Compact Room Temperature-Operated Sensing System for Methanol and Ethanol Mixture Separation and Quantification

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***Abstract*—For practical olfactory sensing with a safe and low-power system, it is important to be able to operate easily at room temperature. However, this has not been a trivial task to achieve with existing conventional gas separation and sensing devices. In this study, a novel compact room temperature-operated sensing system is proposed to separate and quantify each component in a vapor mixture with simple operation. The sensing system consists of a portable and replaceable gas separation column and a sensing module containing a nanomechanical Membrane-type Surface stress Sensor, MSS. Proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) results show that the gas separation column can clearly separate methanol and ethanol in their mixtures. The sensing signals from the column-MSS system are consistent with the peaks measured by PTR-TOF-MS. For mixtures of methanol and ethanol with various ratios, a clear correspondence is observed between the output signals and the theoretically calculated vapor pressure ratios of each mixture. The developed compact room temperature-operated sensing system can discriminate and quantify different methanol and ethanol mixtures, paving the way for practical applications of olfactory sensing devices.**

Keywords*—olfactory sensors; room temperature-operated; real-time; gas mixture; separation; quantification; MSS

I. INTRODUCTION

Each substance has different effects on the human body even with the same functional groups; in particular, ethanol has much fewer side effects on the human body than methanol. Since methanol and ethanol are often found together, it is important to detect the levels of methanol and ethanol in the beverage or in the environment separately and in a timely manner. The most commonly used measurement technique is gas chromatography (GC), which can separate the chemical substances for accurate quantification. However, it is mostly used in laboratories because of its time-consuming operation at elevated temperatures with a bulky and expensive system.

There have been various attempts to realize a practical sensing system for the separation and quantification of methanol and ethanol in their mixture. To reduce the overall size of the system, some studies have attempted to use micro-machined GC columns [1], [2]. For a low-power system, recent studies demonstrated room temperature-operated columns to separate components in a gas mixture [3]. Regarding the sensing elements, sensors capable of methanol and ethanol sensing at room temperature have recently been developed [4], [5]. Despite these advancements, challenges still remain: an integration of all these technologies towards a compact and room temperature-operated system for the rapid separation and quantification of methanol and ethanol mixtures without complex signal processing.

While there are various sensors developed so far, one of the candidates of a sensing element for a room temperature-operated system is a nanomechanical Membrane-type Surface stress Sensor (MSS) [6], [7]. Given the high sensitivity and compact size, MSS holds great promise for further improvement towards a fully room temperature-operated sensing system [8], [9], [10], [11]. While highly sensitive gas sensors like MSS with functional material receptors have been explored to detect and differentiate various mixtures at room temperature [8], they often lack the precise quantification capability that traditional methods like GC provide, especially for gas mixtures with the same functional groups. This general limitation of chemical sensors shows the ongoing need for a sensor system that can rapidly and accurately quantify target compounds.

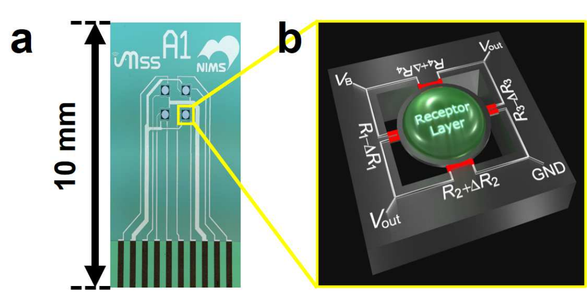

Fig 1. (a) The microscope image of an MSS chip. (b) Schematic of the MSS structure with electrical connections.

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Herein, we introduce a new practical sensing system with the combination of a gas separation technique based on column chromatography and an MSS measurement system. Proton transfer reaction-time of flight-mass spectrometry (PTR-TOF-MS) measurements confirmed that a room temperature-operated compact column can be used for effective gas separation. The gas separation column was integrated into the MSS sensing system, demonstrating clear output signals corresponding to methanol and ethanol vapors. Moreover, the column-MSS system exhibited clear signal differences in mixed samples with different vapor pressure ratios of ethanol/methanol. The resultant signal intensities are confirmed to be linearly related to the theoretical vapor pressure of each component. The demonstration of the room temperature-operated sensing system with gas separation capability will be a model case for the next generation of practical olfactory sensing devices.

II. Materials and Methods

A. Materials

Polystyrene (PS), polycaprolactone (PCL), poly(vinylidene fluoride) (PVF), and poly(4-methylstyrene) (P4MS) were purchased from Sigma-Aldrich and used as the MSS receptor materials in the experiments. *N,N*-Dimethylformamide (DMF; Wako Pure Chemical Industries, Ltd) was used as the solvent of receptor materials. For the sensing measurement, methanol (MeOH; Kanto Chemical Co., Inc.) and ethanol (EtOH; Wako Pure Chemical Industries, Ltd) in analytical grades were used as sample vapors. The material inside the separation column is Tenax TA (2,6-diphenyl-*p*-phenylene oxide; GL Sciences Co., 60/80 mesh). All chemicals were used as purchased.

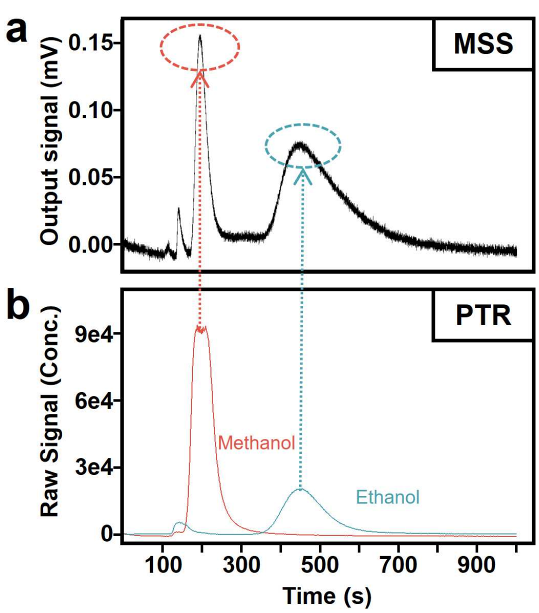

Fig 2. (a) Comparison of MSS output signals and (b) PTR-TOF-MS signals of the methanol and ethanol mixture.

B. Experimental procedure

PS, PCL, PVF, and P4MS were dissolved in DMF to a concentration of 1.0 g/L. Polymer solutions are dropped onto an MSS chip using an inkjet spotter (LaboJet-500SP, MICROJET Corporation) equipped with a nozzle (IJHBS-300, MICROJET Corporation). To enhance the vaporization of DMF, the stage of inkjet was heated at 80 °C.

To fabricate the room temperature-operated separation column, Tenax TA was put into a Teflon tube, and both ends are plugged with quartz wool. To remove the absorbed impurities of Tenax TA, the prepared column was initially purged with nitrogen flow at 100 sccm overnight. The gas sensing was performed with a custom made MSS measurement system, which consists of gas flow lines, mass flow controllers, and a sensor chamber. The MSS sensing measurements were carried out with a bridge voltage of –0.5 V and a sampling rate of 20 Hz. The data collection program was designed using LabVIEW (NI Corporation). The MSS measurement system was connected to the separation column, maintaining the gas flow rate at 25 sccm throughout the experiments. Nitrogen was used as the carrier gas to introduce the sample gas into the separation column and subsequently into the MSS measurement system. The data obtained from MSS were analyzed using Origin 2021b.

The real-time measurements of chemicals with and without the separation column were performed with PTR-TOF-MS (PTR-TOF 6000X2, IONICON Analytik GmbH). The data obtained from PTR-TOF-MS were analyzed using PTR-MS Viewer ver. 3.4.

III. Results and Discussion

A. Comparing PTR-TOF-MS and column-MSS system

The room temperature separation column was connected to a sample containing a mixture of methanol and ethanol. As shown in Fig. 2, the PTR-TOF-MS confirmed that the separation column could effectively separate methanol and ethanol, demonstrating the feasibility of the room temperature-operated separation column. The sensing signals of the

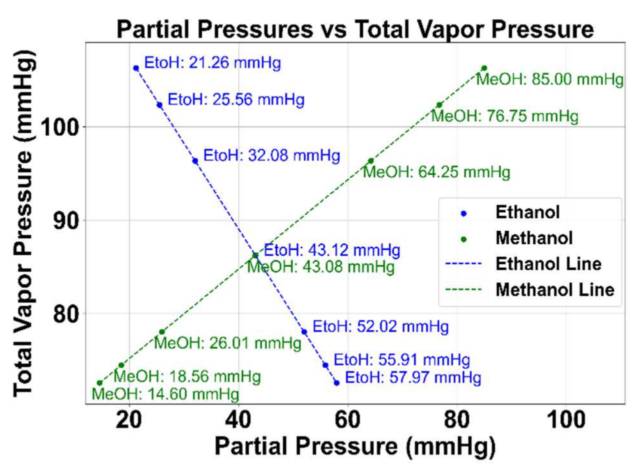

Fig. 3. Partial vapor pressures and total vapor pressures based on Raoult's law.

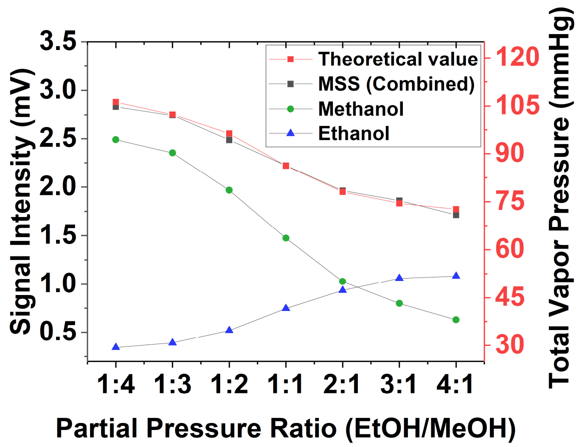

Fig. 4. Signal intensity of different partial pressure ratios of EtOH and MeOH as measured by the column-MSS system. 'MSS (Combined)' refers to the sum of ethanol and methanol maximum signal intensity. 'Methanol' and 'Ethanol' represent the maximum of the output signal for methanol and ethanol. The theoretical values are found in red.

column-MSS system were found to be consistent; both PTR-TOF-MS and MSS exhibited two different peaks (i.e., the first peak was methanol and the second was ethanol) observed at similar retention times, demonstrating the reasonable sensitivity and response time of the column-MSS system.

B. *Sensing signal from ethanol and methanol mixtures with different vapor pressure ratios*

Since the sensing signal of MSS depends on the vapor pressure of the target molecule [12], methanol and ethanol mixtures consisting of different vapor pressure ratios (ethanol/methanol vapor pressure ratios were 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, and 4:1) were prepared. To evaluate these mixtures, the relationship between the partial pressure of each mixture and the total vapor pressure of the different fractions of the mixtures in the ideal gas state was calculated according to Raoult's Law [13]. It was found that for opposite vapor pressure ratios (e.g., ethanol/methanol of 1:4 and 4:1), the partial vapor pressure of methanol was higher than that of ethanol (Fig. 3).

We measured methanol and ethanol mixtures with different vapor pressure ratios using the column-MSS system. As shown in Fig. 4, by increasing ratios of ethanol/methanol vapor pressure, the signal intensity of methanol decreases, while that of ethanol increases. It is shown that mixture vapor pressure decreases with decreasing amount of methanol. The observed MSS signal intensity trend (represented by the black line) closely matches the theoretical values calculated according to Raoult's Law (represented by the red line), indicating that the MSS sensing signal can be used to accurately quantify the mixture vapor. For increasing ratios of ethanol/methanol vapor pressure, the signal intensity of methanol decreases, while that of ethanol increases (Fig. 4). Therefore, with the column-MSS system, the concentration of each component can also be clearly quantified, which is usually challenging with a conventional olfactory sensing system.

IV. Conclusion

We have developed a compact room temperature-operated sensing system to separate and quantify vapor mixtures of methanol and ethanol. Firstly, a gas separation column was prepared, and then the vapor mixture separation performance of the column was verified with PTR-TOF-MS. Next, the column was integrated with the MSS sensing system. The obtained sensing signal of the system was consistent with the result of PTR-TOF-MS. A series of ethanol and methanol mixtures with different vapor pressure ratios were prepared and measured using the column-MSS system. For different vapor pressure ratios of methanol and ethanol mixtures, the sensing signals from the column-MSS system showed a clear correspondence between the output signals and the theoretical values. Since the limit of detection of MSS can be down to ppm, ppb, or even ppt level depending on the physical/chemical characteristics of target molecules [12], the compact room-temperature operated sensing system can effectively separate and quantify diverse ratios of gas mixtures. This study not only demonstrates the feasibility of a room temperature-operated system but also paves the way for the development of olfactory sensing devices in real-world applications. Such advancements hold significant potential for environmental monitoring, healthcare diagnostics, and quality control in manufacturing.

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