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Development of ball SAW gas chromatograph with quantitative analysis of multiple hazard gases

多種類の危険・有害ガス分析のためのボール SAW ガスクロマトグラフの開発

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1. Introduction

It is necessary to analyze multiple gases in the field of hazard gas detection for realizing safe and secure society. Although gas chromatograph (GC) is applicable for multiple gas analysis, it is not portable for its size and weight. We have proposed the ball SAW GC, using the ball surface acoustic wave (SAW) sensor where SAW makes multiple roundtrips without diffusing by the diffraction[1, 2] and a micro separation column fabricated by MEMS (Micro Electro Mechanical System) technology [3], and developed a prototype [4].
Qualitative and quantitative analysis are the main task for f multiple gas analysis using GC. However, previous ball SAW GC has a difficulty in quantitative analysis because of the limited repeatability of manual gas injection using a syringe. In this study, we show the possibility of handy ball SAW GC capable to perform quantitative analysis of multiple gases even if the peaks are overlapped, by developing a gas sampler to inject sample gas automatically and an algorithm using the least square fitting of chromatograms.

2. Development of quantitative analysis method

Figure 1 shows the principle of quantitative analysis. We assume that the peak height in chromatogram is linear to the gas concentration. First, we use M types of gases to take reference chromatograms shown in Fig.1 (a) and sample chromatogram shown as solid curve in Fig. 1 (b). Second, we calculate an fitting error σ; the squared sum of difference between linearly combined reference chromatograms multiplied by coefficients $a_1 \sim a_M$ and the sample chromatogram given by

$$\sigma = \sum_{i=K}^{L} \left(\frac{V_i - V_K}{V_K} - \sum_{i=1}^{M} a_j \frac{V_{ij}^* - V_{Kj}^*}{V_{Kj}^*} \right) \qquad (1)$$

where V and V^* are sample and reference data. K and L are start and end point of calculation range. Finally, we determine the coefficients $a_1 \sim a_M$ by minimizing the fitting error σ using

$$\frac{\partial \sigma}{\partial a_1} = \frac{\partial \sigma}{\partial a_2} = \cdots = \frac{\partial \sigma}{\partial a_M} = 0 \qquad (2)$$

The result of fitting is shown in Fig. (c).

3. Development of gas sampler

Figure 2 shows the concept of gas sampler. Broken lines show closed flow paths cut by valves. Solid lines show opened ones.

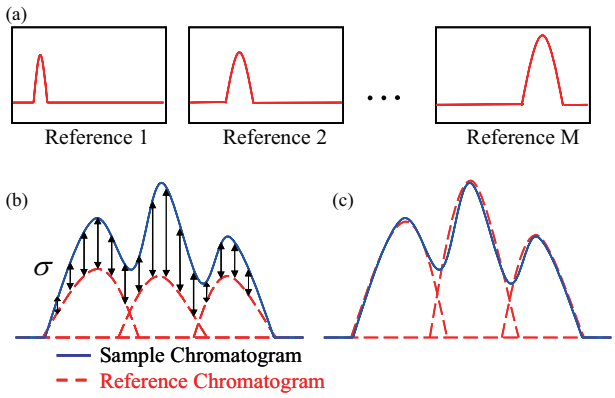

Fig.1 principle of quantitative analysis. (a) Taking reference chromatograms (b) Calculation of σ; (c)Linear combination of reference chromatograms

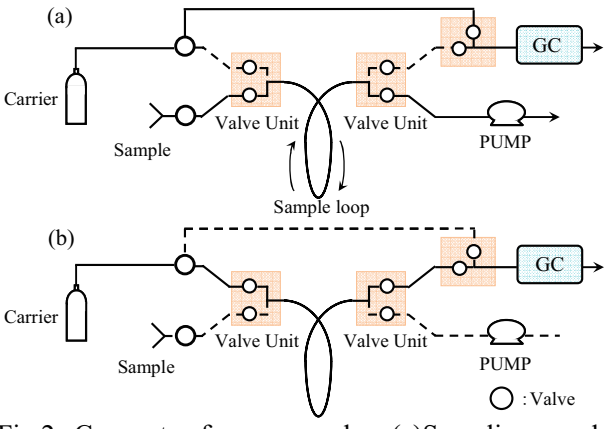

Fig.2 Concept of gas sampler (a)Sampling mode（before switching） (b)injecting mode （after switching）

In Fig.2 (a), carrier gas in the gas bomb flows into the GC, but sample gas is emitted in the atmosphere by the pump after the going through the sample loop. Then flow paths are switched into Fig.2 (b) by valves. Sample gas in the sample loop is pushed into GC by carrier gas. To inject sample gas next time, the operation (a) and (b) are repeated.

This method realizes the automatic injection because valves and the pump can be electrically controlled. Besides, the injection volume can be changed specified by the length. of sample loop

4. Results and discussion

We performed quantitative analysis using ball SAW GC with gas sampler after verified the each response quantity of chromatogram is linear to the each concentration of the gases.

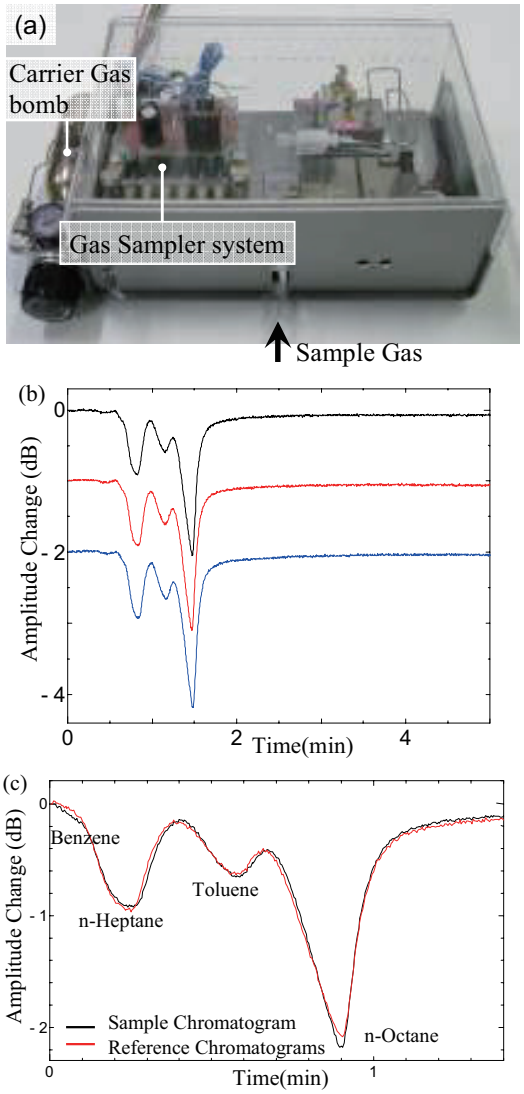

Fig3. Quantitative analysis (a) Ball SAW GC with gas sampler (b) Repeatability of chromatograms (c) Comparison between sample chromatogram and linearly combined reference chromatograms

	Mixed quantity(μl)		Coefficient		Concentration(%)	
	Ref gas	Sample gas	True	Estimated	True	Estimated
Benzene	10 (ref1)	3	0.3	0.17	0.27	0.15
n-Heptane	10 (ref2)	8	0.8	0.77	0.44	0.42
Toluene	10 (ref3)	5	0.5	0.38	0.38	0.29
n-Octane	10 (ref4)	10	1.0	0.83	0.50	0.41

Table1.Result of quantitative analysis

Figure 3 (a) shows the picture of ball SAW GC with gas sampler. Fig.3 (b) shows sample chromatograms of arbitrarily mixed benzene, n-heptane, toluene and n-octane analyzed by ball SAW GC with gas sampler. We succeeded in detecting each of 4 mixed gases using ball SAW GC with gas sampler. Moreover, repeatability of chromatograms was good.

Fig.3 (c) shows the comparison between sample chromatogram and linearly combined reference chromatograms with minimum error σ. The agreement is reasonably good. Table.1 shows the estimated results of coefficient and concentration using quantitative analysis method. The relative order and approximate magnitudes of concentration were reproduced.

5. Conclusion

We developed gas sampler and quantitative analysis method with algorithm using least square method to analyze multiple gases even if the peaks in the chromatogram are overlapped.

We realized automatic injection and good repeatability of chromatograms by introducing gas sampler. Moreover, the linearly combined reference chromatograms almost agreed to sample chromatogram and relative order of concentration was reproduced.

We succeeded in showing the possibility of handy ball SAW GC which is able to quantitatively analyze multiple gases. In the future, we focus on quantitative analysis of lower concentration gases required in the fields.

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