

MEASUREMENT OF GLUTARALDEHYDE IN OCCUPATIONAL INDOOR AIR BY PASSIVE SAMPLER

Yoshika Sekine, Daisuke Oikawa, Kazunobu Saito* and Yasuo Asano**

School of Science, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa, 259-1292 Japan. sekine@keyaki.cc.u-tokai.ac.jp

* TSL Incorporated, 3-5-5 Midorigaoka, Hamura, Tokyo 205-003 Japan.

** Asano Dental Clinic, 5-6-16 Midorigaoka, Zama, Kanagawa 228-0021 Japan.

1. INTRODUCTION

Glutaraldehyde (GA) has been in widespread use in hospitals to sterilize instruments which are not suitable for heat sterilization. Routine exposure to GA is, however, known to cause adverse health effects such as eye irritation, sore throats, skin irritations, dermatitis, short-term memory loss and fatigue, especially for workers in endoscopy, dentistry and other medical departments within hospitals [1].

A solid adsorbent coated with 2,4-dinitrophenylhydrazine (DNPH) was previously used for the determination of GA in air [e.g. 2-4]. Passive samplers, which employ diffusion process based on Fick's law and hence do not require power supply or other services, are suitable for monitoring personal or indoor exposure concentrations of GA in the occupational environment. Then, Authors have evaluated a previous passive diffusion sampler for aldehydes and ketones (DSD-DNPH) [4,5] for the determination of GA in air at ppb level. The sampler is capable of taking samples of GA gas from the atmosphere at a rate controlled by porous polyethylene tube. In the tube DNPH coated silica gel is uniformly packed as a reactive adsorbent. GA permeating through the tube is deposited on the adsorbent surface and collected as DNPH derivative. The product is eluted by acetonitrile and is subsequently determined by high performance liquid chromatography (HPLC). The sampling duration of this device was set for 8 hours to apply to field measurements in workplace.

Using such passive samplers, sampling rate, α is a dominant factor for analytical liability. As shown in Eq.(1), collected amount of GA on adsorbent, W could be converted to air concentration, C using exposure time, t and α , if the adsorbent reduces the concentration of the given analyte at the end of diffusion layer ideally to zero due to sorption or chemical reaction [6].

$$C = \frac{W}{\alpha t} \quad (1)$$

In this study, the sampling rate of the DSD-DNPH against GA was determined by chamber experiments and evaluated in field tests.

2. EXPERIMENTAL

Passive sampler used in this study, DSD-DNPH is commercially available from Supelco. The sampler consists of three parts: porous polyethylene(PE) tube, reservoir made of PE tube and DNPH coated silica gel (See Fig.1). The porous tube is made of sintered PE particles with 34.5% of porosity and work as a diffusion filter (Fig.2). The polyethylene tube is used for reservoir of the adsorbent when eluting DNPH derivatives by passing 10mL of acetonitrile. Amount of impregnated DNPH is 1mg per sampler.

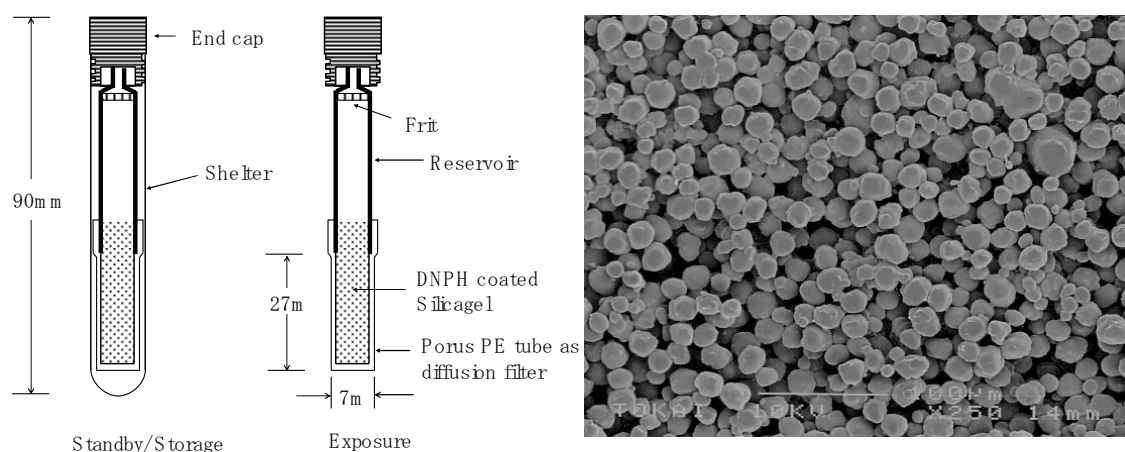


Fig.1 Schematic view of DSD-DNPH Fig.2 SEM image of the diffusion filter ($\times 250$)

The sampling rate was investigated using a small chamber (32L) with a constant gas generation system under controlled temperature. Diffusion samplers were hanged at the center of top of the chamber inside, and GA gas was constantly introduced from a gas generator [7] at a flow rate of 4L/min (air exchange rate=7.5/h). A fan operating thoroughly mixed the air in the chamber. As a reference to passive sampler, active sampling was simultaneously carried out by pulling air through DNPH coated solid cartridge (Supelco, LpDNPH) connected with air pump (Shibata Science., MP-Σ30) at a flow rate of 0.3L/min for 8hrs. To evaluate the sampling rate determined, field tests were conducted in a model laboratory of university and workplace of a dental clinic in Kanagawa, Japan.

After sampling, the adsorbent of the passive sampler was placed in the reservoir tube. DNPH derivatives were eluted by passing 10mL of acetonitrile in 5 min, and determined by HPLC. The HPLC system consists of Shimadzu LC-6A pump with SPD-6A UV-Vis detector. The following conditions were used: column, 4.6mm \times 150mm, 5 μ m, Inertsil ODS-80A (GL sciences); eluent, 60/40 acetonitrile/distilled water at 1.5mL/min (isocratic) ; detection, 360nm, Injection volume, 20 μ L. Diluted GA-DNPH (0.1mg/mL, in acetonitrile, Supelco) was used as analytical standard. Duplicate injections were made for standards, samples and blanks. Analytical procedure of active samplers followed described here.

3. RESULTS AND DISCUSSION

3.1 HPLC analysis

Glutaraldehyde reacts with DNPH and gives possible three geometric isomers of hydrazone: *syn-syn*, *syn-anti* and *anti-anti*. However, two peaks were seen in the HPLC chromatogram. The ratios between major and minor peak areas were not constant: 5.2 ± 0.14 in the standard solution ($0.05\text{--}0.15 \mu\text{g/mL}$, $n=4$), 3.2 ± 0.23 in eluted solutions from active samplers ($n=16$) and 3.4 ± 0.25 in eluted solutions of passive sampler ($n=16$) used for chamber and field measurements. Therefore, we added up the two peaks for calibration and determination. Coefficient of variations for repeated injections of $1 \mu\text{g/mL}$ of standard solution were 2.3% in peak area and 1.1% in retention time ($n=4$). It had been known that peak area varied with time because of unstable properties of DNPH derivatives of certain aldehydes and ketones after elution. Then, just after passive and active sampling in the chamber, DNPH derivatives were quickly eluted and time-series analysis were made for both samplers. As shown in Fig.3, for example, the peak response of the active sampler gradually increased and became constant by 3 hours after elution (the sample solution was stored at 25°C). However, such an increase was not found when the active sampler was stand in the room at least 3 hours before elution. This leads conclusion that sampler or sample solution should be stand at least 3 hours at room temperature before analysis.

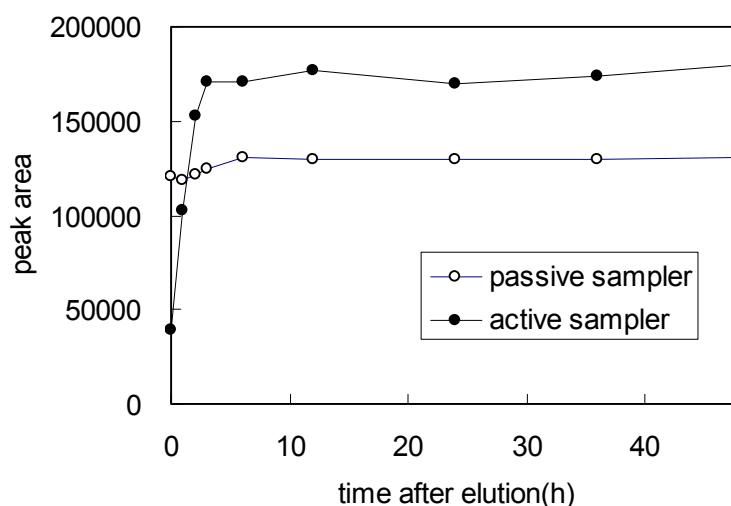


Fig.3 Variations of peak areas after elution of GA-DNPH derivatives from the passive and active sampler (eluted solution was stored at 25°C).

3.2 Sampling rate

Sampling rate of the sampler was determined by chamber experiments. As air concentration, C can be described in volume basis (ppm) and mass basis (mg/m^3), the rates are expressed as follows.

$$\alpha_v(\mu\text{g/ppm/h})=W(\mu\text{g})/C(\text{ppm})/t(\text{h}) \quad (2)$$

$$\alpha_w(\mu\text{g}/(\text{mg/m}^3)/\text{h})=W(\mu\text{g})/C(\text{mg/m}^3)/t(\text{h}) \quad (3)$$

Fig.4 shows relationship between air concentration, C (ppm) measured by the active sampling method and collected amount of GA per hour, W/t on adsorbents of the passive sampler at 25°C. Even though the simultaneous exposure tests were conducted with varying relative humidity from 35 to 71%, the collected amounts of GA by passive samplers showed good linearity against air concentrations in the chamber. This meant sampling rate of GA gas was constant and independent on the relative humidity. By adapting Eq.(2) to this relationship, the sampling rate of passive sampler can be derived from the slope of a linear regression analysis and resulted in 9.7 ± 0.38 ($\mu\text{g/ppm/h}$) for GA. Similarly, the rate resulted in 2.4 ± 0.11 ($\mu\text{g}/(\text{mg/m}^3)/\text{h}$) using mass concentrations. Alternatively, the sampling rate can be written in 40mL/min, which is 6.8 times greater than that of the badge type passive sampler [8].

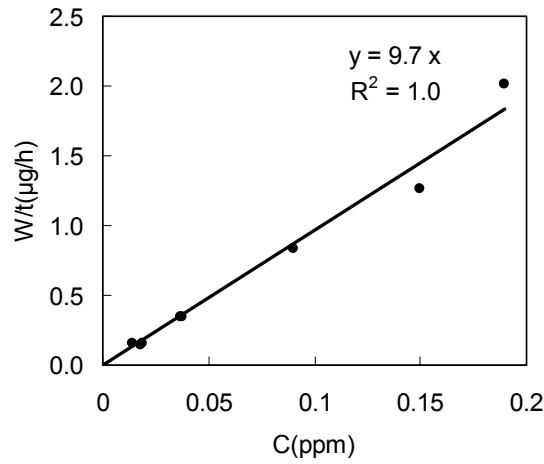


Fig.4 Scatter diagram between C and W/t.
(chamber experiment ,25°C,RH 35-71%)

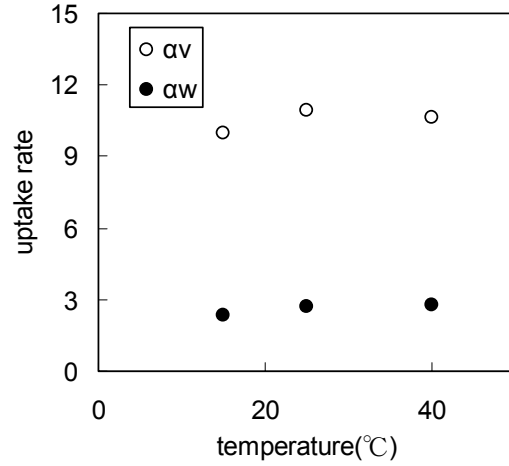


Fig.5 Derived sampling rates plotted against temperature.

The sampling rate of this sampler is potentially depends on temperature; diffusion coefficient usually increases to the absolute temperature raised to the 1.66-1.83 power, air concentration varies inversely with absolute temperature according to the ideal gas law, increase in temperature decreases physical adsorption efficiency of the gas molecule, and heterogeneous reaction rate increases exponentially with absolute temperature obeying an Arrhenius law, if the gas molecule could be first trapped on the surface of silica gel and then fixed as DNPH derivatives. Then, temperature tests were performed at 15, 25 and 40°C, which seems to be realized in a hospital atmosphere. Effect of temperature was not apparent on the rates under at least given conditions as shown in Fig.5. This tendency was similar to the result of previous study on formaldehyde [5].

3.3 Field evaluation

The sampling rates were then validated in the field measurement. Indoor air concentrations of GA were measured by the passive sampler and co-located active samplers in two fields. Sampling duration was set at 8 hours. At first, a model laboratory in a university facility was used. The dimension of the room was approximately 7.9m (length) × 3.0m (width) × 3.8m (height). About 1L of 3w/v% GA solution, generally used for sterilizer (Maruishi Pharmaceutical, STERISCOPE®) was poured in a plastic bucket (32cm×25cm×11.5cm) and set on a self-standing chair 90cm above from the floor. Air ventilation system was not operated during the samplings. Secondary, the simultaneous measurements were conducted in a dental clinic located in Kanagawa, Japan, where the GA solution is normally employed for sterilizing tools and equipments. The sterilizer was stand in a plastic bucket (32cm×25cm×11.5cm) loosely covered by a plastic cover at the side of the examination room. Measurements were carried out in July 2003 and January 2004, on the days the clinic was closed. Fig.6 illustrates good agreement of the passive sampler response with that of the active method for the determination of 4~180 ppb of GA using the sampling rate derived from the chamber experiment. The results show excellent linearity of the technique and suggest that reasonable accuracy can be expected after establishing the sampling rate under given exposure conditions.

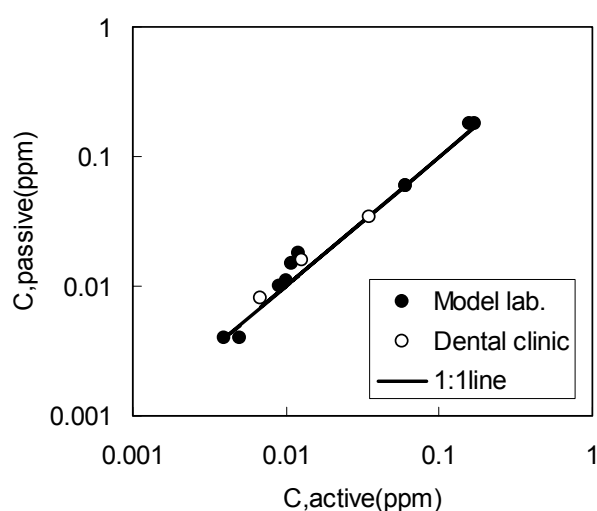


Fig.6 Scatter diagram of field measured concentrations between passive and active sampling methods.

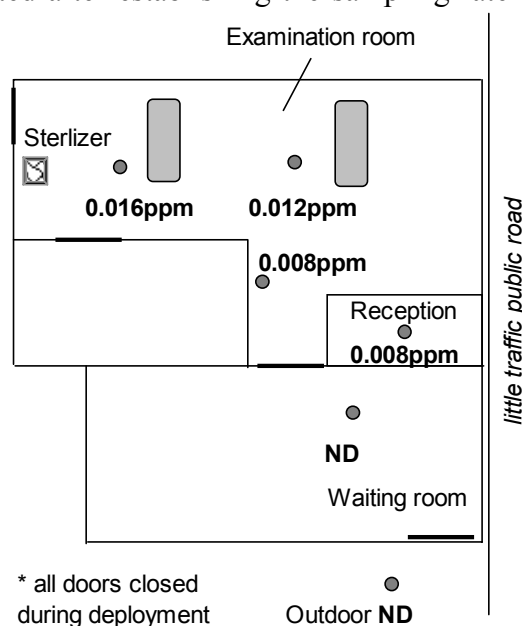


Fig.7 Indoor air GA concentrations at the dental clinic (26 Feb.,2004)

3.4 Quality assurance

The precision of the passive sampling method was assessed by field triplicate measurements conducted in the university laboratory. Relative standard deviations (RSD) were 0.78% for 4.0 ppb of air concentration and 0.17% for 180 ppb. Since significant

contamination by field handling and during storage was not detected in transport and storage blanks, limit of detection (LOD) of the sampler was defined as 3 times HPLC baseline noise level ($S/N=3$) and resulted in 1.2 ppb of GA in air for 8h sampling duration following the analytical procedure described above. Similarly, limit of quantitation (LOQ) was defined as 10 times the noise ($S/N=10$) and 3.9 ppb of LOQ was obtained.

3.5 Distribution of GA in dental clinic

Based on the results, distribution of indoor concentration was measured by the passive sampler in the examination room, reception and waiting room of the dental clinic at a height of 1.2m above the floor. There is usually a breathing zone of Japanese adult around the height. Results were illustrated in Fig.7. The GA concentrations shown in this figure were obtained using sampling 8-hour period at 5 sites in 26 February 2004. Relatively higher concentrations were observed in the examination room, where the sterilizer usually used by dentist, while GA was not detected in the waiting room partitioned from the emission source.

4. CONCLUSION

A sampling rate of DSD-DNPH was determined by chamber experiments and resulted in 9.7 ($\mu\text{g/ppm/h}$) for GA. Effects of temperature and humidity on the rate were not apparent. The sampling rates were then validated in the field measurements comparing with a previous active sampling method. The diffusion sampler was successfully used for determination of GA and gave similar results to active sampling in indoor air of the dental clinic located in Kanagawa, Japan. LOD of the diffusion sampler was defined as 10 times standard deviation of HPLC baseline noise and resulted in 3.9 ppb for 8-hour exposure in air.

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