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Diffusive Personal Sampler for Methyl Acetate Monitoring

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Methyl acetate is an organic solvent present in some industrial materials such as paints and adhessives (Kumai et al., 1983), and to a lesser extent in degreasers (Inoue et al., 1983); experience shows a mixture of methanol and methyl acetate is used for removal of styrene monomer-containing uncured resin from brushes in fiber-reinforced plastics production. Furthermore, additional attention has been recently paid to this ester as a possible source of methanol in sniffing thinner. Ogawa et al. (1988) studied a case of acute optic neuropathy after thinner sniffing, and suspected methyl acetate as a causative agent in the thinner; one paint thinner which the patient used to sniff contained this ester by 20% (in addition to methanol by 20%), this ester is more volatile with higher vapor pressure at saturation than methanol, readily absorbed, and quickly hydrolyzed to methanol and acetate when taken into body. Interestingly, this ester is not only lipophilic as an organic solvent, but partly soluble also in water. Because of this physico-chemical characteristics, application of conventional personal diffusive samplers such as those equipped with carbon cloth (Hirayama and Ikeda, 1979) or water (Uchida et al., 1990) as an absorbent is associated with difficulties due to rapid spontaneous desorption.

A new diffusive sampler is developed in the present study in which silica gel is employed as an absorbing material. The details are described in this communication.

MATERIALS AND METHODS

Silica gel (A gel with a relative surface area of 790 m^2/g, 20-30 mesh; Kida Chemicals, Tokyo, Japan) was a

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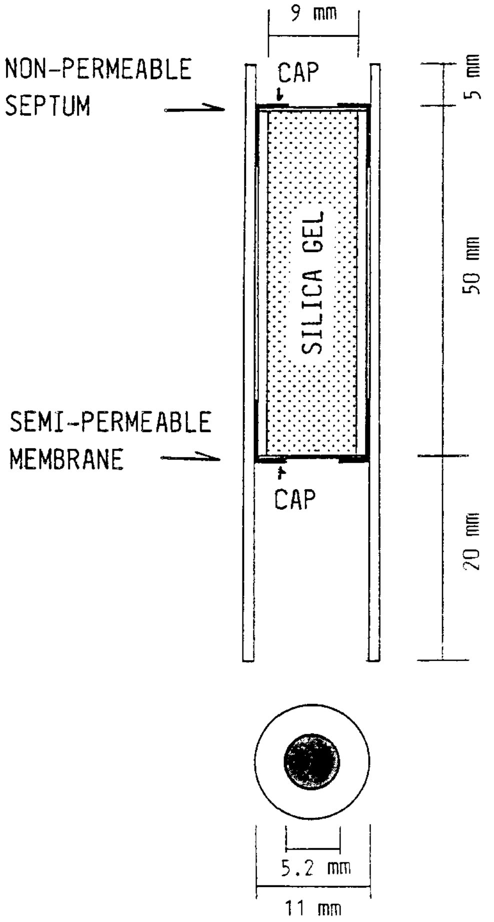

Figgure 1. Structure of the sampler with silica gel as an absorbent

Silica gel, 1.2 g, in a cylindrical container is exposed to the ambient air across a semi-permeable membrane (Cellpore® NW-11; Sekisui Chemical Co., Osaka, Japan) to absorb solvent vapor, e.g., methyl acetate. The lower part of an outer cylinder serves also a wind-killer.

kind gift from Komyo-Rikagaku & Co., Tokyo, Japan. Other reagents were purchased from Nacalai Tesque, Inc., Kyoto, Japan.

The structure of the newly designed sampler is depicted in Fig. 1. The main part of the sampler is a poly-propylene cylinder (25 mm in length and 9 mm in inner diameter) containing ca. 1.2 g of silica gel. One end of the cylinder is air-tightly sealed. The other end is sealed with a semipermeable polypropylene membrane (Cellpore ® NW-11; Sekisui Chemical Co., Osaka, Japan); the membrane allows free passage of methyl acetate vapor. The entire cylinder is protected by another larger polypropylene cylinder (60 mm in length and 13 mm in inner diameter) that serves also as a wind-killer. The sampler can be used as a personal sampler (attached to the chest of an exposed worker) as well as a stationary sampler, keeping sealed end up and wind-killer part down so that the silica gel is in a direct contact with the semipermeable membrane so that methyl acetate vapor after passing through the membrane will be absorbed by the silica gel.

Samplers were tested in a servo-mechanized solvent vapor exposure chamber system (Koizumi and Ikeda, 1981; Kumai et al., 1984). The vapor concentration in the chamber was measured automatically every 13 min, and performance was such that the mean of the measured concentrations was almost 100% of the nominal concentration with a coefficient of variation of less than 4%.

Under standard conditions, i.e., unless otherwise specified, the exposed silica gel was quantitatively transferred to a glass container, and shaken vigorously for 10 min in the presence of 3 ml of ethanol (spiked with methanol by 0.1%, v/v, as an internal standard). The extract was subjected to GC analysis on 30-m DB-WAX capillary column at 40°C with flame-ionization detectors as previously described (Kawai et al., 1991a and b). Under the conditions employed, it was possible to complete one analysis in 7 min.

For comparison, two other types of samplers, i.e., the one equipped with carbon cloth (Hirayama and Ikeda, 1979) and the other with water (Uchida et al., 1990), were also exposed to methyl acetate. The procedures of the GC analysis were as previously described (Hirayama and Ikeda, 1979; Uchida et al., 1990). Regression analysis and *t*-test were employed when necessary.

RESULTS AND DISCUSSION

To examine the recovery, 1.2 g of silica gel spiked with 300 µg of methyl acetate was extracted with 3 ml of ethanol containing 0.01% methanol for a period of 10 min. Recovery of methyl acetate was 100.6% (with a coefficient of variation of 0.95% after 5 measurements) based on GC analysis of methyl acetate in 10 µl ethanol. Under the conditions studied, methanol remained in ethanol and was not lost in air or absorbed by silica gel. Similar recovery experiments with water, carbon disulfide and ethyl acetate in the place of ethanol disclosed that the recovery was about 38.2±4.7% (average±SD of 5 determinations) with water, and none with carbon disulfide. In the case of ethyl acetate, a large peak for ethyl acetate over-lapped with a small peak for methanol in the chromatogram under the GC conditions employed, which made it difficult to study

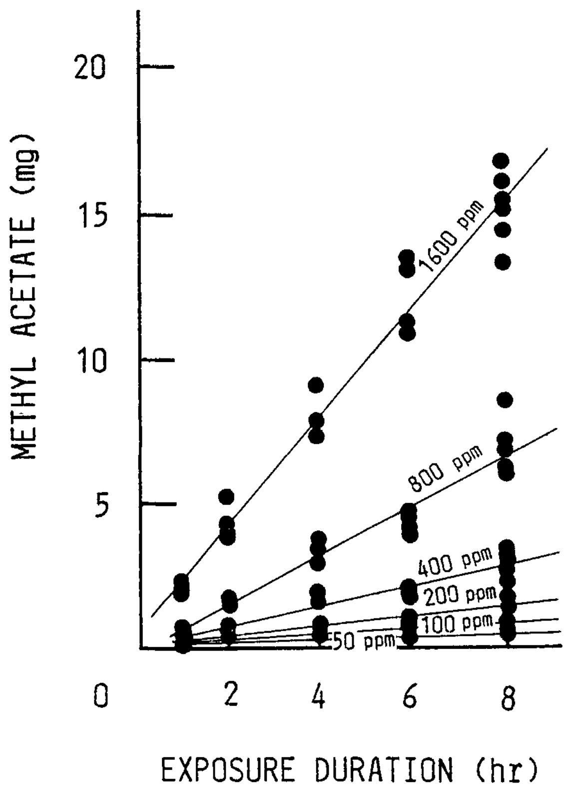

Figure 2. Absorption of methyl acetate by silica gel as a function of exposure duration

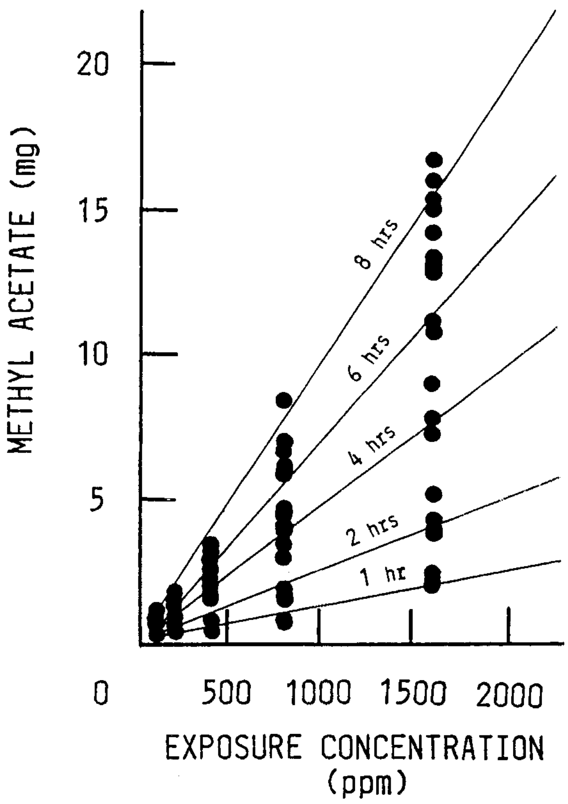

Figure 3. Absorption of methyl acetate by silica gel as a function of exposure concentration

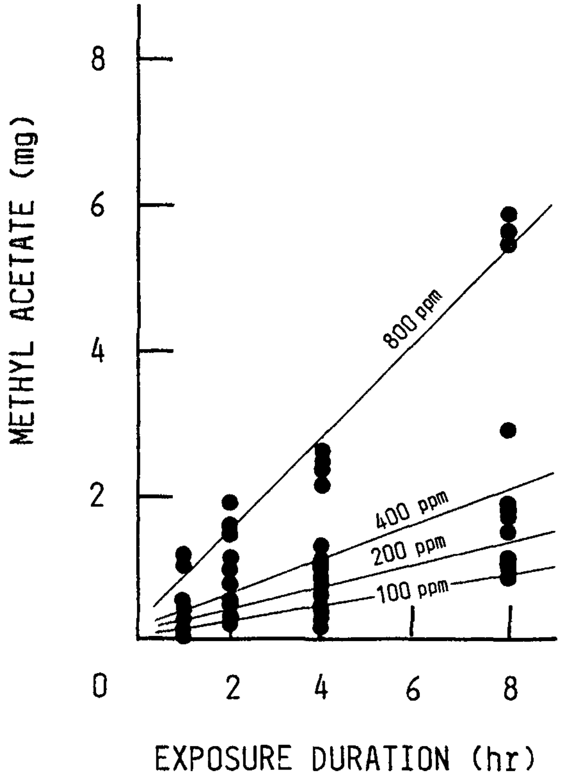

Figure 4. Absorption of methyl acetate by water as a function of exposure duration

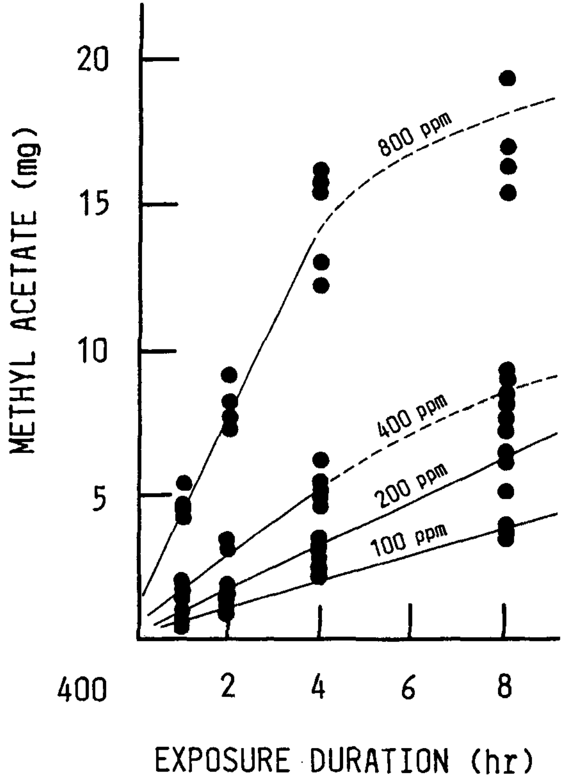

Figure 5. Absorption of methyl acetate by carbon cloth as a function of exposure duration

the recovery.

Silica gel-equipped samplers were exposed to methyl acetate at 100, 200, 400, 800 and 1600 ppm for 1, 2, 4, 6 and 8 h. At each concentration and exposure duration, 2 to 3 samplers were taken out of the exposure chamber and analyzed for the amount of methyl acetate absorbed. The results are depicted in Figs. 2 and 3 taking exposure duration and exposure concentration on the horizontal axis, respectively. It is evident from the figures that the amount of methyl acetate absorbed is linearly related to both the exposure duration up to 8 h and to exposure intensity up to 1600 ppm. It was possible to calculate from the data that the average amount of methyl acetate absorbed should be 1.354 µg/ppm/h.

Similar experiments with water-equipped samplers showed that the amount methyl acetate absorbed was linearly related to the exposure duration (the maximal duration tested; 8 h) and the exposure concentration (the maximal concentration tested; 800 ppm) as shown in Fig. 4. The rate of methyl acetate absorption was 124,7 ng/ppm/h. When carbon-cloth equipped samplers were exposed to methyl acetate at up to 800 ppm for up to 8 h, however, a leveling-off in the amount of methyl acetate was observed after long time exposure at high concentrations; the amount was no longer proportional to exposure time at 8 h at 400 and 800 ppm, whereas it was proportional up to 4 h at 400 and 800 ppm, or up to 8 h at 200 ppm (Fig. 5). The absorption rate was 5.581 µg/ppm/h when the data were selected where the linearity was held.

Several samplers equipped with silica gel (i.e., the present device), carbon cloth or water were impregnated with methyl acetate at 1000 ppm for 1 h. They were then kept in fresh air for 48 h or more after the termination of the exposure; 3 samplers were analyzed at each time period. When logarithm of the amount of methyl acetate detected in the absorbent was graphed against the time in fresh air, it was found that methyl acetate disappeared spontaneously from the absorbent with a half-time of about 11.0 h and 9.6 h for carbon cloth- and water-equipped samplers, respectively. In contrast, essentially no decay in the methyl acetate amount was observed during the period of the study (for 84 h) with silica gel-equipped samplers; the calculated half-time was 335 h (Table 1).

In order to examine if the silica gel-equipped sampler has a capacity to respond quantitatively to a short term peak exposure, 7 samplers were simultaneously

Table 1. Decay half-time for methyl acetate in the 3 types of samplers

Sampler	Absorbent	Desorbent	Study duration (h)	Half-time (h)
1	Silica gel	Ethanol	84	334.8
2	Carbon cloth	CS_2	48	11.0
3	Water	_____	48	9.6

exposed to 1600 ppm methyl acetate for 15 min and the amount of methyl acetate was determined. In practice, 590.5±84.8 μg (mean±SD of 10 determinations) methyl acetate was detected. Because the measured methyl acetate vapor concentration was 1600 ppm, the 15 min exposure should result in the absorption of 544 ug methyl acetate. Thus the response rate was 108.5± 15.6%; mean±SD). Similar experiments with samplers of other two types showed that the response rate was 116.4% and 130.7% with carbon cloth- and water-equipped samplers, respectively.

The present study has clearly demonstrated that personal diffusive sampling can be applied to monitor methyl acetate exposure, when silica gel with a large relative surface is employed as an absorbent; the amount of methyl acetate absorbed is proportional to the exposure duration up to 8 h and to the exposure concentration up to 1600 ppm (or 8 times the current occupational exposure limit of 200 ppm; American Conference of Governmental Industrial Hygienists 1991; Deutsche Forschungsgemeinschaft, 1991; Japan Association of Industrial Health 1991). The response of the sampler to a short term peak exposure is also satisfactory (i.e., 108.5%).

In practice, one of the question to be settled is the choice of the solvent for extraction. The solvents present in the working environment or those interfering with GC analysis must be excluded. Carbon disulfide is seldom used in usual solvent workshops other than rayon industries, but failed to extract methyl acetate from silica gel. Extraction with water also gave poor results (i.e., ca. 40%) although the rate was reproducible. Ethanol with an extraction rate of 100% appears to be the solvent of choice because it is present in industrial solvent preparations only on very limited occasions (Kumai et al., 1983; Inoue et al., 1983), even though the prevalence might be higher among home-use products (Saito and Ikeda, 1988).

It was also found that samplers of both carbon cloth (Hirayama and Ikeda, 1979) and water types (Uchida et al., 1990) can quantitatively absorb methyl acetate at low concentrations such as 200 ppm (Fig. 4 and 5). The difficulty is associated with rather rapid spontaneous desorption of methyl acetate from the absorbents; the desorption half-time was calculated to be 9.6 h for water-equipped samplers and 11.0 h for carbon cloth-equipped samplers (Table 1). When an extreme case is assumed such that an extensive exposure takes place only at the beginning of an 8-h workshift followed by essentially no exposure during the rest of the shift, the half-time values suggest that about 34% and 40% loss in methyl acetate in the absorbent will be expected for the former and the latter samplers, respectively, before the termination of the shift.

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REFERENCES

American Conference of Governmental Industrial Hygienists (1991) 1990-1991 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. ACGIH, Cincinnati OH, U.S.A.

Deutsche Forschungsgemeinschaft (1991) Maximum Concentrations at the Workplace and Biological Tolerance Values for Working Materials, 1991. VCM, Weinheim, Germany

Hirayama T, Ikeda M (1979) Applicability of carbon felt to the dosimetry of solvent vapor mixture. Am Ind Hyg Assoc J 40:1091-1096

Inoue T, Takeuchi Y, Hisanaga N, Ono Y, Iwata M, Ogata M, Saito K, Sakurai H, Hara I, Matsushita T, Ikeda M (1983) A nationwide survey on organic solvent components in various solvent products: Part I. Homogeneous products such as thinners, degreasers and reagents. Ind Hlth 21:175-183

Japan Association of Industrial Health (1991) Recommended occupational exposure limits. Jpn J Ind Hlth 32:381-401 (in Japanese with English translation)

Kawai T, Yamaoka K, Uchida Y, Ikeda M (1991) Exposure to vapors of benzene and other aromatic solvents in tank truck loading and delivery. Bull Environ Contam Toxicol 46:1-8

Kawai T, Mizunuma K, Yasugi T, Horiguchi S, Uchida Y, Iwami O, Iguchi H, Ikeda M (1991) Urinary methylhippuric acid isomer levels after occupational exposure to a xylene mixture. Int Arch Occup Environ Hlth 63:69-75

Koizumi A, Ikeda M (1981) A servomechanism for vapor concentration control in experimental exposure chambers. Am Ind Hyg Assoc J 42:417-425

Kumai M, Koizumi A, Saito K, Sakurai H, Inoue T, Takeuchi Y, Hara I, Ogata M, Matsushita T, Ikeda M (1983) A nationwide survey on organic solvent components in various solvent products: Part II. Heterogeneous products such as paints, inks and adhesives. Ind Hlth 21:185-197

Kumai M, Koizumi A, Morita K, Ikeda M (1984) An exposure system for organic solvent vapor. Bull Environ Contam Toxicol 32:200-204

Ogawa Y, Takatsuki R, Uema T, Seki Y, Hiramatsu K, Okayama A, Morimoto K, Kaneko Z (1988) Acute optic neuropathy induced by thinner sniffing: Inhalation of mixed organic solvent containing methyl alcohol and methyl acetate. Ind Hlth 26:239-244

Saito J, Ikeda M (1988) Solvent constituents in paint, glue and thinner for plastic miniature hobby. Tohoku J Exp Med 155:275-283

Uchida Y, Kawai T, Yasugi T, Ikeda M (1990) Personal monitoring sampler for acetone vapor exposure. Bull Environ Contam Toxicol 44:900-904

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