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A Novel Chemical Sensor Utilizing Surface Plasmon Resonance For Quality Control of Japanese Sake

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A chemical sensor based on surface plasmon resonance (SPR) with four channels is studied for the quality control of the fermentation process of Japanese sake. Each channel of the SPR sensor responds to a change in quality of the *moromi* (fermented for 5, 14 and 23 days), which is sake in the final stage of fermentation. The responses of each channel of the SPR sensor clearly change with the number of fermentation days, indicating that an SPR sensor with four channels is useful for quality control of the production of Japanese sake. The SPR sensor, in which distilled water is used as the reference liquid, also responds to different kinds of Japanese sake. This result strongly suggests that the SPR sensor is useful for the identification of the type of Japanese sake.

1. Introduction

Surface plasmon resonance (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 film has, therefore, been recognized as a promising technique for sensitive detection of chemical species.(1) 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,(2) wavelength modulation,(3) intensity modulation(4) and phase modulation.(5)

The objective of this study is to demonstrate a novel chemical sensor using the SPR phenomenon for quality control in the fermentation of Japanese sake and the identification of different kinds of Japanese sake.

2. Experimental

Optical SPR sensors are sensitive to changes in the refractive index of a sample near the sensor surface. The SPR was measured using a Kretschmann configuration (Nihon Denki Kagaku: SPR-20), illustrated in Fig. 1, with a prism and a thin, highly conductive gold metal layer deposited on the base of the prism. 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) is measured by coupling transverse magnetically polarized monochromatic light into the prism and measuring the reflected light intensity of the ray exciting the prism versus the angle of incidence.

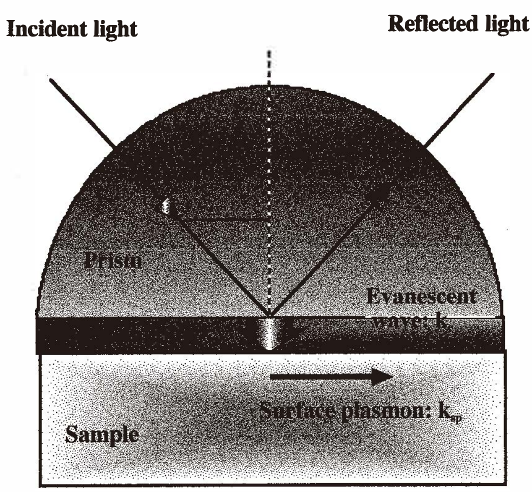

Fig. 1. Kretschmann-type SPR configuration.

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, as shown in Fig. 2, were observed using the CCD camera, because the image of the CCD can be divided into four channels using computer software. The schematic configuration of the SPR system is shown in Fig. 2. The volume of the sensor unit cell is 2.5 ml.

To utilize this system as a sensor for measuring the changes in quality of Japanese sake, distilled water or diluted ammonia (4%) was used as the reference liquid.

The *moromi* samples with different numbers of fermentation days and the eight kinds of Japanese sake used were supplied by the Shata-syuzou Co., Ltd. As-fermented *moromi* samples were used in the experiments.

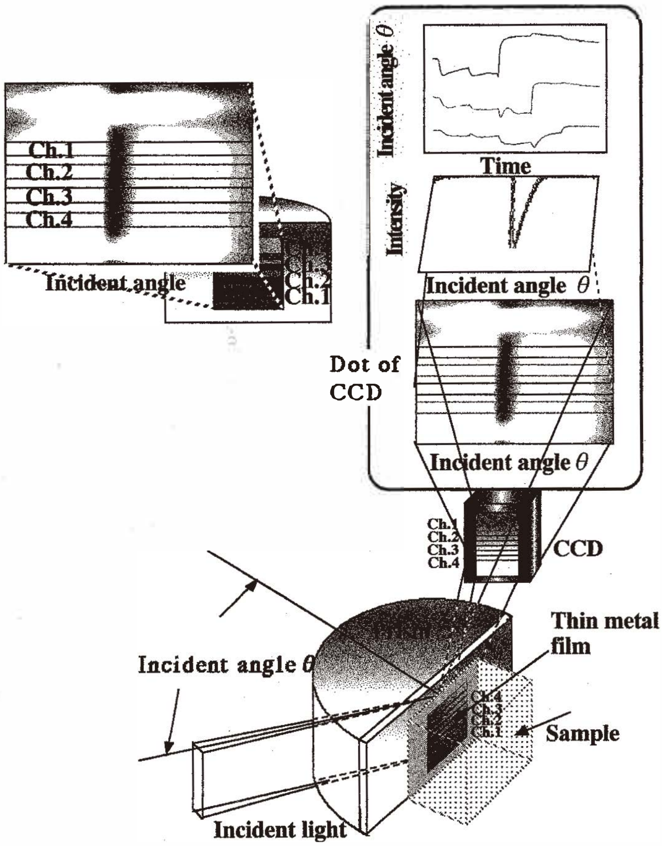

Fig. 2. Schematic diagram of the SPR sensor system.

3. Results and Discussion

3.1 *Responses to the* moromi *of Japanese sake at different fermentation stages*

The *moromi* process is the final one in the fermentation of Japanese sake. Usually, the fermentation of the *moromi* is carried out for about 20–25 days. During fermentation, the specific gravity, alcohol content, acidity and amino acidity change with the time of fermentation. In this experiment, we pay attention to the change in specific gravity and acidity of the *moromi* samples. Two kinds of experiments were carried out as follows: (1) Distilled water was used as a reference liquid to observe changes in the *moromi* properties corresponding to changes in specific gravity. In this experiment, 80 μl of *moromi* was injected using a microsyringc into the sensor unit cell which was filled with distilled water, and then the SPR signal (Ch. 1–Ch. 4), which is a change in the resonance angle, was measured just after injection. (2) To observe the changes in *moromi* properties corresponding to changes in acidity, diluted ammonia (pH 10) was used as the reference liquid.

The specific gravity, alcohol content, acidity and amino acidity of the *moromi* at different fermentation times (5 days, 14 days and 23 days) measured by Shata-syuzou Co., Ltd., are listed in Table 1. The specific gravity of the *moromi* decreases as the number of fermentation days increases and the acidity increases with the number of fermentation days.

Figures 3, 4 and 5 show the responses of each channel (Ch. 1–Ch. 4) to *moromi* samples A, B and C fermented for 5, 14 and 23 days, respectively, when each *moromi* sample is injected in the distilled water as the reference liquid. The following features are noted:

(a) For *moromi* sample A fermented for 5 days, the SPR peak angle shift ($\Delta\theta$) of Ch. 1 is more dominant than that of Ch. 3 and 4. This is due to the specific gravity of sample A (5 days fermentation) being larger than that of distilled water (specific gravity = 1), and consequently, the *moromi* sample injected into the cell diffuses toward the bottom of the cell.

(b) In contrast, the SPR peak angle shift of Ch. 3 and 4 for *moromi* sample C, fermented for 23 days, is more dominant than that of *moromi* samples A and B, fermented for 5 days and 14 days, respectively. The specific gravity of *moromi* sample C fermented for 23 days is lower than that of distilled water, and consequently, the *moromi* sample does not diffuse toward the bottom of the cell.

Table 1
Specific gravity, alcohol content, acidity and amino acidity of the *moromi* samples.

Samples	Fermentation days	Specific gravity	Alcohol content [%]	Acidity	Amino acidity
A	5	1.0502	7.4	1.7	1.0
B	14	1.0077	16.3	2.3	1.7
C	23	0.9979	18.7	2.7	2.2

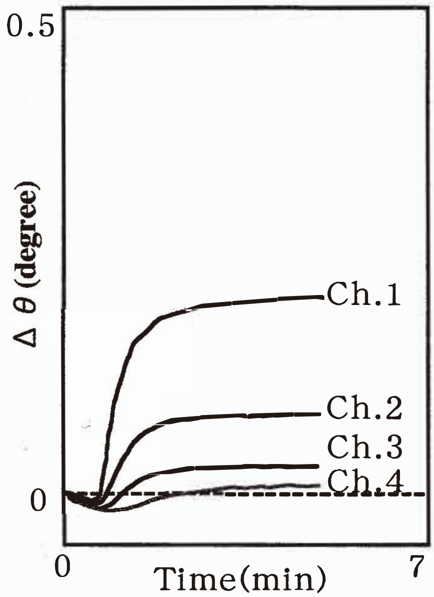

Fig. 3. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to a *moromi* sample fermented for 5 days, where distilled water was used as the reference liquid.

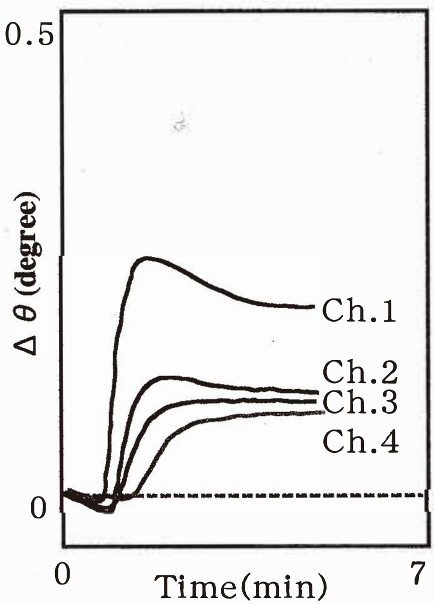

Fig. 4. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to a *moromi* sample fermented for 14 days, where distilled water was used as the reference liquid.

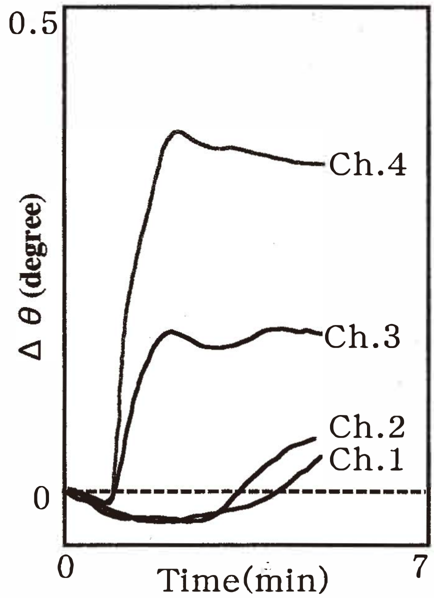

Fig. 5. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to a *moromi* sample fermented for 23 days, where distilled water was used as the reference liquid.

Figures 6, 7 and 8 show the responses of each channel to each *moromi* sample when diluted liquid ammonia at pH = 10 is used as the reference liquid. The following features should be noted:

(c) For *moromi* sample A fermented for 5 days, which has a low acidity, the responses of each channel are similar to those of the SPR sensor when distilled water is used as the reference liquid.

(d) The response of each channel of the SPR sensor to *moromi* sample B fermented for 14 days when diluted ammonia is used as the reference liquid is different from that of each channel when distilled water is used.

(e) For *moromi* sample C fermented for 23 days, which has the highest acidity at pH = 2.7, an SPR peak angle shift in Ch.1 and Ch. 2, when diluted ammonia is used as the reference liquid, is observed as well as in Ch. 3 and Ch. 4. However, an SPR peak angle shift for *moromi* sample C fermented for 23 days when distilled water is used as the reference liquid is not observed.

These results indicate that the SPR sensor responds to the index change of the mixture of the *moromi* sample and the reference liquid due to changes in the quality of the *moromi* with the changing duration of fermentation.

It was confirmed that there is good reproducibility of the SPR responses for several trials using the same *moromi* samples. Using an SPR sensor, we can establish the suitable duration of *moromi* fermentation from pattern recognition of the SPR signal in each channel, which changes with changes in the quality during the fermentation of *moromi*.

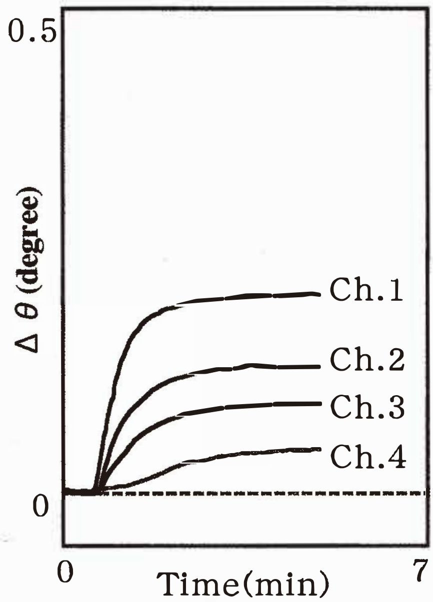

Fig. 6. Typical responses of each channel (Ch.1–Ch.4) of the SPR sensor to a *moromi* sample fermented for 5 days, where diluted ammonia was used as the reference liquid.

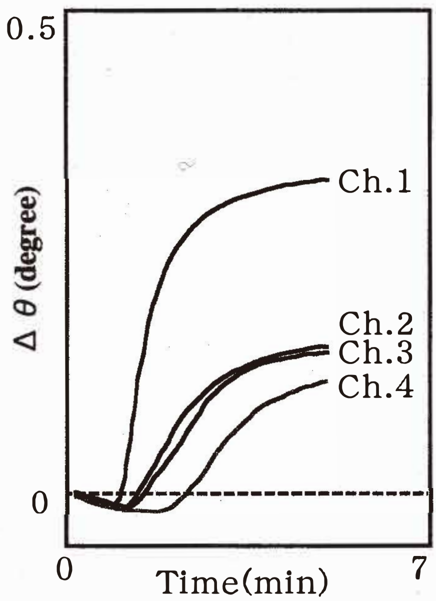

Fig. 7. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to a *moromi* sample fermented for 14 days, where diluted ammonia was used as the reference liquid.

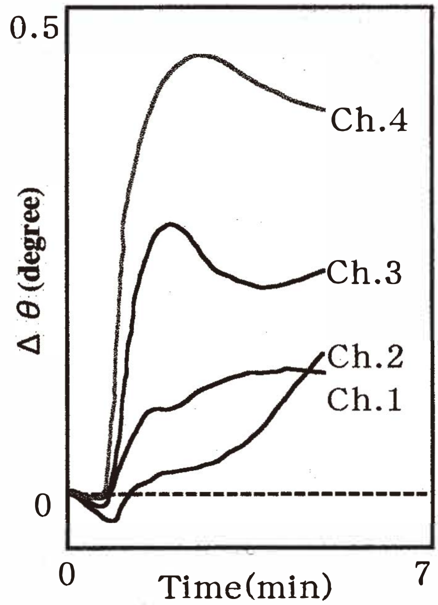

Fig. 8. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to a *moromi* sample fermented for 23 days, where diluted ammonia was used as the reference liquid.

3.2 *Responses for several types of Japanese sake*

Eight types of Japanese sake, as listed in Table 2, were used as the samples. Yamahai yeast fungus was used as the brewer's yeast for fermentation of *Yamahai-ginzyou* and *Yamahai-zyunmai.* Sokuzyou yeast was used for the fermentation of other samples such as *Gin-kouburi*, *Kokosyu-ginzyou*, *Bunsei-rokunen*, *Yawara* and *Tokuzyou.* A mixture of Yamahai and Sokuzyou yeasts was used for the fermentation of *Taka.* Yamadanishiki is the name of the raw rice used for preparing the malt of *Gin-kouburi*, *Kokoshu-ginzyou* and *Yamahai-ginzyou.* Gohyakumangoku rice was also the raw rice used for other Japanese sakes such as *Bunsei-rokunen*, *Yawara*, *Yamahai-zyunnmai*, *Tokuzyou* and *Taka.* Brewing alcohol was blended in the brewing process for six types of Japanese sake except for *Yawara* and *Yamahai-zyunmai.*

Figure 9 shows typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Gin-kouburi* sample, which has the highest quality among the samples, where distilled water was used as the reference liquid. The response of Ch. 4 is dominant compared with other channels. Figures 10 and 11 show typical responses of the SPR sensor to the *Kokosyu-ginzyou* and *Bunsei-rokunen* samples which have the same specific gravity as the *Gin-kouburi* sample listed in Table 2. The response of Ch. 4 is dominant in all samples but the response of each channel varies from sample to sample.

Figures 12 and 13 show typical responses of the SPR sensor to the *Yamahai-ginzyou* and *Yamahai-zyunmai* samples in which Yamahai yeast fungus was used as the brewing

Table 2
Specific gravity, alcohol content, acidity, amino acidity and other conditions for different types of Japanese sake.

Sample	Specific gravity	Alcohol content[%]	Acidity	Amino acidity	Raw rice	Brewers Yeast
Gin-kouburi	0.9962	16.6	0.95	0.80	Yamada-nishiki	Sokuzyou
Kokoshu-ginzyou	0.9962	16.5	1.05	0.80	Yamada-nishiki	Sokuzyou
Yamahai-ginzyou	0.9958	16.3	1.15	0.80	Yamada-nishiki	Yamahai
Bunsei-rokunen	0.9962	15.8	1.20	1.15	Gohyakumangoku	Sokuzyou
Yawara	0.9969	15.9	1.40	1.70	Gohyakumangoku	Sokuzyou
Yamahai-zyunmai	0.9972	15.9	1.70	2.10	Gohyakumangoku	Yamahai
Tokuzyou	0.9952	15.9	1.20	1.35	Gohyakumangoku	Sokuzyou
Taka	0.9972	15.8	1.30	1.40	Gohyakumangoku	Yamahai & Sokuzyou

yeast. The responses of the SPR sensor to the *Yawara*, *Tokuzyou* and *Taka* samples are shown in Figs. 14, 15 and 16, respectively. The following features are noted:

(a) All channels of the SPR sensor respond to the *Yamahai-ginzyou* and *Yamahai-zyunmai* samples which are produced using Yamahai yeast fungus, although Ch. 1 and Ch. 2 of the SPR sensor did not respond to the samples which were produced using Sokuzyou yeast fungus.

(b) In particular, Ch. 4 of the SPR sensor exhibits a dominant change for the *Gin-kouburi* sample.

It was confirmed that the responses of the SPR sensor exhibit good reproducibility for several trials using the same samples. The results as described above strongly suggest that pattern recognition of the responses of each channel of the SPR sensor using a computer is useful for the discrimination of the type of Japanese sake, because the response of the SPR sensor is different from sample to sample.

To explain the response of the sensor to various types of Japanese sake, experiments using pure ethanol, *shouchu* and whisky are now in progress, and in the near future the results will be reported.

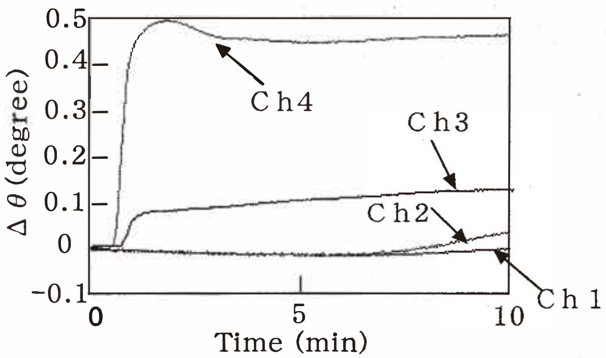

Fig. 9. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Gin-kouburi* sample, where distilled water was used as the reference liquid.

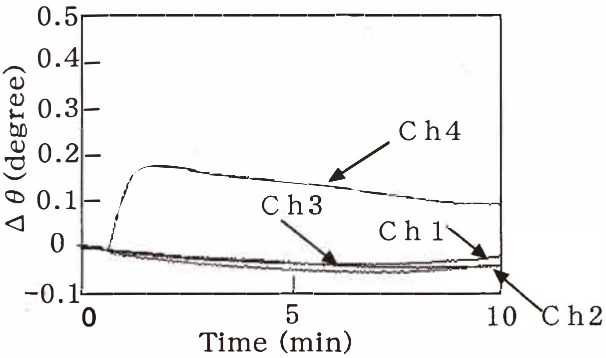

Fig. 10. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Kokosyu-ginzyou* sample, where distilled water was used as the reference liquid.

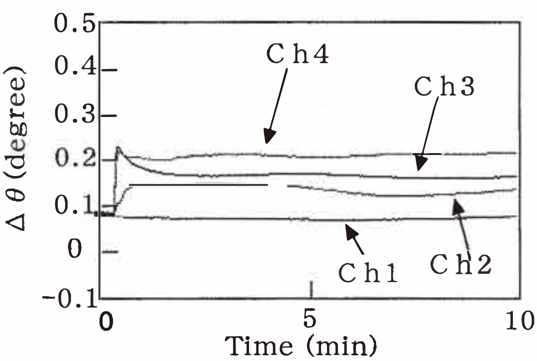

Fig. 11. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Bunsei-rokunen* sample, where distilled water was used as the reference liquid.

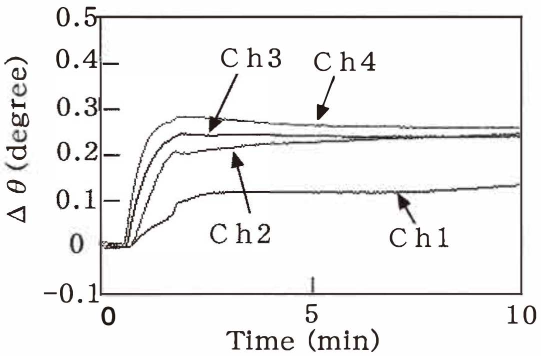

Fig. 12. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Yamahai-ginzyou* sample, where distilled water was used as the reference liquid.

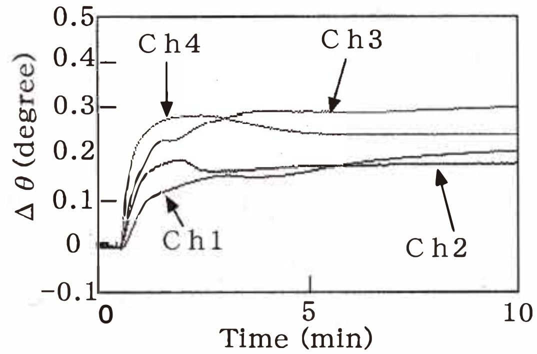

Fig. 13. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Yamahai-zyunmai* sample, where distilled water was used as the reference liquid.

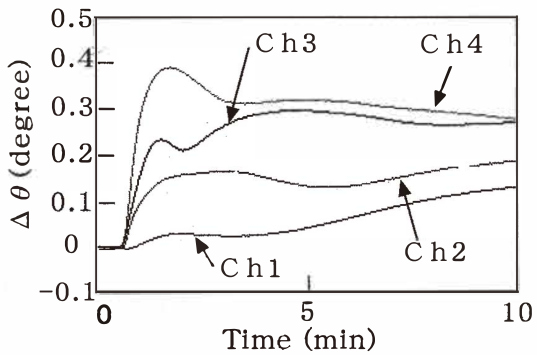

Fig. 14. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Yawara* sample, where distilled water was used as the reference liquid.

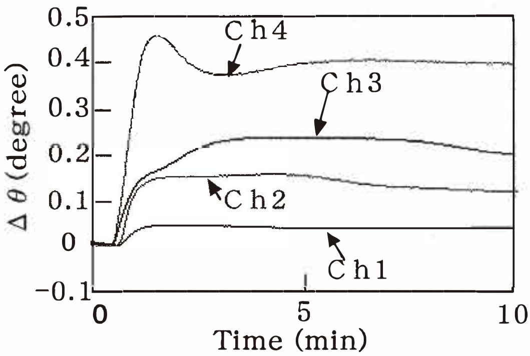

Fig. 15. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Tokuzyou* sample, where distilled water was used as the reference liquid.

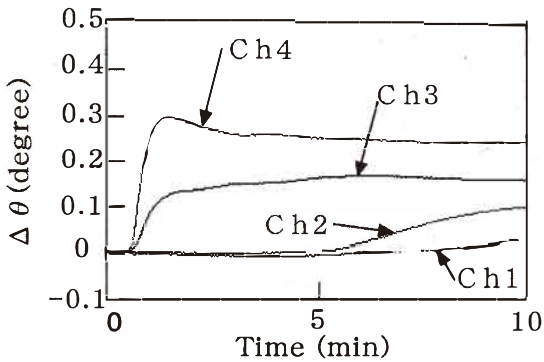

Fig. 16. Typical responses of each channel (Ch. 1–Ch. 4) of the SPR sensor to the *Taka* sample, where distilled water was used as the reference liquid.

4. Conclusions

The responses of an SPR sensor with four channels to the *moromi* samples (fermented for 5, 14 and 23 days) of Japanese sake were studied by measuring the response of each channel of the SPR sensor when specific amounts of "*moromi*" were injected into distilled water or diluted ammonia as the reference liquid. Each channel of the SPR sensor responded to the changes in the quality of the *moromi* samples (fermented for 5, 14, and 23 days), indicating that the SPR sensor is useful for quality control in Japanese sake production.

The SPR sensor with four channels exhibited different behavior for each Japanese sake such as *Gin-kouburi*, *Kokosyu-ginzyou*, *Yamahai-ginzyou*, *Bunsei-rokunen*, *Yawara*, *Yamahai-zyunmai*, *Tokuzyou* and *Taka*, the quality of which is subtly different from sample to sample.

These results strongly suggest that an SPR sensor with four channels using distilled water or diluted ammonia as the reference liquid is a promising candidate for quality control of Japanese sake and for identification of types of Japanese sake.

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References

1 B. Liedberg, C. Nylander and I. Lundstrom: Sensors and Actuators **4** (1983) 299.
2 E. Kretschmann: Z. Phys. **241** (1971) 313.
3 K. S. Johnston, S. R. Karlson, C. Jung and S. S. Yee: Mater. Chem. Phys. **42** (1995) 242.
4 B. Chadwick and M. Gal: Jpn. J. Appl. Phys. **32** (1993) 2716.
5 S. Nelson, K. S. Johnston and S. S. Yee: Sensors and Actuators B **35–36** (1996) 187.