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Personal Diffusive Sampler for Methanol, a Hydrophilic Solvent

Toshio Kawai,[1] Tomojiro Yasugi,[1] Yoko Uchida,[2] and Masayuki Ikeda[2,3]

[1]Osaka Occupational Health Service Center, Osaka 550, Japan and [2]Department of Public Health, Kyoto University Faculty of Medicine, Kyoto 606, Japan

Diffusive samplers are badge-type exposure monitors which take advantage of diffusion of vapor for sampling volatile pollutants in atmospheric air (Ikeda and Okuno 1988). Attention has been paid (e.g., Berlin et al. 1987) to occupational and environmental health use of diffusive samplers because of its practicality, and it has been shown that the device is especially valid for the measurement of time-weighted average exposure of individual workers in solvent workplaces (Yin et al. 1987; Liu et al. 1988; Inoue et al. 1988 and 1989). The use of activated carbon cloth, which is the most popular absorbent for variety of organic solvents, has been however hampered by the serious problem that carbon has only limited capacity to retain water-soluble solvents such as methanol (Koizumi and Ikeda 1982; Kasahara and Ikeda 1987). Accordingly, personal sampling device with an absorbent suitable for methanol sampling has been searched for, as methanol is gaining it popularity not only among various industrial solvent preparations (Inoue et al. 1983; Kumai et al. 1983) but in home-use solvent products (Saito et al. 1989).

This article is to describe the results of experiments to show that a commercial product, Pro-Tek® Badge originally designed for formaldehyde monitoring, can be successfully applied for monitoring occupational exposure to methanol, utilizing water as the absorbent.

MATERIALS AND METHODS

Pro-Tek® Formaldehyde Badge (Series II, Type C-60; from Du Pont, Wilmington, DE, U.S.A.) was employed. The sampler consists of two bags sealed in succession in a 63 mm x 68 mm plastics sheet (for details, see Kring et al. 1981 and 1984). One bag in a upper half of the

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[3]Correspondence/reprint requests to: Prof. M. Ikeda

sheet which contains 'blank solution' was ignored throughout. The other bag in a lower half has a plastic piece ('diffuser'; ca. 3 mm x 55 mm in space and ca. 6 mm tall) which allows penetration of some organic volatile chemical (e.g., formaldehyde for which it was originally designed) with no leakage of water, when the sampler is placed vertically and the plastic piece is located at the bottom. A tiny hole was made at an upper end of the lower bag for the supply/removal of the absorbent (2.0 ml of water) and also washing of the bag by means of a disposable 2.5 ml clinical syringe and needle. The hole was sealed with a small piece of adhesive tape during the exposure of the sampler. A preliminary experiment showed that washing 3 times with water (2.0 ml, each) was enough to clean-up the bag.

A servomechanized exposure chamber (Koizumi and Ikeda 1981) was used for experimental exposure of the sampler. Methanol vapor at known concentrations was generated by bubbling of air through liquid methanol, followed by dilution with fresh air, and the concentration in the chamber was monitored periodically at 6-25 min (depending on the schedule) by means of automated FID-gaschromatography (GC). Performance was previously described (Koizumi and Ikeda 1981; Kumai et al. 1984); in the case of methanol exposure, the observed mean concentration was 98-102% of the ordered concentration with a small (about 1%) coefficient of variation.

After exposure of the sampler to methanol at the known concentration for a known duration was terminated, the exposed water was taken out, of which 1 ul/injection was injected into a FID-GC as previously described (Kawai et al. 1987) with one modification that the column was heated at 75°C in the place of 55°C. Namely, the GC (Shimadzu GC-15A) was equipped with a glass column (3.2 mm in inner diameter and 4.1 m in length; packed with 10% SBS-100 on Shimalite TPA, 60-80 mesh), and was connected with an automatic sample injector and an electronic integrator. The temperature of the oven and the injection port was 75°C and 180°C, respectively, and nitrogen gas, hydrogen gas and air were supplied at 1.8, 0.6 and 0.5 kg/cm^2, respectively.

RESULTS AND DISCUSSION

First, the relationship between air concentration, exposure duration and the amount of methanol absorbed was examined. Thus, samplers, 3 to 5 per exposure condition, were exposed to methanol at a constant concentration of 400 ppm for different durations up to 8 hr, and the amount of methanol was examined if it was

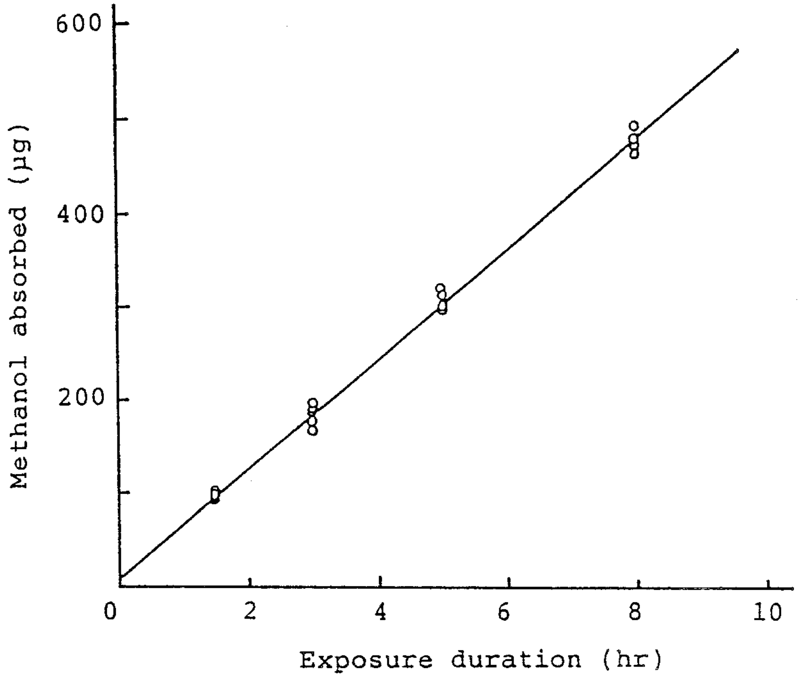

Figure 1. The amount of methanol absorbed in proportion to the exposure duration up to 8 hr. Samplers, 4 at each time, were exposed at 400 ppm.

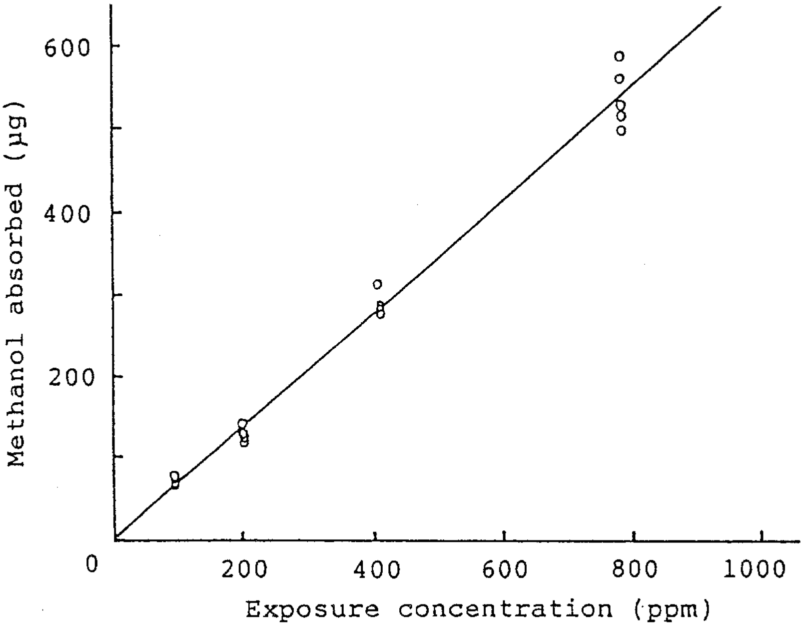

Figure 2. Linear relationship between the exposure concentration and the amount of methanol absorbed. Samplers, 5 at each concentration, were exposed for 4 hr.

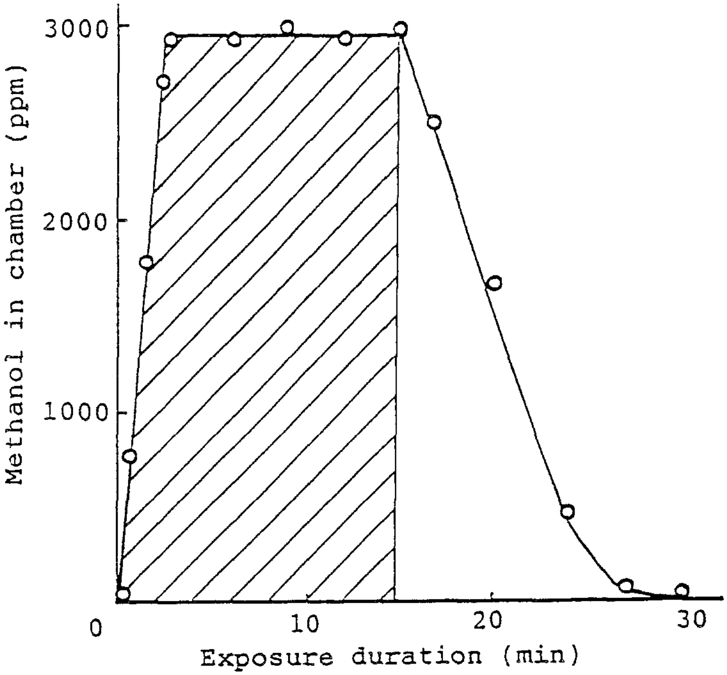

Figure 3. The design of short-term peak exposure of the samplers to methanol vapor. The shaded area shows the concentration and the duration of the exposure. The experiment revealed that an efficiency rate of 100.9% is established.

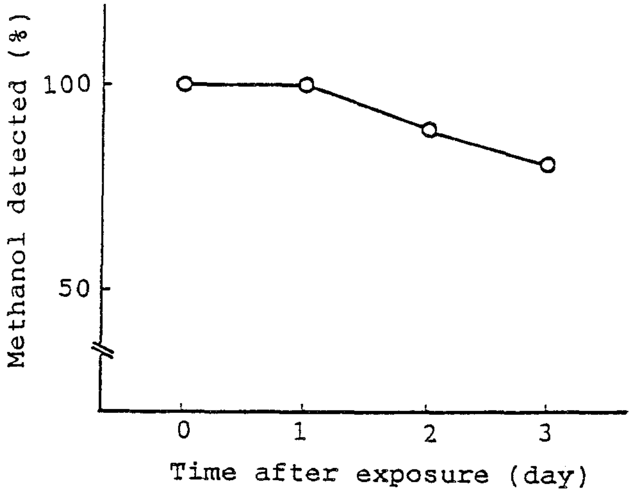

Figure 4. Disappearance of methanol from a sampler after exposure. Samplers were exposed to methanol at 2000 ppm for 30 min, and methanol in water was measured on Day 0 (i.e., on the day of exposure), 1, 2 and 3 after exposure. The mean amounts of 3 samplers are shown, taking the Day 0 value as 100 (%).

proportional to the exposure duration. The experiment clearly demonstrated that a linearity holds between the exposure duration and the amount of methanol absorbed (Fig. 1). It was further proved that the amount of methanol absorbed after 10 hr exposure at 200 ppm (i.e., 2000 ppm·hr exposure) precisely agrees with the estimate from the regression line in Fig. 1. Similarly, the amount of methanol absorbed was proportional to exposure concentrations of up to 800 ppm for a fixed duration of 4 hr (Fig. 2). Such findings were in contrast to the previous observation with activated carbon cloth that methanol absorbed on the carbon cloth is not linearly related to the exposure time but levels off (Koizumi and Ikeda 1982), due to spontaneous desorption of methanol from the carbon (Kasahara and Ikeda 1987). The variation in the amount of methanol among the 5 samplers exposed simultaneously was small; the coefficient of variation in the worst case observed was about 5%, indicating high reproducibility.

One of the critical performance needed to be achieved is a quantitative response to a short-term peak exposure. To test this function, methanol concentration in the exposure chamber was rapidly elevated in 3 min to reach ca. 3000 ppm, maintained there for 12 min, and then allowed to decrease as depicted in Fig. 3. Samplers were taken out of the chamber at 15 min after the initiation of the exposure so that they were exposed to methanol at the concentration and the duration shown by the shaded area below the curve (i.e., 40,535 ppm·min; Fig. 3). It is possible to deduce from the regression line in Fig. 2 [$Y = 0.6767X$, here Y is the amount (µg) of methanol absorbed after 4 hr (or 240 min) exposure at X ppm] that 338.35 µg methanol will be absorbed after 120,000 ppm·min exposure. Thus, the amount of methanol absorbed after 40,535 ppm·min exposure was estimated to be 114.29 µg. The carbon cloth after the 15 min exposure contained 113.7 µg methanol (or 99.5% of the estimate) in one experiment and 116.8 µg methanol (102.2%) in the other. The average efficiency of 100.9% indicates that the absorption is rapid enough to respond such a short-term peak exposure.

Finally, possible decay in methanol concentration in the absorbent (water) was examined. Samplers were impregnated with methanol by exposure at ca. 2000 ppm for 30 min, and then left in fresh air for 3 days. The methanol in the water measured on Day 0 (i.e., on the day of exposure), 1, 2 and 3 are depicted in Fig. 4. It is clear that there was a gradual decrease in methanol amount as a function of time; the decrease was insignificant ($p>0.10$) on Day 1 but a significant

($p<0.05$) loss was detected on Day 2 (by 12%) and Day 3 (by 20%), suggesting that the back diffusion of the methanol from the water to air in 2 days was small but not negligible. When the water was taken out of the sampler immediately after exposure and kept in a glass-stoppered bottle at room temperature, the decrease in methanol concentration was insignificant ($p>0.10$) till Day 3 but barely significant on day 4 ($0.05<p<0.10$), as observed by Bartley et al. (1988). Thus, it is recommendable to transfer water to a small tube when exposure was terminated, and analyze it within 3 days.

The present findings show that the sampler tested can absorb methanol vapor in linear relation to the exposure duration up to 10 hr and to exposure concentration up to 800 ppm, the maximum duration and concentration tested, respectively, that the response to short-term peak exposure is rapid enough, and that no spontaneous desorption will take place. Thus, it is possible to conclude that the difficulty in personal monitoring of methanol encountered when carbon cloth was employed as absorbent (Kasahara and Ikeda 1987) is cleared up, and that time-weighted average exposure of methanol in occupational setting can be monitored by the sampler tested. One problem still remaining would be possible leakage of water when the water bag is accidentally pressed. This problem would be solved by improving the structure of the diffuser portion.

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