

Development of Ball SAW Gas Chromatograph for Natural Gas Analysis

天然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

Today, the production and consumption of natural gas are increasing due to its low environmental load. Moreover, the improvement of digging technique of the shale gas in the USA brought a profitable digging boom, resulting in an excitement for being free from dependence on the Middle East gasses (Figure 1 shows a surprising photo of a rig breaking the skyline of Fort Worth, Texas [1]). Therefore, it is possible that the supply plan of the natural gas is reviewed and new markets other than the USA are searched in the Middle East region [2].



Fig. 1 Rig for digging natural gas in Fortworth, USA[1]

In producing countries of natural gas, the composition is different among area and gas field. On the other hand, in consumer countries, the city gas composition provided by the Wobbe Index (WI) indicating combustion performance and by the maximum combustion potential (MCP) is different among countries. Thus gas chromatograph (GC) is used for composition monitoring in digging and

purification. However, present GC is too large for online (OL) monitoring, small and light CG is required. In this study, we improve our ball SAW GC [3-6] by forward flush method [7] and apply it to the natural gas analysis.

2. Standard of city gas

The city gas in Japan is regulated by a standard with MCP and WI as shown in Table I. MCP is given by

$$MCP = \frac{\sum (S_i f_i A_i)}{\sum (f_i A_i)} (1 - K) \tag{1}$$

where S_i is a burning velocity of combustible each gas, f_i is a coefficient of combustible each gas, A_i is a content rate of combustible gas (vol %), and K is an attenuation coefficient given by

$$K = \frac{\sum A_i}{\sum (\alpha_i A_i)} \left\{ \frac{2.5CO_2 + N_2 - 3.77O_2}{100 - 4.77O_2} + \left(\frac{N_2 - 3.77O_2}{100 - 4.77O_2} \right)^2 \right\} \tag{2}$$

where CO_2 , N_2 and O_2 are content rate of each gas in the city gas (vol %), α_i is a correction coefficient of combustible each gas (table II). And WI is given by

$$WI = \frac{Hg}{\sqrt{s}} \tag{3}$$

where Hg is gross heating value of city gas (MJ/m^3), s is a specific gravity of the gas to

Table I Standard of city gas

| | 13A | 12A | 6A | 5C | L1 | L2 | L3 |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| MCP | 35 - 47 | 34 - 47 | 34 - 45 | 42 - 68 | 42.5 - 78 | 29 - 54 | 35 - 64 |
| WI | 52.7 - 57.8 | 49.2 - 53.8 | 24.5 - 28.2 | 21.4 - 24.7 | 23.7 - 28.9 | 19.0 - 22.6 | 16.2 - 18.6 |

Table II Value used to calculate

| | H2 | CO | CH4 | C2H6 | C2H4 | C3H8 | C3H6 | C4H10 | C4H8 | Other HC |
|------------|------|-------|------|------|------|------|------|-------|------|----------|
| Si | 282 | 100 | 36 | 41 | 66 | 41 | 47 | 38 | 47 | 40 |
| fi | 1.00 | 0.781 | 8.72 | 16.6 | 11.0 | 24.5 | 21.8 | 32.7 | 28.5 | 38.3 |
| α_i | 1.33 | 1.00 | 2.00 | 4.55 | 4.00 | 4.55 | 4.55 | 5.56 | 4.55 | 4.55 |

air.

Because of this, there is a freedom in the gas composition even in the same standard. And efficient purification and addition matching composition of the source gas would make profit. This is because OL monitoring with GC is quite desirable.

3. Ball SAW gas chromatograph

Figure 2 shows a prototype ball SAW GC system. To separate and detect higher hydrocarbons, we fabricated a micro electro mechanical system (MEMS) column coated with 5% phenyl 95% polydimethylsiloxane (PDMS) in the channel. And a $\phi 3.3$ mm langasite ball SAW sensor was coated with PDMS sensitive film by using off axis spin coating [3,4]. To separate and detect lower hydrocarbons, we fabricated a MEMS column packed with styrene divinylbenzene micro beads by introducing a compression jacket [5]. Then we fabricated a ball SAW GC system combining them with a small carrier gas bomb, an injector, and a detector circuit. By using this system, we detected the model gas containing natural gas elements at the room temperature. By using this system, we detected a model gas sample containing representative natural gas components.

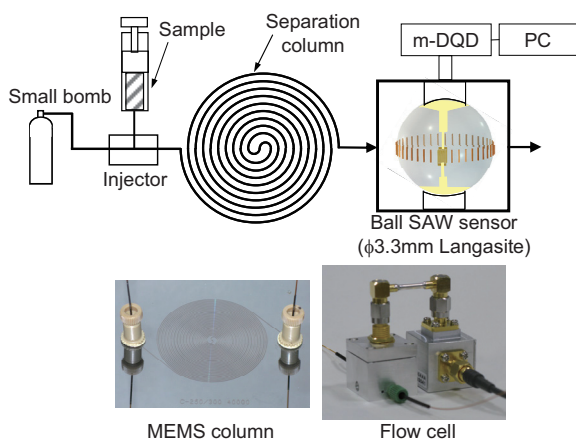


Fig. 2 Prototype of ball SAW GC system

4. Result and discussion

Figure 3(a) shows a chromatogram of the delay time change and the amplitude change due to six mixed hydrocarbons by a ball SAW sensor at 30 turn multiple roundtrips. We successfully separated and detected higher hydrocarbons more than hexane. We consider that the delay time change is depend on the mass loading effect and the amplitude change is depend on the viscoelastic effect because of sensitive organic film. Fig. 3(b) shows a chromatogram of amplitude change to detect methane, ethane and propane mix gas by 30 times

multiple roundtrips of ball SAW sensor. We successfully separated and detected 3 mix gases. The signal was obtained with the leaky loss whose measurement is a typical advantage of a ball SAW sensor over planer SAW sensors [6].

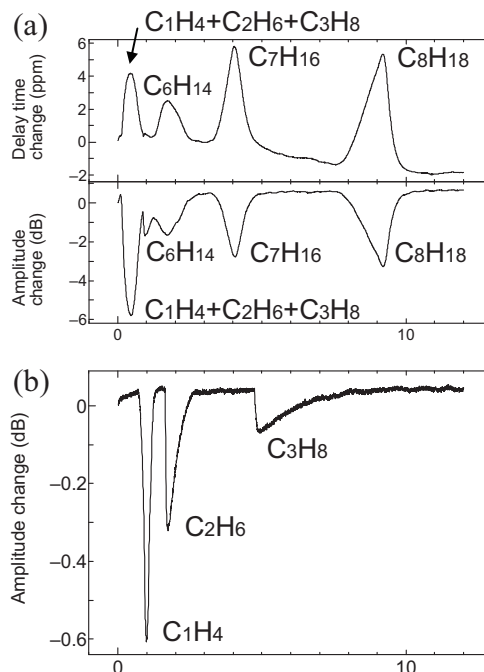


Fig. 3 Gas chromatogram of C1H4, C2H6, C3H8, C6H14, C7H16 and C8H18 (a) Separation by OT MEMS column (b) Separation by Packed MEMS column

5. Conclusion

For a social requirement of the process monitoring of the natural gas, Ball SAW GC could detect the natural gas element by the room temperature. For this reason, using gas forward flash method with multiple columns and sensors we can expect the application as small CG for the process monitoring of the natural gas.

References

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