Monitoring of Residential Air Quality by Formaldehyde Biochemical Gas Sensor for Indoor Public Health

High sensitive (sub-ppb) bio-sniffer for residential VOC assessment

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***Abstract*— An optical fiber biochemical gas sensor (bio-sniffer) for assessment of indoor formaldehyde was fabricated and tested. The bio-sniffer measures formaldehyde vapor as fluorescence of reduced nicotinamide adenine dinucleotide (NADH), which is the product of formaldehyde dehydrogenase (FALDH) reaction. Usually, an enzyme loses its specific activity in the gas phase. This makes biochemical gas monitoring difficult. We used a micro flow-cell with a FALDH immobilized membrane to prevent the FALDH from deactivation. An ultraviolet light emitting diode (UV-LED) with peak emission of 335nm was employed as an excitation light source. Emission of the UV-LED was introduced to the optode through an optical fiber and fluorescence of NADH was picked up coaxially at the optode. In order to improve the sensitivity, a photomultiplier tube was utilized as a photodetector. Consequently, continuous FA monitoring with biochemical method was successfully conducted with high sensitivity and high selectivity. A real-sample test was also carried out with the bio-sniffer. According to the results, it is expected to be useful in fast and convenient monitoring of indoor FA.**

Keywords- residential formaldehyde; bio-sniffer; volatile organic compound; public health.

I. INTRODUCTION

Formaldehyde (FA) is a reactive and flammable aldehyde which is well known as one of the harmful volatile organic compounds (VOCs). Although FA is also produced in natural processes [1], it is mainly emitted to the living environment by human activities. One of the main emission sources of indoor FA is urea-formaldehyde resins in pressed wood products, such as particleboard and fiberboard used in cabinetry and furniture. A combination of respiratory disease, allergic dermatitis and other ailments so called sick building syndrome (SBS), is associated with chronic exposure to FA [2-3]. Therefore, indoor FA levels are occasionally utilized to assess indoor air qualities. The guideline for indoor FA is determined to 80 ppb from its acute toxicity by world health organization (WHO). Although the WHO standard is held in many countries, there are still serious health problems caused by chronic exposure to FA even less than 80 ppb.

The relationship between the indoor FA levels and related health damages are usually investigated using chromatographic methods [4]. However, these methods are too time-consuming to monitor the daily fluctuation of indoor FA levels. Hence, solid-state gas sensors with gas-sensitive oxides are expected in monitoring of indoor VOCs for their stability, reduced cost and fast response [5-10]. Considering the monitoring of indoor FA, it is also important to enhance the selectivity to other chemicals since the measurement is conducted under the presence of many chemicals. Improving the selectivity of real-time gas monitoring in mind, we previously reported a biochemical gas sensor (bio-sniffer) that utilizes enzyme to recognize the target substance [11].

In this work, we have constructed a fiber-optic biochemical gas sensor for continuous monitoring of indoor formaldehyde with high sensitivity and tested by monitoring fluctuation of FA levels using real-sample. We report the design, structure, characteristics and latest result of indoor FA monitoring.

II. EXPERIMENTAL

A. Design and Fabrication

The bio-sniffer measures FA as fluorescence of nicotinamide adenine dinucleotide (NADH), which is the product of formaldehyde dehydrogenase (FALDH) reaction given as following equation.

$$FA + NAD^{+} + H_2O \xrightarrow{FALDH} \text{formic acid} + NADH + H^{+} \quad (1)$$

The bio-sniffer consists of an UV-LED-based excitation system, a photomultiplier tube (PMT) and an optical fiber probe with a flow-cell. The UV-LED based excitation system was constructed by attaching an UV-LED (UVTOP® BL335, Sensor Electronic Technology, Inc., USA) on a custom-fabricated UV-LED power supply (KLV CO., LTD., Japan) with an adjustable SMA connector.

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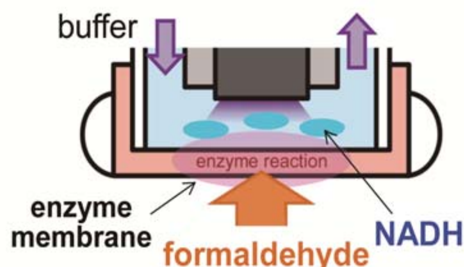

Figure 1. Principle of the fiber-optic bio-sniffer for FA vapor.

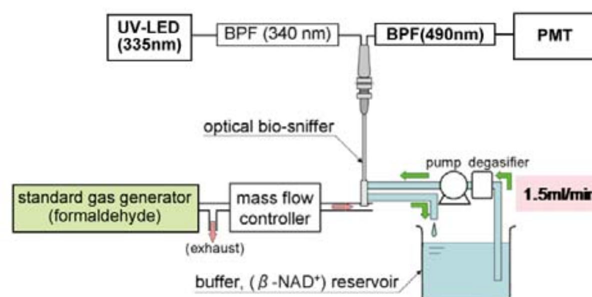

Figure 2. Experimental set-up for characterization of the bio-sniffer.

The excitation system and the PMT (C9692, Hamamatsu Photonics, Co., Ltd, Japan) were connected to an optical fiber probe (F1000-900, core diameter: 1.0 mm, Ocean Optics Inc., USA) using an optical fiber assembly (BIF600-UV/VIS, Ocean Optics Inc., USA). The excitation light and the fluorescent light were filtered using a band-pass filter (BPF: 490-510 nm) and a long-pass filter (LPF: >400 nm) purchased from Asahi Spectra Co. LTD. (Japan), respectively. A flow cell, on which an enzyme immobilized membrane, was attached at the end of the optical fiber probe. The enzyme membrane was prepared as follows: FALDH (FALDH, EC 1.2.1.1, 1 units/mg, solid, from Pseudomonas sp., Funakoshi Co., Ltd., Tokyo, Japan) with an activity of 1 unit mg^{-1} of protein was first immobilized onto a hydrophilic PTFE (H-PTFE) membrane filter (Porosity: 80 %, Pore size: 0.2 µm, JGWP14225, Millipore Co., USA) by curing a mixture of 2-methacryloyloxyethyl phosphorylcholine (MPC) copolymerized with 2-ethylhexyl methacrylate (EHMA) solution (1µl cm^{-2}) and FALDH (50 units cm^{-2}) on the H-PTFE membrane filter (4 °C, 180 min).

Figure 1 represents the working principle of the bio-sniffer. Since the enzyme is immobilized at the hydrous sensing membrane, the FA vapor at the neighborhood of the probe is easily dissolved into the flow-cell. As explained in eq (1), FALDH produces formic acid and NADH under the presence of FA and NAD^+. Fluorescence of the NADH is coaxially introduced into the optical fiber probe and measured with the PMT. Phosphate buffer which contained NAD^+ is continuously circulated in the flow-cell to prevent enzyme from deactivation, to remove the products of enzyme reaction and to rinse the excessive substrate. The NADH produced at the sensing region is immediately removed from the sensing region. Therefore, the output of the fiber-optic bio-sniffer is determined by the trade-off of the FA level and the removal rate of NADH (i.e. flow-rate of the phosphate buffer). This indicates that the sensing region of the bio-sniffer is always refreshed by the circulation of the phosphate buffer which contained NAD^+.

B. Characterization of the FA bio-sniffer

Characterization of the bio-sniffer was carried out using a standard gas generator (Permeater, Type: PD-1B, Gastec Corp., Kanagawa, Japan) [12]. Figure 2 shows the experimental set-up for characterization of the fiber-optic bio-sniffer. The UV-LED was operated with a constant forward current of 20 mA for excitation of NADH. The excitation light was coupled into the optical fiber and guided to the probe. During the measurement, phosphate buffer (pH 8.0, 80 mM) with NAD^+ (20 mM) was circulated into the flow-cell (flow rate: 1.5 ml/min). Various concentrations of standard FA vapor were supplied with the standard gas generator. The flow-rate of the sample gas was fixed at 200 ml/min. Fluorescent signal was measured with the PMT and the signal was recorded using a laptop PC.

In order to confirm the usefulness of our system for real indoor airs, fluctuation of the FA levels induced by a real-indoor air was also investigated using the bio-sniffer in real-time.

III. Results and Discussion

A. Spectral response to FA vapor

First of all, spectral response to formaldehyde vapor was investigated. Fluorescent spectrum of NADH was measured by replacing the PMT with a fiber-optic spectrometer. A cut on wavelength of 400nm was employed instead of the BPF (490nm). Figure 3 shows the spectral responses of the bio-sniffer. The line labeled 0 ppm represents the initial response and 5.0 ppm is the spectral response to 5.0 ppm FA vapor. In both cases, phosphate buffer which contained NAD^+ was circulated. Fluorescence increased as the concentration of the gaseous FA increased. The peak wavelength of the spectrum was 491nm, which is consistent with our previous reports [11]. The result indicates that NADH was successfully produced by enzyme reaction of FALDH (eq.1).

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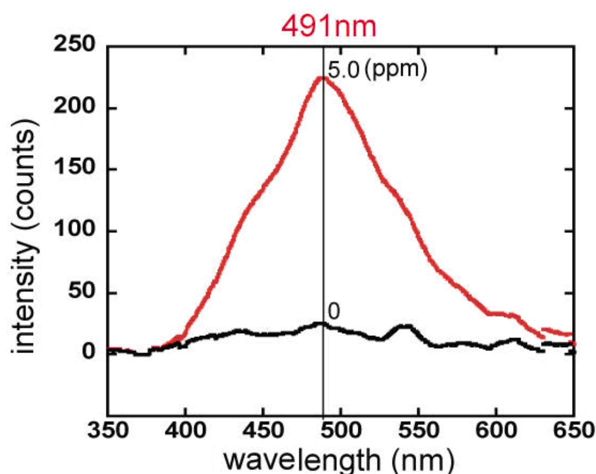

Figure 3. Spectral response of the bio-sniffer.

B. *Characteristics of the bio-sniffer for FA vapor*

After the spectral investigation, characterization of the bio-sniffer was carried out using the PMT as a photodetector and the BPF (490 nm). At first, the dynamic response to the FA exposure was investigated. Figure 4 shows the change of fluorescent response to FA. Exposure to Standard FA was conducted from 2 to 10 min. Only the carrier gas, which impurities were removed with activated carbon filter, was flown into the sensing region before and after the measurement.

At the beginning of FA exposure, the fluorescent signal increased immediately and became stable in approximately 90 seconds. And the signal decreased down to the initial value after the switching into carrier gas. The increase of the signal can be associated with the production of NADH as mentioned above, and the decrease of the signal is the resulted by the circulation of phosphate buffer. Considering the working mechanism, the fluorescent signal can be increased by reducing the flow-rate of the buffer circulation. The lower detection limit was 2.5 ppb, with the simple single LED excitation system. This can be improved by increasing the intensity of the excitation light by using multiplied LED system. The selectivity of the bio-sniffer was also investigated. Acetaldehyde, acetone, benzene, methanol and ethanol (5.0 ppm) was also tested using the bio-sniffer with FALDH. The maximum fluorescence was 1.3% of FA in case of acetaldehyde and no significant crosstalk was found in case of other chemicals.

In order to confirm the possibility of indoor FA monitoring, we also conducted a real-sample test. First the pure carrier gas was applied and confirmed the initial level. After that, air in the laboratory was applied to the sensing region. As a result, the fluorescence increased immediately and the FA level was estimated to 20 ppb at that time while it varies by the temperature or position in the room.

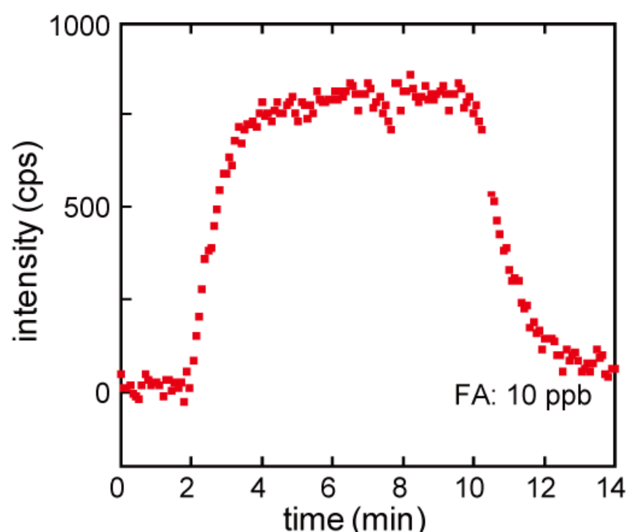

Figure 4. Typical change of the fluorescece during FA exposure. Standard FA vapor (10.0 ppb) was applied to the sensing region from 2 min to 10 min.

IV. CONCLUSIONS

A bio-sniffer for FA vapor was fabricated and confirmed to be useful for indoor FA monitoring. Since the bio-sniffer uses an enzyme for molecular recognition, high selectivity was achieved. The optical measurement system also reduces the effect of interferences in comparison with electrochemical methods. High sensitive detection system with the PMT provided high sensitivity to FA vapor. Using the optimized multi-LED system, it is expected to be able to monitor sub-ppb level FA in real-time.

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REFERENCES

[1] R. Guicherit and F.L. Schulting, “The occunence of organic chemicals in the atmosphere of the Netherland,” Sci Total Environ. 43, 1985, pp. 193–219.

[2] J. Gamble, “Effects of formaldehyde on the respiratory system.” In: Gibson JE, ed. Formaldehyde toxicity. Hemisphere & McGraw Hill, Washington DC, 1983, pp. 175-197.

[3] H. Maibach, “Formaldehyde: Effects on animal and human skin.” In: Gibson JE, ed. Formaldehyde toxicity. Hemisphere & McGraw Hill, Washington DC, 1983, pp. 166-174.

[4] J. Levin, K. Andersson, R. Linndahl, and C. Nilsson, “Determination of sub-parts-per-million levels of formaldehyde in air using active and passive sampling on 2,4

dinitrophenylhydrazine-coated glass fibre and high-performance liquid chromatography," Anal. Chem. 57, 1985, pp. 1032–1035.

[5] J.A. Dirksen, K. Duval, and T.A. Ring. "NiO thin-film formaldehyde gas sensor," Sens. Actuator-B 80, 2001, pp. 106–115.

[6] T. Seiyama, A. Kato, K. Fujiishi, and M. Nagatani, "A new detector for gaseous components using semiconductive thin films," Anal. Chem. 34, 1962, pp. 502–1506.

[7] M. Tonoike, "Current status and future view of development for odorantsensors," Bull. Electrotechn. Lab. 52, 1988, pp. 63–79.

[8] Y. Hiranaka, T. Abe, and H. Murata, "Gas-dependent response in the temperature transient of SnO2 gas sensors," Sens. Actuators-B 9, 1992, pp. 177-182.

[9] T. Maekawa, J. Tamaki, N. Miura, and N. Yamazoe, "Development of SnO2-based ethanol gas sensor," Sens. Actuators-B 9, 1992, pp. 63–69.

[10] P. Lv, Z.A. Tang, J. Yu, F.T. Zhang, G.F. Wei, Z.X. Huang, and Y. Hu. "Study on a micro-gas sensor with SnO2-NiO sensitive film for indoor formaldehyde detection," Sens. Actuators-B 132, 2008, pp. 54-80.

[11] H. Kudo, M. Sawai, Y. Suzuki, X. Wang, T. Gessei, D. Takahashi, T. Arakawa, and K. Mitsubayashi, "Fiber optic bio-sniffer (biochemical gas sensor) for high selective monitoring of ethanol vapor using 335 nm UV-LED," Sens. Actuator B-Chem, 147, 2010, pp. 676-680.

[12] Mitsubayashi K., Nishio G., Sawai M., Saito T., Kudo H., Saito H., Otsuka K., Noguer T., and Marty J-L., A bio-sniffer stick with FALDH (formaldehyde dehydrogenase) for convenient analysis of gaseous formaldehyde. Sens. Actuators B 130, 2008, pp. 32-37.