1P2-15

Separation and Detection of Odorous Compounds at Parts-Per-Billion by Volume Levels Using Ball SAW Gas Chromatograph

ボール SAW ガスクロマトグラフによる ppbv レベルのにおい物質の分離・検出

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1. Introduction

There are broad range of requirements for on-site analysis of voratile organic compounds (VOCs) at parts-per-billion by volume (ppbv) levels. For example, food quality control by monitoring the ordorous compounds and early detection of desease by analysis of biogas are expected. Gas chromatograph (GC) is useful for such analyses, but conventional GCs are too large to be applied for on-site analysis. We have developed a portable ball surface acoustic wave (SAW) GC [1] using ball SAW sensor where SAW makes multiple roundtrips without diffraction [2, 3]. In this study, we developed a preconcentrator (PC) for very trace gases and an injector of sample gases to further improve the sensitivity of the ball SAW GC, and measured VOC mixtures at ppbv levels. As a demonstration, we analyzed the odorous compounds of soy sauce.

2. Ball SAW GC

A schematic diagram of ball SAW GC equipped with a PC is shown in **Fig. 1**. The PC was a stainless steel tube filled with Tenex®TA (GL Sciences) as absorbents and a nichrome wire was wound around the tube for resistive heating. Sample gas is drawn through the PC by a pump and trapped by the absorbents. Then by switching valves and quickly heating the PC, the trapped gas components are desorbed and injected into a separation column with reverse flow to the sampling mode (backflush). Each component is separated because of different retention time due to adsorption to stationary phase coated on the inner surface of the column, and is detected by delay time or amplitude changes of the SAW by adsorption to the sensitive film coated on the ball SAW sensor. In this study, we used a 3.3 mm quartz ball SAW sensor (150 MHz) coated with polydimethylsiloxane (PDMS) or Siponate DS-10™ as the sensitive film.

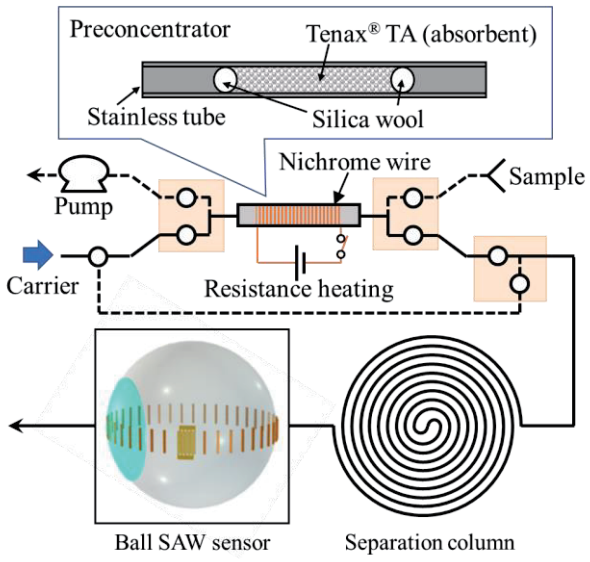

Fig. 1 Schematic diagram of ball SAW GC.

3. Separation and detection of mixture at ppbv levels

We measured a mixture containing 4 kinds of VOCs in nitrogen with each concentration of 80 ppbv using the ball SAW GC. Sample gas was trapped for 28 minutes at a flow rate of 70 ml/min. As a column, we used InertCap®1 (GL Sciences) cutting into 3 m. The response of ball SAW sensor (Siponate DS-10) is shown in **Fig.2**. Each component is separated and detected as clearly separated peak.

In addition, we measured mixture of 3 kinds of odorous compounds (800 ppbv) contained in foods.

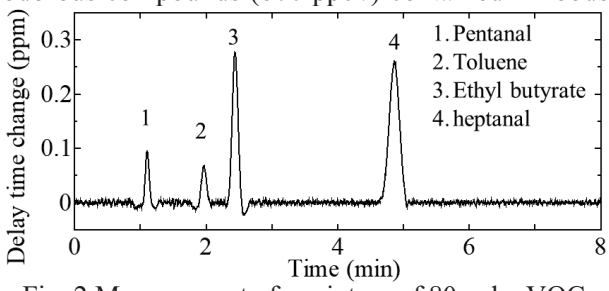

Fig. 2 Measurement of a mixture of 80 ppbv VOCs in nitrogen using ball SAW GC.

Sample gas was trapped for 20 minutes at a flow rate of 60 ml/min. A 30 m long InertCap® Pure-WAX column (GL Sciences) in a desktop GC was used. **Fig. 3** shows the response of ball SAW sensor (Siponate DS-10). Each component was clearly separated and detected as a peak.

Therefore, it was demonstrated that VOCs and odorous compounds at ppbv levels can be separated and detected by the ball SAW GC with a PC.

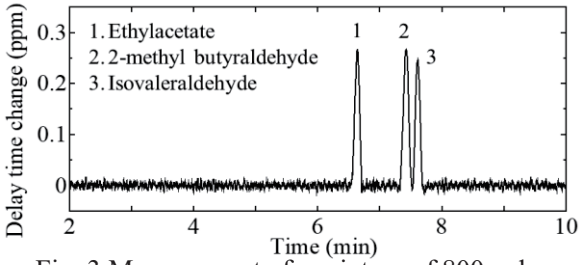

Fig. 3 Measurement of a mixture of 800 ppbv odorous compounds.

4. Analysis of headspace gas of soy sauce

Fig.4 shows a procedure of concentration and injection of headspace gas sample. Soy sauce was stored in a vial and the headspace gas was trapped by the PC for 10 minutes at a flow rate of 44 ml/min (Fig.4 (a)). Then, unadsorbed gas staying in the PC was exhausted with backflush by switching a valve (Fig.4 (c)). By switching valves and heating the PC to 200 ℃, the trapped gases were desorbed and introduced into a column (Fig. 4 (d)). The column and measurement conditions were the same as those shown in Fig.3. This system can also be applied to the "purge and trap" to trap the sample gas more effectively by bubbling liquid (Fig.4 (b)).

A chromatogram of headspace gas of soy sauce was obtained by the ball SAW GC (PDMS) in **Fig. 5** (a). Introducing the gas measured by the ball SAW sensor into a desktop GC, another chromatogram was obtained by a flame ionization detector (FID) in Fig. 5 (b). It is confirmed that the positions of both peaks agreed well. Since ethyl alcohol shows the highest response in soy sauce headspace analysis by FID [4, 5], peak 4 can be identified as ethyl alcohol. Moreover, comparing Fig.3 and Fig. 5, peak 1, 2, and 3 can be identified as ethylacetate with a fruit odor like pineapple, 2-methyl butyraldehyde with a chocolate flavor, and isovaleraldehyde which is an odorous compound of liquors and fruits, respectively. Since the amounts of these gases vary depending on the type yeast and the ripening time of koji (malted rice), they are indicators of the maturation status of soy sauce [5, 6].

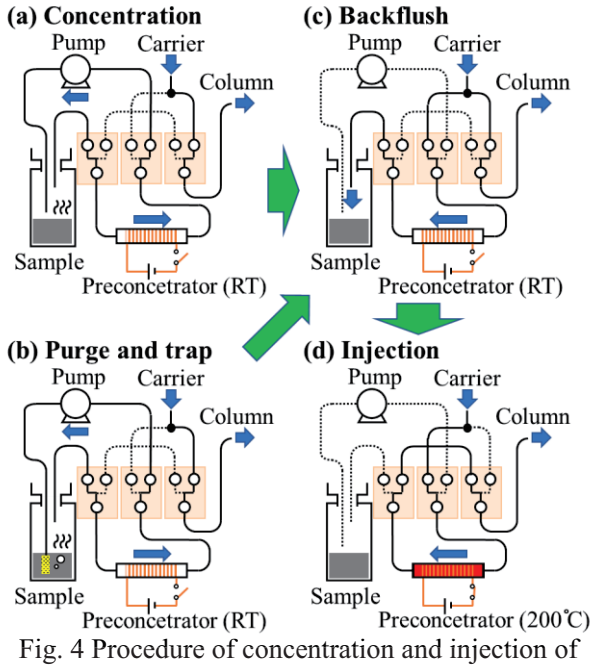

Fig. 4 Procedure of concentration and injection of headspace gas sample.

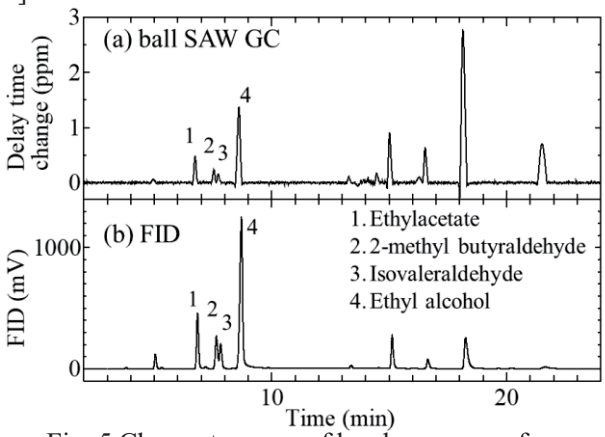

Fig. 5 Chromatograms of headspace gas of soy sauce by ball SAW GC (a) and FID (b).

5. Conclusions

We achieved separation and detection of VOC mixture at ppbv levels by ball SAW GC with a PC. We measured headspace gas of soy sauce and succeeded in detection and identification of odorous compounds which are indicators of the maturation status of soy sauce. Therefore, ball SAW GC is expected to be applied to analysis of odorous compounds in food manufacturing processes.

References

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