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Odorant analysis of sake by using ball SAW gas chromatograph
ボールSAWガスクロマトグラフによる日本酒の香気成分分析

Shingo Akao[1†], Takamitsu Iwaya[1], Tatsuhiro Okano[1], Nobuo Takeda[1], Yusuke Tsukahara[1], Toru Oizumi[1], Hideyuki Fukushi[1], Tomoki Tanaka[1], Maki Sugawara[1], Toshihiro Tsuji[2,1], Ryoko Hiraoka[1], Akinobu Takeda[1], and , Kazushi Yamanaka[1,2] ([1]Ball Wave Inc.; [2]Tohoku Univ.)
赤尾慎吾[1†]，岩谷隆光[1]，岡野達広[1]，竹田宣生[1]，塚原祐輔[1]，大泉透[1]，福士秀幸[1]，田中智樹[1]，菅原真希[1]，辻俊宏[2,1]，平岡領子[1]，武田昭信[1]，山中一司[1,2] ([1]ボールウェーブ, [2]東北大)

1. Introduction

On-site analysis of many kinds of volatile organic compounds (VOC) has various needs. For example, for safety of workers in factories, monitoring of atmospheric gas, quality control by aroma component analysis in food production can be expected. A gas chromatograph (GC) is effective for multi-type gas analysis, but in general, GC is large and difficult to apply in the field.

On the other hand, we have developed a portable GC using ball surface acoustic wave (SAW) sensors (ball SAW GC) [2-4] where the SAW makes multiple roundtrips on a spherical piezoelectric crystal [1]. Recently, the ball SAW GC succeeded in analyzing VOCs at ppbv levels by the development of a preconcentrator (PC) that traps and injects VOCs by thermal desorption [5].

In this study, the ordarants of sake, a brewed beverage, were analyzed using the ball SAW GC.

2. Ball SAW GC with preconcentrator

Fig. 1 shows a schematic diagram of a ball SAW GC equipped with a PC. As for PC, about 2 mg of Tenax®TA as an adsorbent was filled in a stainless steel pipe having an outer diameter of 1.61 mm and a wall thickness of 0.18 mm, and a nichrome wire for resistance heating was wound around the outer circumference. The sample gas is pumped and collected by the adsorbent of PC. After that, when the valve is switched and the temperature of the PC is rapidly raised by the resistance heater, the collected components are instantly desorbed by heat, and the hydrogen carrier gas is introduced into the separation column by backflushing in the opposite direction to the time of collection. Each component is separated by the difference in the absorptivity to the stationary phase coated on the inner surface of the column, and is adsorbed on the sensitive film formed on the ball SAW sensor, so that it is detected as a delay time change or amplitude change.

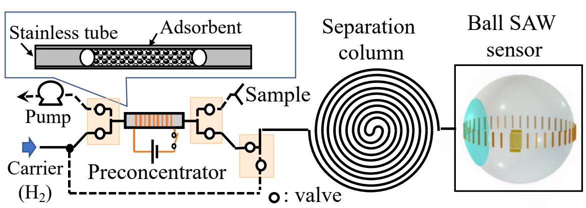

Fig. 1 Schematic diagram of a ball SAW GC equipped with PC.

3. Experiment

Headspace gas of sake was analyzed using a ball SAW GC with a PC. The sample sake was put in a vial and the headspace gas was collected on the PC at 21 ml/min for 5 minutes. For the preliminary examination of the column, a tabletop GC InertCap® Pure-Wax (GL science) 30 m was used. The column temperature was maintained at 40°C for 5 minutes by using a tabletop type GC oven, and then the temperature was raised to 230°C at 6°C/min.

As the ball SAW sensor, a 3.3 mm crystal quartz (150 MHz) coated with Poly-dimethylsiloxane (PDMS) was used, and each component was detected by the change in SAW delay time. A flame ionization detector (FID) was installed in series as a reference sensor.

Honjozo-shu A, B, C and Ginjo-shu D, E, F of different brands were prepared as samples, and headspace gas was analyzed immediately after opening. Then, it was left at room temperature for 4 days and analyzed under the same conditions.

4. Result and discussion

Fig. 2 shows the chromatograms obtained by analyzing Honjozo-shu A and Ginjo-shu D. The upper graph is the ball SAW sensor and the lower graph is the FID. In each case, the odorant of sake was detected, and the results were different in the component composition depending on the brand.

The peaks 1 to 5 of each component could be identified by 1: ethyl acetate, 2: ethanol, 3: isoamyl acetate, 4: isoamyl alcohol, and 5: ethyl caproate. On the other hand, 6-8 are currently unconfirmed.

Comparing the two detectors, the ball SAW sensor was able to detect clearer peaks than FID in water and the long retention time components 6-8.

The peak of component 7 was remarkably large in D in Ginjo-shu, but the estimation by Nagai et al. [6] suggests that component 7 is ethyl caprate. As a result, we have found that the ball SAW sensor is useful in detecting aromatic esters.

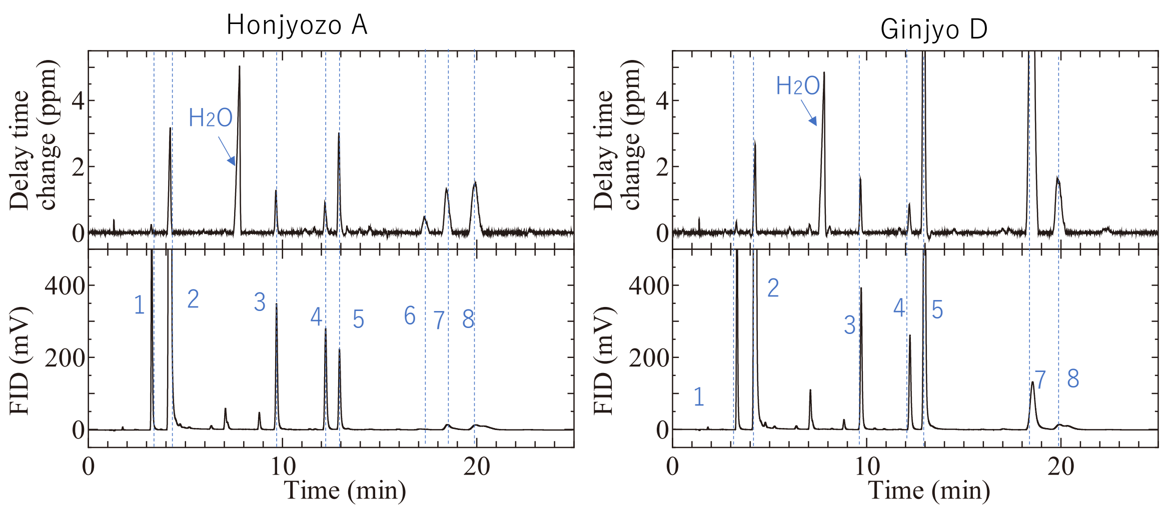

Fig. 2 Chromatograms obtained by analysis of Honjozo-shu A and Ginjo-shu D.

Fig. 3 shows a chromatogram obtained by analyzing the Honjozo-syu A left at room temperature for 4 days using a ball SAW sensor. A decrease in the peak area of each odorant was observed. This indicates that the odorant of sake is reduced.

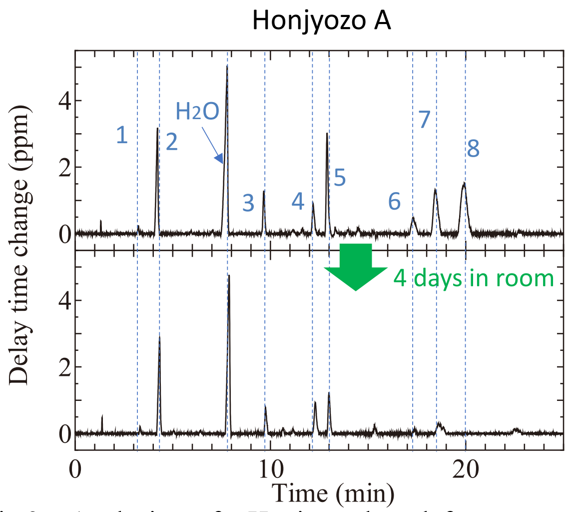

Fig.3 Analysis of Honjozo-shu left at room temperature for 4 days.

Fig. 4 shows the comparison results of the peak areas of ethyl caproate (component 5) for the three types of Honjozo-shu and the three types of Ginjo-shu that were analyzed at the same time for the sample immediately after opening and for the sample left for 4 days. In all the samples, the peak area of ethyl caproate was smaller after being left for 4 days than after opening.

Comparing the peak areas of Honjozo-shu A, B, and C and Ginjo-shu D, E, and F, the peak area of Ginjo-shu was wider than that of Honjozo-shu, regardless of the time after it was opened. It is presumed that this reflects the difference in the fruity aroma of Ginjo-shu liquor due to the manufacturing method such as rice polishing [7].

akao@ballwave.jp

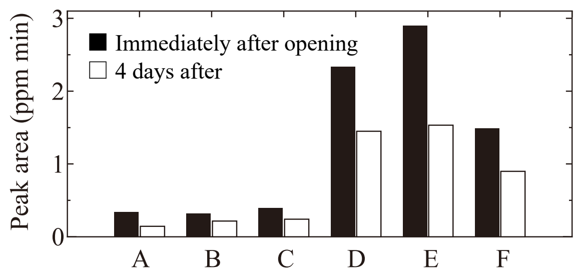

Fig.4 Change in peak area of ethyl caproate after being left at room temperature for 4 days.

5. Conclusion

The headspace gas of sake was concentrated and analyzed by the GC using a ball SAW sensor coated with PDMS film. It was shown that the ratio of the peak area of odorant was different depending on the brand of sake. From this, it was found that the ball SAW GC is useful in quality control in the brewing process and analysis of substances produced in the development of yeast cultivation.

References

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