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有人宇宙環境測定のための可搬型ボール SAW ガスクロマトグラフの開発とその地上における応用

Development of portable ball SAW gas chromatograph for measurement of manned space environment and its application on the ground

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1. Introduction

In solar system exploration, a portable gas chromatograph (GC) that can analyze multiple volatile gases is an important instrument for the in-situ analysis of the surface of the moon, planets, and small bodies. It is useful to monitor cabin atmosphere in spacecraft and the International Space Station for human exploration. In addition, there are various needs for portable GC on the ground, such as quality control by in-site measurement of harmful gas in factories and odor analysis at food transportation / manufacturing sites is desired.

We have developed a GC system equipped with a ball surface acoustic wave (SAW) sensor [1,2]: a ball SAW GC [3-5]. The key features of our ball SAW GC are the multiple roundtrips of the SAW on a spherical crystal and a metal micro-electro-mechanical-system (MEMS) column coated with a stationary phase in a 3 m long microchannel formed by diffusion bonding of etched stainless-steel plates.

In this study, we fabricated three-layered metal microchannel with the length of 10 m to improve gas separation and developed two types of metal MEMS column using the channels. We succeeded to minimize the size of the ball SAW GC to a 10 cm cube including these metal MEMS columns. The performance of this system was examined by analyzing multiple volatile gases. In addition, as part of the study of ground uses of ball SAW GC, we report an experiment in which a palm-sized prototype was developed and the odorants of sake, a brewed beverage, were analyzed.

2. Principle of ball SAW sensor

As shown in **Fig. 1**, the SAW excited with the width of the geometric mean of the diameter and wavelength on the spherical element realizes naturally collimated beam and makes multiple roundtrips without the diffraction loss, enabling a dramatic long-distance propagation [1,2]. When gas molecules are adsorbed on the sensitive film coated on the SAW propagation path, the amplitude and delay time of the SAW change due to the interaction with the sensitive film. Since these changes increase with the length of the SAW propagation, ball SAW sensor can detect gases with high sensitivity by measuring changes of amplitude and delay time after multiple roundtrips.

The ball SAW sensor is highly versatile because it can handle many gases by changing the sensitive film or forming multiple sensitive films on one sensor. In addition, since it operates at room temperature, it can save power and is suitable

for portable GC. In this study, we used a crystal quartz with a center frequency of 150 MHz and a diameter of 3.3 mm as the ball SAW sensor.

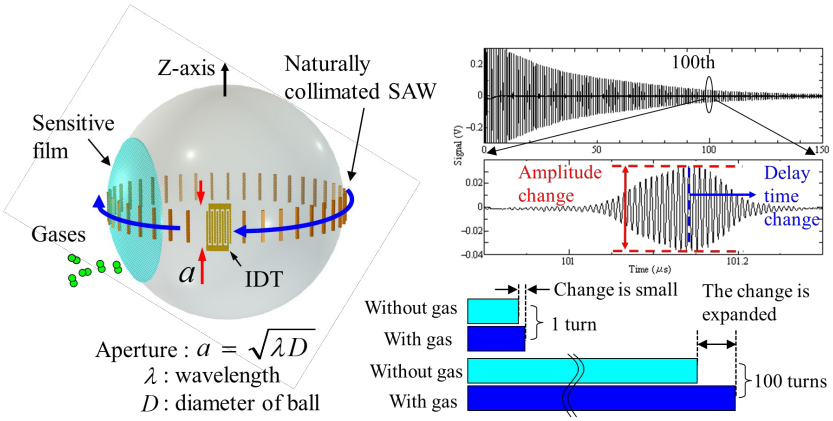


Fig. 1 Principle of ball SAW sensor

2. Three-layered metal MEMS column

Fig. 2 (a) shows the fabrication process of the three-layered microchannel. First, channels with 330 μm width and 185 μm depth were formed by wet etching on both sides of a stainless-steel plate (SUS304, 0.5 mm thick). Next, a through hole of φ0.25 mm was drilled to connect channels of both sides. Finally, the plate was sandwiched between two stainless-steel plates (0.2 mm thick), each of which with through holes for connecting the outside and the channel, and the three plates were joined by using the diffusion bonding. Fig. 2 (b) shows a photo of the column. A 10 m channel was formed in the area of 71 x 43 mm and 0.9 mm thick. The inlet of the channel is at the center of the protruded part, and the outlet is at the same position on the back side. Consequently, the channel length can be increased by stacking the columns via O-rings.

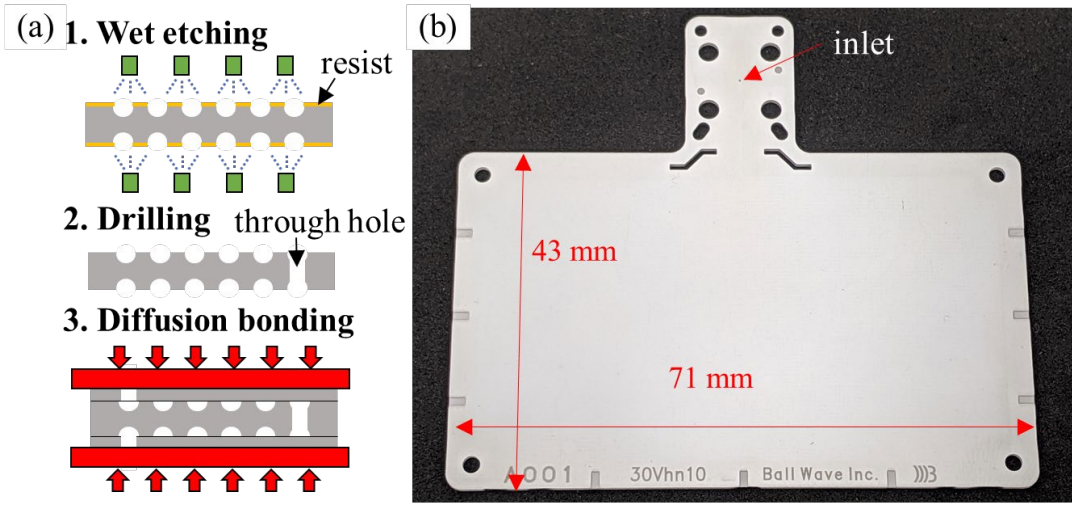


Fig. 2 Three-layered microchannel. (a) fabrication process. (b) photo.

To evaluate the fabricated channel, we performed the nondestructive testing using an acoustic microscope operated at 200 MHz. **Fig. 3 (a)** shows an acoustic image of the microchannel focused at bonding interface. **Fig. 3 (c)** shows the reflected waveforms at three positions in the enlarged image of **Fig. 3 (b)**. Position 1 is located on the bonding area and 2 is located on the channel. The large amplitude echo S at 6.95 μs and echo C at 7.02 μs represent reflection from the surface and interface of the channel, respectively. Position 3 is supposed to be in the bonding area, but echo I with the same propagation time as echo C was confirmed, suggesting a defect with a risk of connecting neighboring channels. A possible cause of this

defect is an excessive etching by delamination of the resist, or inclusion of foreign matters during the bonding. Such defects might branch off the flow path leading to unintended peaks in the chromatogram or cause inhomogeneous thickness of the stationary phase reducing the gas separation performance.

Then, we selected defect-free channels and coated each column with 5% diphenyl - 95% polydimethylsiloxane (PDMS) and polyethylene glycol (PEG) as the stationary phases.

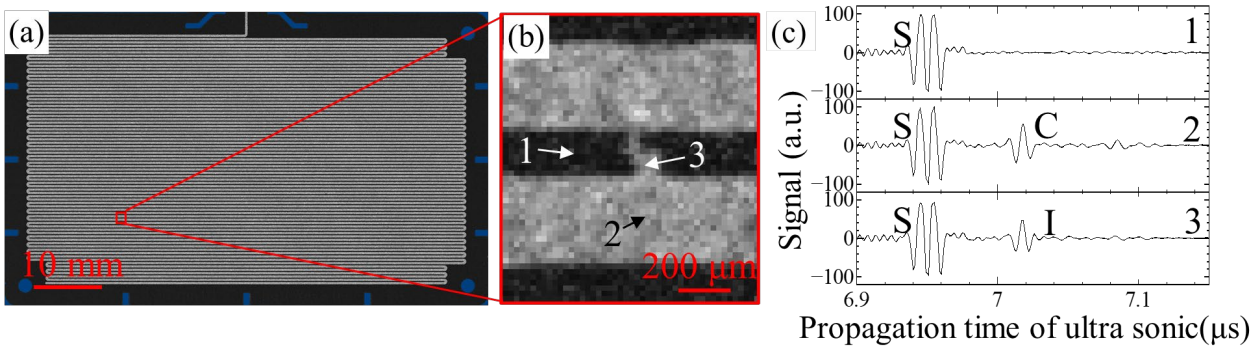


Fig. 3 Nondestructive testing of a channel by an acoustic microscope.
(a) Full image. (b) Enlarged image. (c) Waveforms at point 1, 2 and 3.

4. 10cm ball SAW GC using metal MEMS column

Using the developed three-layer metal MEMS column, we developed a portable ball SAW GC that implements the forward flush method [4,5]. The fundamental of the forward flush method is shown in **Fig. 4**. This system consists of a pre-concentrator (PC) [6] that collects and injects sample gas, two gas separation columns (CL1, CL2), and two ball SAW sensors (BS1, BS2). First, the pre-concentrator is rapidly heated with CL1-BS1-CL2-BS2 connected in series, and the gas collected in the pre-concentrator is injected into CL1 (**Fig. 4 (a)**). Components with weaker holding power than CL1 are non-destructively detected by BS1 as peaks that pass through CL1 without being separated. On the other hand, the component with strong holding power is retained in CL1. Next, switch the valve and connect CL1-BS1 and CL2-BS2 in parallel (**Fig. 4 (b)**). The components remaining in CL1 are separated by CL1 and detected by BS1, and the components that have passed without being separated by CL1 are separated by CL2 and detected by BS2. By using two types of columns in this way, it is possible to separate gases that are difficult to separate with a single column in a short time.

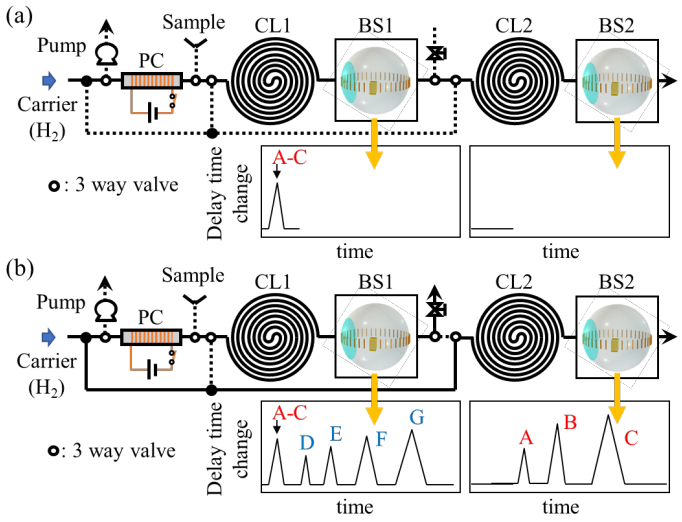


Fig. 4 Forward flush method: (a)serial connection and (b) parallel connenction.

Fig. 5 shows the prototyped ball SAW GC. The carrier gas was supplied from a hydrogen storage canister, and the flow rate was controlled by a pressure regulator. The pre-concentrator was a stain-less steel tube with an outer diameter of 1.6 mm and a wall thickness of 0.18 mm filled with two types of adsorbents, Carboxen® 1000 (Sigma-Aldrich) and Tenax TA (GL science). The first column (CL1) was a 10 m long metal MEMS column coated with 5% diphenyl - 95% PDMS. The second column (CL2) was a 30 m long column connecting three 10 m long metal MEMS columns coated with PEG. The column temperature was controlled by seat heaters mounted on both sides of the column and cooling fans. The first sensor (BS1) with a PDMS sensitive film was connected to the outlet of CL1, and the second sensor (BS2) with poly-N-vinylpyrrolidone sensitive film was connected to the outlet of CL2. In addition, it included a gas sampler unit equipped with a pre-concentrator, a detection circuit for operating a ball SAW sensor, and a control circuit for valves and heaters. This GC was 10 x 10 x 10 cm in size and weighed 762 g.

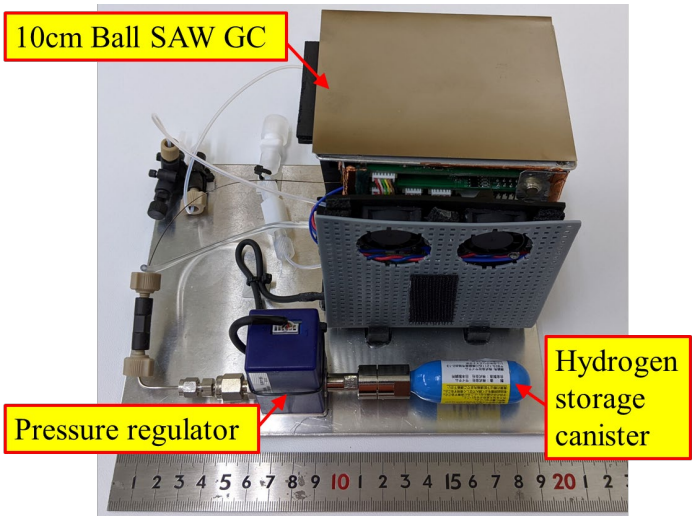
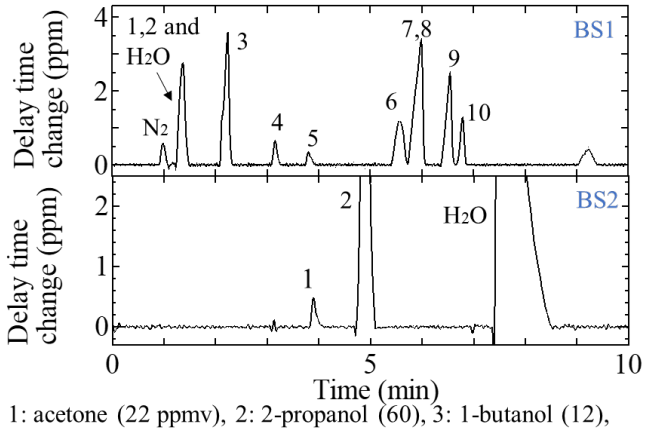


Fig. 5 10cm ball SAW GC.

A 10 cm ball SAW GC was used to analyze the mixed gas of aerial pollutants in a spacecraft. Ten kinds of gases specified in NASA's Spacecraft Maximum Allowable Concentrations for Airborne Contaminants (SMAC) [7] were mixed at the maximum permissible concentration for a 180-day exposure period. The sample gas was collected at a flow rate of 33 ml/min for 2 minutes. The column temperature was maintained at 40 °C for 5 minutes and then raised to 140 °C at 10 °C/min. The chromatograms are shown in **Fig.6**. Acetone, 2-propanol and H_2O which is mixed during the sample preparation were not separated by CL1 and detected as one peak by BS1. They were separated by CL2 and detected by BS2. Other gases were separated by CL1 and detected as clear peaks 3 to 10 by BS1.



1: acetone (22 ppmv), 2: 2-propanol (60), 3: 1-butanol (12), 4: toluene (4), 5: n-octane (3), 6: ethylbenzene (12), 7: m-xylene (8.5), 8: p-xylene (8.5), 9: o-xylene(8.5), 10: nonane (3)

Fig. 6 Chromatograms by 10cm ball SAW GC. The number in parentheses indicates concentration.

5. Palme-sized ball SAW GC

For the purpose of studying application of ball SAW GC on the ground, we developed a palm-sized ball SAW GC [8] with a simple configuration of one pair of a column and a sensor (**Fig. 7**). The pre-concentrator was filled with Tenax TA only. The column was made smaller by processing a commercially available metal capillary column UltraALLOY® (flow path length 30 m) coated with PEG as a stationary phase into a coil with a diameter of 27 mm and a length of 65 mm. The ball SAW sensor was coated with PDMS as a sensitive film.

Using this prototype, we analyzed the aroma components of sake, which is a brewed beverage. Honjozo-shu A, B, C and Ginjo-shu D, E, F of different brands were prepared as samples, and the headspace gas of each sake was collected at 16 ml/min for 2 minutes. The column temperature was maintained at 40 °C for 5 minutes and then raised to 140 °C at 10 °C/min.

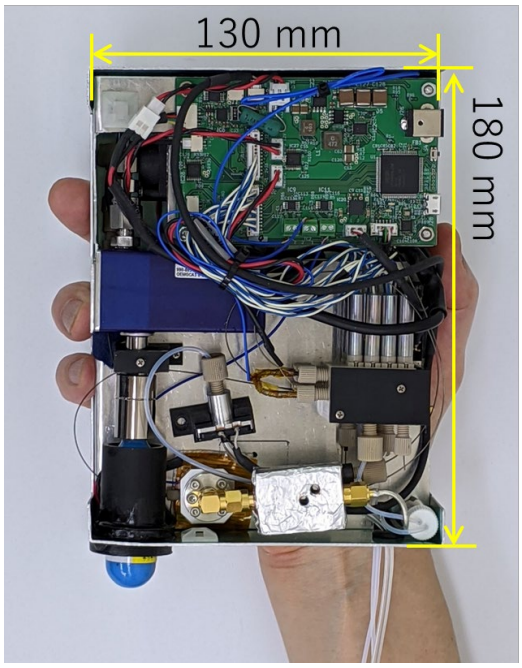


Fig. 7 Palm-sized ball SAW GC.

Fig. 8 shows the chromatograms of the headspace gas of Honjozo-shu A and Ginjo-shu D obtained by analysis using this prototype. The components of each peak could be identified by 1: ethyl acetate, 2: ethanol, 3: water, 7: isoamyl alcohol, 9: ethyl caproate, and 10: ethyl caprylate. In addition, peak 5 with a retention time of 8.6 minutes is isoamyl acetate, and peaks 4, 6 and 8 appearing before and after that are currently unidentified.

The peak areas of isoamyl acetate, which is a characteristic of Honjozo-shu, and ethyl caproate and ethyl caprylate, which are Ginjo-shu incenses, are shown in **Fig. 9**.

In the case of isoamyl acetate, the values of Honjozo-shu A to C and Ginjo-shu D were high, and in ethyl caproate, the values of Ginjo-shu D to F were high. In the past report [9], the value of Ginjo-shu D was high for ethyl caprylate, but it was about the same as F in this experiment. It is possible that the component volatilized during the storage period of the sample, or that fermentation progressed and the sample was transformed into another component. Ginjo-shu D has both the Ginjo incense of ethyl caproate and ethyl caprylate and the Honjozo incense of isoamyl acetate. We confirmed with brewers that the yeast from Ginjo-shu and Honjozo-shu were used together.

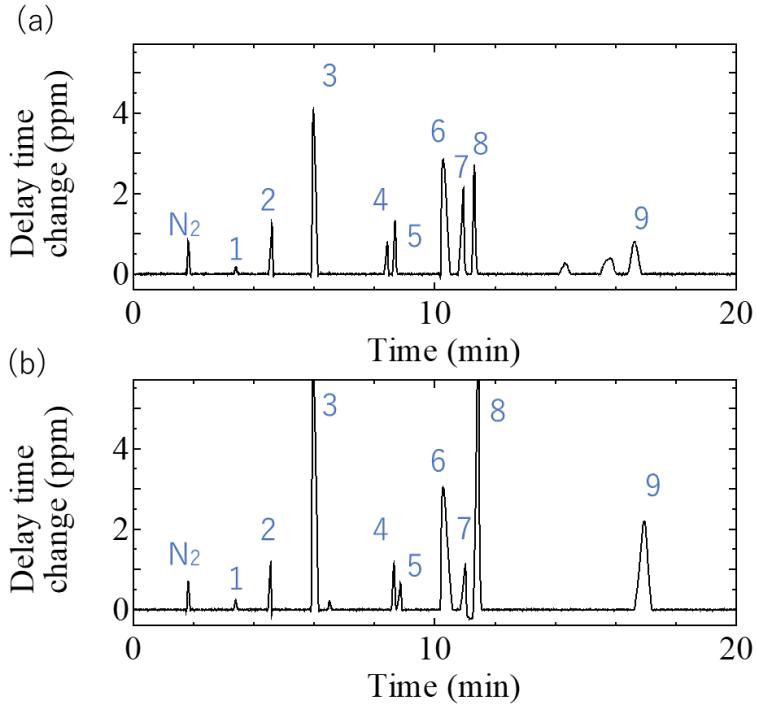


Fig. 8 Chromatograms obtained by analysis of (a) Honjozo-shu A and (b) Ginjo-shu D.

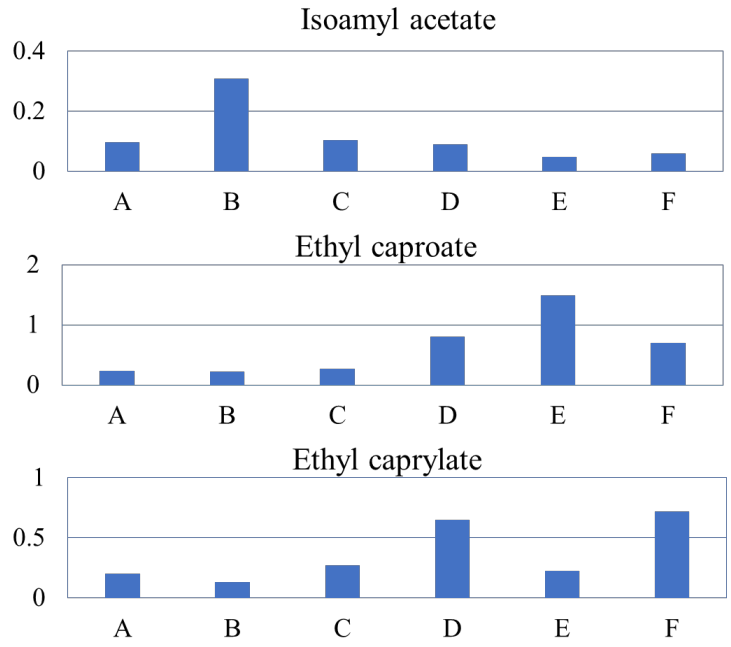


Fig. 9 Peak areas of aroma components of each brand.

The flavor wheel is known as an index that links the odorants obtained from chromatograms to the sensory evaluation. Although the words and phrases have been organized several times in the long history of sake, a system using the analysis results as standard terms was compiled in 2006 [10]. Flavor wheels have different odors and tastes in each class. Class 1 is lined with Ginjo incense, fruity incense, ester, alcohol, and flowery incense.

Fig. 10 shows a radar chart of the peak areas of the chromatograms in their odorants. Since human sensory perception is proportional to the logarithm of the concentration of a substance, we plotted the logarithm of the peak area of the chromatogram.

Although the peak area values of Honjozo-shu A, B, and C were different, their shapes of the radar chart were very similar. The radar charts of Ginjo-shu D, E, and F were also similar. Their shapes differed from the radar chart of Honjozo-shu in that they were elongated in the vertical direction.

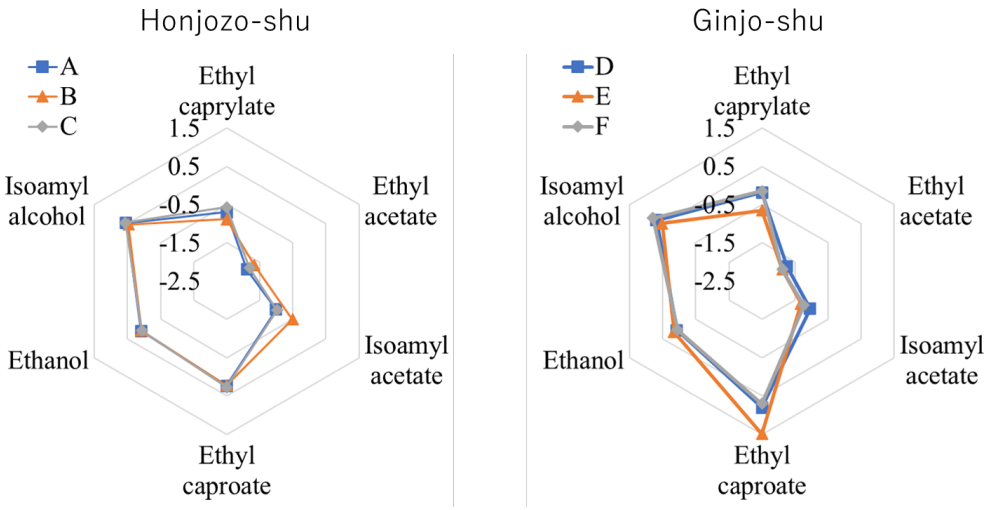


Fig. 10 Radar chart of each brand according to the flavor wheel

6. Conclusion

We have developed two types of three-layered metal MEMS columns with different stationary phases, evaluated by the nondestructive testing using an acoustic microscope. Using these columns, we have developed the prototyped ball SAW GC of 10 cm cube and 762 g weight. This GC equipped with the same functions as those of the desktop GC that include the sampler, the pre-concentrator, and the column temperature controller. It was succeeded in separating and detecting 10 kinds of gases within 10 minutes measurement and showed the capability of the in-site analysis of multiple gases.

Furthermore, as application of ball SAW GC on the ground, we have developed a palm-sized ball SAW GC using one metal capillary column. Using this GC, we analyzed 6 types of headspace gas of sake and showed that the peak areas of the main components differed depending on the brand of sake. We also founded a characteristic difference in shape between Honjozo-shu and Ginjo-shu by using a radar chart based on the flavor wheel.

Therefore, the ball SAW GC is expected to be useful not only for monitoring cabin atmosphere in spacecraft, but also for applications on the ground such as quality control of the brewing process and in-site analysis of produced substances in yeast cultivation and development.

Acknowledgment

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