol* was also measured as a reference of aromatic constituent of rose and its pattern was shown in Fig. 13. This shows similar pattern as Fig. 12. This means the possibility that the main aromatic constituent of these roses is *citronellol*.

Fig. 14 shows the other similar patterns of *Snow white* (white), *Love* (red), and *First love* (pink). These roses showed another very similar pattern, in which #1, #4 and #3 elements reacted well. These patterns are similar to the pattern of 2-phenyl ethanol which is also well known constituent of roses (Fig. 15).

We also measured another well known constituent of roses, *Geraniol*. This pattern is shown in Fig. 16 and is different from Fig. 12 and 14. The authors are now trying to analyze numerically by the mixing of these rose constituents to estimate the containing ratio in each rose.

By using the QCR odor sensor with $CaCl_2$ desiccant, the authors successfully measured RFS curve for 6 kinds of roses in the natural environment eliminating moisture influences. By the numerical calculation of a newly proposed pattern recognition method, it was found that we can classify into two groups those having similar patterns. Further, we have found an interesting result that there is no correlation between color and aroma of these roses. By the comparison between the pattern of pure reference aroma; *citronellol*, 2-phenyl ethanol, and *geraniol*, and the ones of measured rose’s, one group pattern is similar to *citronellol*, and the other is similar to 2-phenyl ethanol. It can be speculated that these are the main constituents of these roses, respectively.

**Literature Cited**


**Figures**

Fig. 1. Structure of QCR.

Fig. 2. Setup of the odor sensing system.

Fig. 3. QCR type odor sensing system.

Fig. 4. Sensor elements.
Fig. 5. Experimental setup.

Fig. 6. Time course of RFS for Ambient air.

Fig. 7. (a) Time course of RFS for 100% relative humidity. (b) Time course of RFS for ambient air with desiccant (CaCl₂).
Fig. 8. (a) Time course for ambient air with $\alpha$-pinene. (b) Time course of RFS for ambient air mixed with $\alpha$-pinene using desiccant (CaCl$_2$).

Fig. 9. Tested roses and sampling of aroma.

Catherine Deneuve (pink-orange)  Star light (yellow)  Snow white (white)

White Christmas (white)  Love (red)  First love (pink)

Fig. 10. Time course of RFS for Catherine Deneuve.
Fig. 11. Radar chart for Catherine Deneuve.

Fig. 12. Radar charts of the similar pattern to Catherine Deneuve.

Fig. 13. Radar chart for Citronellol.

Fig. 14. Radar charts of the other similar pattern than Fig. 12.

Fig. 15. Radar chart for 2-phenyl Ethanol.

Fig. 16. Radar chart for Geraniol.