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A Novel Chemosensor System Using Surface Plasmon Resonance Taste Sensor and Metal Oxide Odor Sensor for Quality Control of Vinegar

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A taste sensor based on surface plasmon resonance (SPR) with four channels is studied for quality control of the fermentation process of vinegar. Each channel of the SPR taste sensor responds to the change in quality of the vinegar which has been fermented for 1 day, 7 days and 14 days. The responses of each channel of the SPR taste sensor clearly change with the number of fermentation days, indicating that the SPR taste sensor will be useful for quality control in the preparation of vinegar. The SPR taste sensor also responds to different types of vinegar such as *kome-su*, *junkome-su* and *gousei-su*. It is also found that the commercially available odor sensor using a metal oxide semiconductor responds to the change in the odor intensity of the vinegar which is estimated using the human nose. These results suggest that a sensor system using an SPR taste sensor and a metal oxide odor sensor will be useful for identification of the types of vinegar.

1. Introduction

In recent years, chemosensors such as odor sensors based on the resistance change in metal oxide semiconductors (MOS), odor sensors based on the resonance frequency change in quartz resonator microbalances (QCM) and both odor and taste sensors using

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surface plasmon resonance (SPR) have been extensively studied for application to the quality control of foods and beverages in the food industry.(1–3) Recently, these types of chemosensors have been labeled "kansei biosensors" in Japan, because a chemosensor array system which consists of taste and odor sensors offers the possibility of measuring the kansei quantity which corresponds to that of humans.(2)

SPR is an optical phenomenon in which incident light excites a charge-density wave at the interface between a highly conductive metal and a dielectric material. The conditions for excitation are determined by the permittivities of the metal and the dielectric material. The SPR transduction principle is widely used as an analytical tool for measuring small changes in the refractive index of a thin region adjacent to the metal surface. The optical excitation of surface plasmon on a thin metallic region has, therefore, been recognized as a promising technique for the sensitive detection of chemical species by taste and odor sensors.(4) Several methods have been employed to monitor the excitation of SPR by measuring the light reflected from the sensor interface. These include analysis of angle modulation,(5) wavelength modulation,(6) intensity modulation(7) and phase modulation.(8)

We have previously reported that a chemosensor based on SPR responds to quality changes in Japanese sake and is useful for quality control in the fermentation process and identification of the type of Japanese sake.(9–11) The main objective of this study is to demonstrate a novel chemosensor system using an SPR taste sensor and a metal oxide semiconductor odor sensor for quality control in the case of vinegar.

2. Experimental

Optical SPR sensors are sensitive to changes in the refractive index of a sample placed near the sensor surface as described above. In the experiment, SPR was measured using a Kretschmann configuration(5) (Nihon Denki Kagaku: SPR-20) with a prism and a thin highly conductive gold metal layer. An LED emitting 660 nm light was used as the light source to excite the SPR. The SPR reflection spectrum (intensity of reflected light versus angle of incidence with respect to the normal of the metal/dielectric interface) was measured by coupling transverse magnetically polarized monochromatic light into the prism as shown in Fig. 1.

The reflected light was measured using a charge-coupled device (CCD) camera attached to a personal computer. The angle at which the minimum reflection intensity occurs is the resonance angle at which coupling of energy occurs between the incident light and the surface plasmon waves. Four channel images (Ch.1 – Ch.4) of reflected light were observed using the CCD camera, because the CCD image can be divided into four channels using computer software. The volume of the sensor unit cell was 2.5 ml. To utilize this system as a sensor for measuring quality changes in vinegar, distilled water was used as the reference liquid as shown in Fig. 2.

Commercially available MOS odor sensors such as those listed in Table 1 were used for detecting the odor from vinegar. Vinegar samples were fermented for different numbers of days, and the three kinds of vinegar used were supplied by Takanosu Co., Ltd. The types of vinegars used in the experiment, their acidities, additions of NaCl, additions of acetic acid and the raw materials are listed in Table 2.

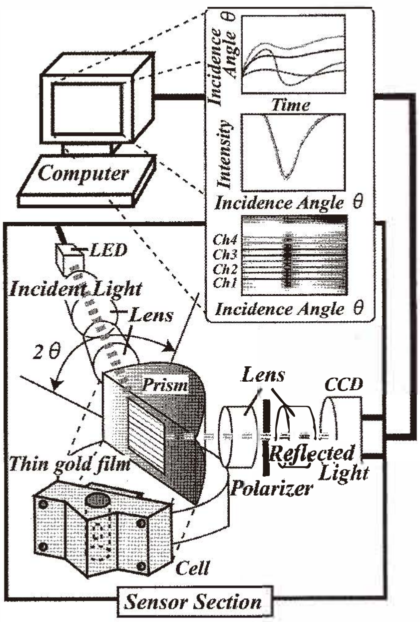


Fig. 1. Schematic diagram of the SPR taste sensor system.

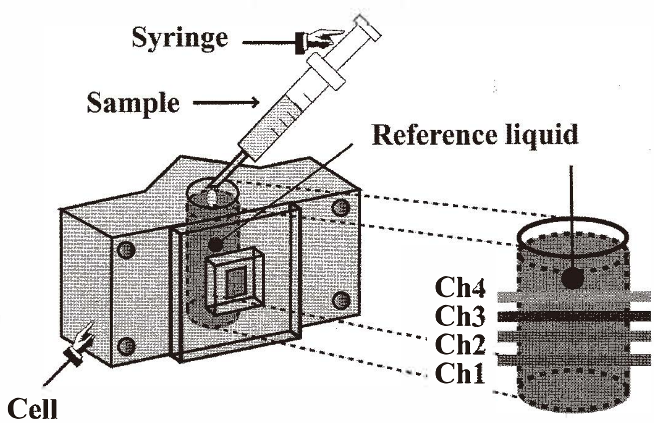


Fig. 2. Schematic diagram of the sensing cell of SPR taste sensor.

3. Results and Discussion

3.1 *Responses of SPR taste sensor to vinegar*

Conventionally, the fermentation of vinegar is carried out for about two weeks using Japanese sake as a starting material. During the fermentation process, the specific gravity and acidity change with the duration of the fermentation. Figures 3(a), (b) and (c) show typical responses of each channel of the SPR taste sensor to each sample fermented for different fermentation periods (1 day, 7 days, and 14 days, respectively). The acidity of each fermented sample is listed in Table 3. Figures 4(a) and (b) show the typical responses of each channel of the SPR sensor for Japanese sake and *kome-su* (typical Japanese vinegar fermented from rice), respectively. It can be seen that the responses of the SPR sensor for Japanese sake and vinegar differ. Regarding the results shown in Fig. 3, we can say that the response of the SPR sensor changes from that of sake to that of vinegar with changing (increasing) the number of fermentation days. It was found from the results of a detailed experiment performed for fermented vinegar samples at different fermentation stages (from 1 day to 14 days) that the fermentation period of about 3 days is necessary to bring about the change from Japanese sake to vinegar. This result suggests that we can identify the suitable fermentation period for vinegar from the change in response of the SPR sensor.

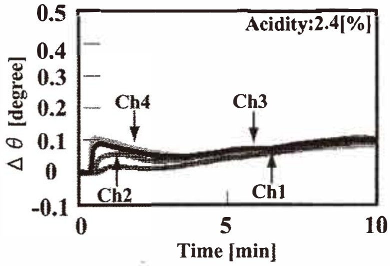
The resonance angles of the SPR sensor for three types of vinegar, *junkome-su*, *kome-su* and *gousei-su,* in comparison with that for distilled water, are listed in Table 4. The responses of the SPR sensor for three types of vinegar are shown in Fig. 5, where a mixture of acetic acid and distilled water of resonance angle about the 71.5 degrees is used as the reference liquid. It can be seen that discrimination among the three vinegar samples can be performed using such a reference liquid, indicating that the identification of the type of vinegar from the response of the SPR sensor is possible .

Table 1
Employed odor sensors fabricated by New COSMOS Inc. of Japan.

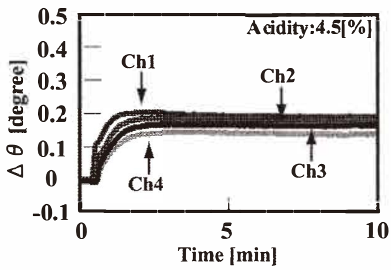
Type	Material	High sensitivity gases and odors
CH-E2	SnO_2	VOC, CH_3CH, CH_4, alcohol
CH-E3	SnO_2	High sensitivity type for CH-E2
CH-N	SnO_2	NH_3, C_2H_5OH, CH_3OH
AET-S	ZnO_2	H_2S, CH_3SH, CH_3SCH_3, CH_3SSCH_3

Table 2
Acidity, addition of NaCl, addition of acetic acid and raw material of each vinegar.

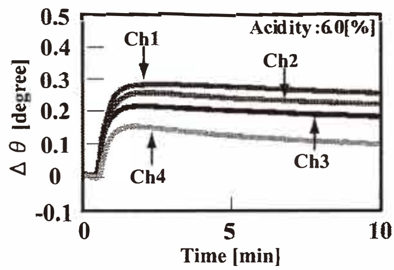
Sample	Acidity [%]	NaCl	Acetic acid	Raw material
Junkome-su	5.0	×	×	Rice
Kome-su	4.6	○	×	Rice
Hachimitsu-su	4.2	×	×	Honey
Gousei-su	11.0	○	○	Rice



(a) fermented 1 day.



(b) fermented 7 days.

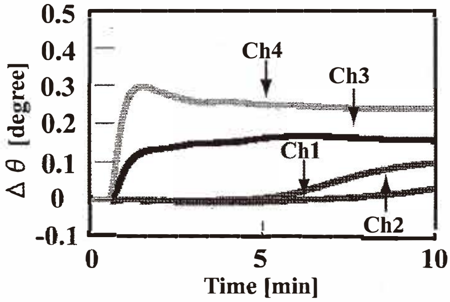


(c) fermented 14 days.

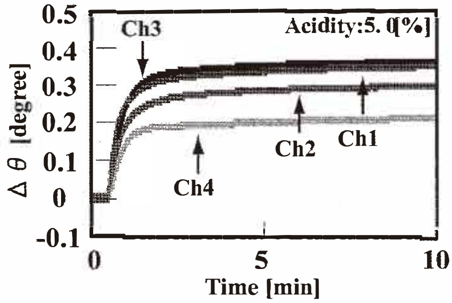
Fig. 3. Responses of SPR taste sensor for vinegar with different fermention periods: (a) 1 day, (b) 7 days and (c) 14 days.

Table 3
Fermented vinegar samples with different fermentation periods.

Sample	Acidity [%]
Vinegar fermented for 1 day	2.4
Vinegar fermented for 7 days	4.5
Vinegar fermented for 14 days	6.0



(a) Japanese sake.



(b) *kome-su*.

Fig. 4. Response of SPR taste sensor for Japanese sake (a) and *kome-su* (b).

Table 4
Resonant angles for three kinds of vinegar.

Sample	Degree [θ]
Junkome-su	70.3
Kome-su	70.7
Gousei-su	72.2

3.2 *Responses of MOS odor sensor for aromas from vinegar*

Figure 6 shows typical responses of six kinds of commercially available MOS odor sensors supplied by New Cosmos Co., Ltd. The responses of MOS odor sensors were measured immediately after a constant amount of aroma from vinegar was injected into the sensing chamber for 10 min.[12] It can be seen that the AET-S odor sensor had the highest output (sensitivity) for aroma from vinegar among the six kinds of odor sensors. Figures 7

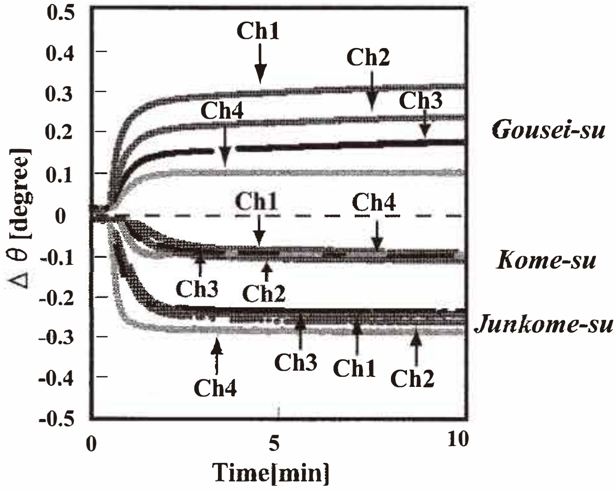


Fig. 5. Responses of SPR taste sensor for each type of vinegar, where a mixture of acetic acid and distilled water was used as the reference liquid.

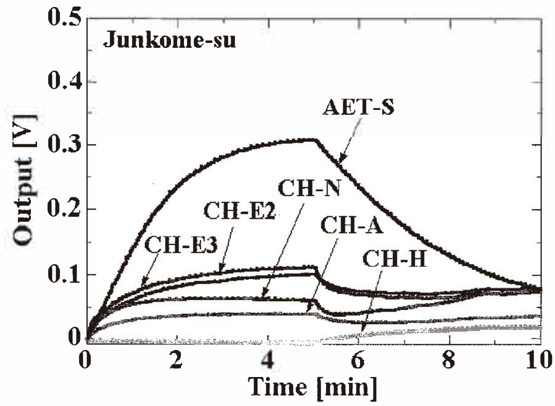


Fig. 6. Responses of commercially available odor sensors for aroma from *junkome-su.*

and 8 show typical responses of the AET-S odor sensor and CH-E3 odor sensor for aromas from *junkome-su* and *gousei-su*, respectively, where the odor intensity of *gousei-su* estimated using the human nose is higher than that from *junkome-su*. It is noted that the output of AET-S odor sensors for aroma from *gousei-su* is higher than that of *junkome-su,* though the output of the CH-E3 odor sensor for *gousei-su* is almost the same as that for *junkome-su.*

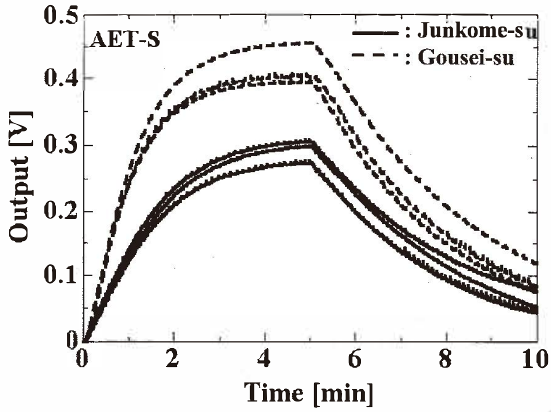


Fig. 7. Responses of AET-S odor sensor for aromas from *junkome-su* and *gousei-su*. The measurement of the response for aroma from each type of vinegar was carried out three times.

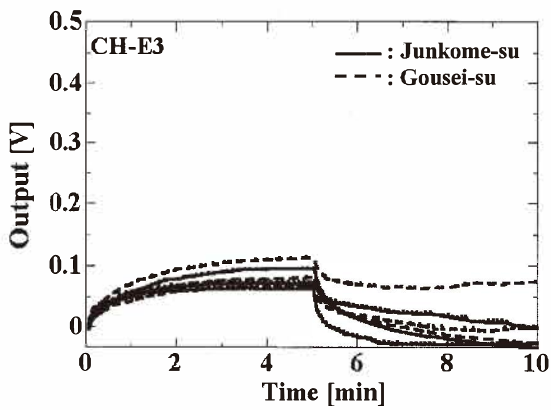


Fig. 8. Responses of CH-E3 odor sensor for aromas from *junkome-su* and *gousei-su*. The measurement of the response for aroma from each type of vinegar was carried out three times.

The output of the CH-E3 odor sensor as a function of the output of the AET-S odor sensor is plotted in Fig. 9. It is clear that plots for the individual aroma from each vinegar tend to cluster in discrete sections with well-defined boundaries. This result strongly suggests that the measurement of aromas from vinegar using two kinds of MOS odor sensors is useful for discrimination of the type of vinegar. Detailed experiments on many types of vinegars are now underway.

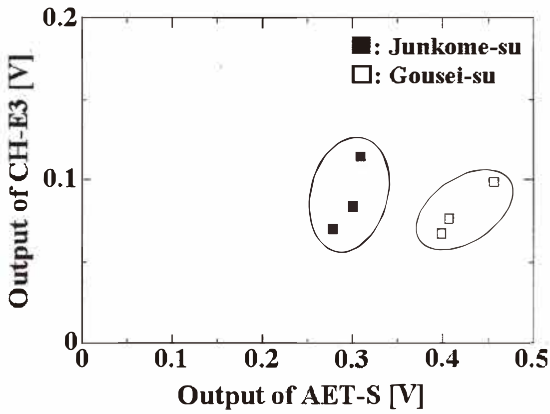


Fig. 9. Plots of CH-E3 odor sensor output as a function of the AET-S odor sensor output.

4. Summary

The responses of chemosensors based on the SPR phenomenon to vinegar were measured for vinegar samples with different fermentation periods. The results obtained are as follows: (1) The responses of the SPR taste sensor for vinegar and Japanese sake differ. (2) The SPR taste sensor responded to a change in quality of the vinegar with different fermentation periods. (3) The SPR resonance angle changed depending upon the type of vinegar. The results described above suggest that the SPR sensor will be useful for the quality control of vinegar.

The discrimination of the type of vinegar is also possible using the MOS odor sensors.

Thus, we can say that sensor fusion, involving the use of information from different types of chemosensors such as SPR taste sensors and MOS odor sensors, will be useful for the estimation of the quality of vinegar.

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