

A Simple and Simultaneous Analysis of Volatile Halogenated Hydrocarbons in Indoor Air Using Personal Sampler

Won-Tae Jung¹⁾ and Dong-Hun Sohn²⁾

¹⁾Department of Pharmaceutical Science, National Institute of Public Health, Shirokanedai 4-6-1, Minato, Tokyo 108, Japan

²⁾College of Pharmacy, Chungang University
Heuksok 221, Dongjak, Seoul 156-756, Korea
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Abstract

To understand the human exposure levels of volatile halogenated hydrocarbons in ambient air, a new rapid and convenient analytical method for determination of the compounds in gaseous phase was evaluated and established. The method is based upon passive diffusion to personal sampler containing adsorbent and solvent extraction followed by purge trap/ on-column cryofocusing method. A new method needs no special instrumentation for gas collection because it is based upon the passive diffusion principle. The typical chromatogram obtained in this study proved that rapid and simultaneous determination of target analytes was possible with good resolution. The developed method was successfully applied to determine the volatile halogenated hydrocarbons in indoor air and the values obtained by this new method were compared with those by direct suction method. The concentration of carbon tetrachloride, 1,1,2-trichloroethylene, chloroform showed the values below $400 \mu\text{g}/\text{m}^3$ except the maximum of $1,513 \mu\text{g}/\text{m}^3$ of chloroform. 1,1,1-Trichloroethane showed approximately 1,000 to $5,000 \mu\text{g}/\text{m}^3$ range of diurnal fluctuation in indoor air.

KEYWORDS

Volatile halogenated hydrocarbons ; concentration ; indoor air ; personal sampler, passive diffusion

1. INTRODUCTION

Volatile halogenated hydrocarbons (VHHs) have been widely used in large quantities as degreasing solvents to produce integrated circuits in frontier technological industries, as raw materials for chloro-fluoro carbon (CFC) gas and as solvents for dry cleaning (Jung et al, 1991a). Recently,

VHHs have received increasing attention as airborne environmental pollutants which are thought to be demolishing the stratospheric ozone layer (Noy et al, 1989). This demolition of the stratospheric ozone increases ultraviolet-B region (280~320nm) radiation which might be hazardous to animate nature. It is presumed that about 40~70% of VHHs and their related com-

pounds used in industries is exhausted into the atmosphere(Tanada et al, 1992). It has also been found that VHHs are moved to the soil through the air and rain and contaminate groundwater which is the major source of drinkable water. In spite of many regulations, these compounds are still found in ground water(Scott, 1988), and even in grain-based foods(Heikes et al, 1986). VHHs are also being broadly detected in local areas(Ohta et al, 1976) and in a global atmosphere. In early 1980s, considerable public and analytical interest was directed towards the occurrence of VHHs in groundwater of Silicone valley, U.S.A. at levels exceeding maximum acceptable concentrations. This finding generated public and hygienic concerns to groundwater of Japan in 1984. The results of surveys in Japan showed grave contaminations by VHHs(Hirobumi, 1988).

VHHs demonstrate general toxicities by causing vertigo, headache, dizziness and fatigue depending on the depress of the central nervous system, and if inhaled, can cause liver or kidney lesions. Futhermore, a certain species of VHHs is considered to be carcinogenic because it causes liver cancer in mice(Kimbrough et al, 1985). Therefore understanding the distribution

and fate of VHHs has recently become a high priority in environmental science(Cothern et al, 1986). We previously reported elsewhere on purge trap/on-column cryofocusing method and its analytical conditions(Fujita et al, 1991;Jung et al, 1991a;Jung et al, 1991b) and on VHHs levels in rainwater(Jung et al, 1992a;Sohn et al 1992) and in urine samples (Jung et al, 1992b). The method used ensured that sub ppb levels of VHHs in small amount of sample could be measured with better resolutions and repeatabilities than other methods such as headspace method and solvent extraction method. But those methods need an apparatus of analytical instrumentation which cannot easily transported. So, these methods cannot be applicable to determining the VHHs in indoor air in which we are exposed for about 70% of a day time. The authors focussed on a more rapid and easy method to determine the trace levels of VHHs in indoor air of usual domicile without restriciton of sampling area. Personal samplers, commercially available are based upon a passive diffusion principle and are being used to trap the organic compounds in gaseous sample. The personal samplers need no special apparatus such as pump for sampling and could

Table 1. The Characteristic Properties of VHHs.

| Compounds | Formulas | b.p.(°C) | m.p.(°C) | Toxicities |
|-----------------------------|---|----------|----------|--|
| Chloroform | CHCl ₃ | 61-62 | -63.5 | hypotension, respiratory & myocardial depression, carcinogenic |
| 1,1,1-Trichloroethane | C ₂ H ₃ Cl ₃ | 113-114 | -35 | irritant, narcotic effect CNS depression |
| Carbon tetrachloride | CCl ₄ | 76.7 | -23 | nausea, vomitting, diarrhea, headache, liver injury, carcinogenic* |
| 1,1,2-Trichloroethylene | C ₂ HCl ₃ | 86.7 | -84.8 | CNS depression, narcotic effect, liver, injury, hepatocellular carcinoma |
| 1,1,2,2-Tetrachloroethylene | C ₂ Cl ₄ | 121 | -22 | dermatitis, narcotic effect CNS depression |

be easily set up at a place to determine the target compound without disturbance of daily activities of persons. In this paper, the evaluation and comparison of results obtained from direct suction by purge trap/on-column cryofocusing method and those from personal samplers fol-

lowed by solvent extraction are described.

2. MATERIALS AND METHODS

2.1. REAGENTS

The characteristic properties of used VHHs

standards are tabulated in Table 1. All VHHs of reagent grade were purchased from Wako Pure Chem.(Japan). Normal-Hexane and toluene for

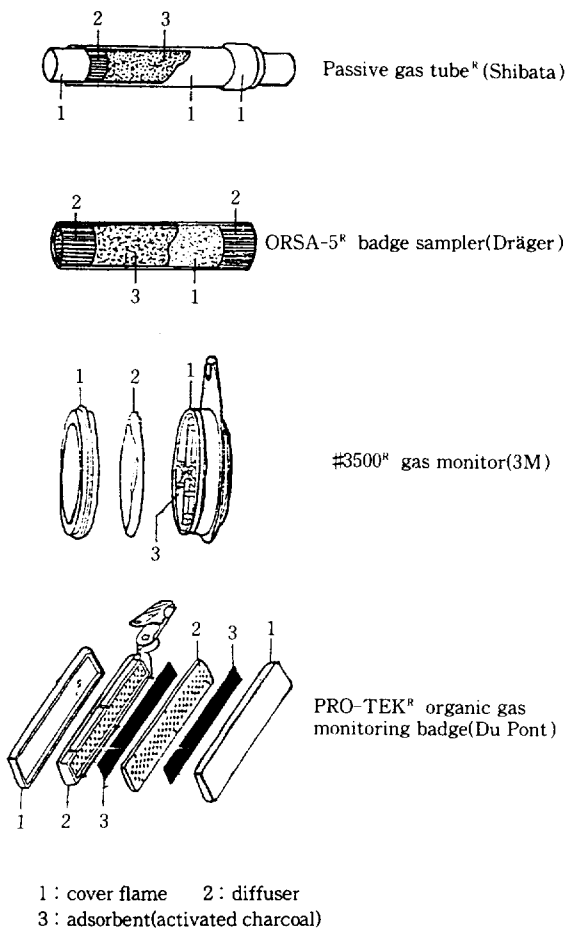


Fig. 1. Exploded Shapes of Various Personal Samplers.

extraction were of pesti-cide analysis grade of Wako Pure Chem. VHHs standards were diluted in π -hexane to contain chloroform 0.72ng, 1,1,1-trichloro-ethane 3.69ng, carbon tetrachloride 0.83ng, 1,1,2-trichloroethylene 0.29ng and 1,1,2,2-tetra-chloroethylene 0.098ng in 1ml.

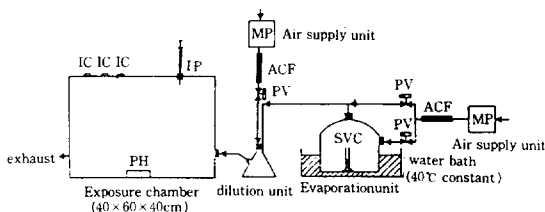
2.2 PERSONAL SAMPLERS

The used adsorbent for gaseous VHHs were 4 kinds of commercially available personal samplers based upon passive diffusion. Passive gas

tube(Shibata, Japan), ORSA-5^R badge sampler (Dräger, Germany), #3500^R gas monitor(3M, U.S. A) and PRO-TEK^R organic gas monitoring badge (Du Pont, U.S.A.) were compared and evaluated for the suitability to determine the VHHs in indoor air. The exploded shapes of personal samplers used are illustrated in Figure 1.

2.3 EXPOSURE CHAMBER

Preliminary analysis of VHHs in indoor air by direct suction-purge trap/on-column cryofocusing method showed that the levels were changed with large variation. Therefore, an exposure chamber as illustrated in Figure 2 was used to make personal sampler, to be exposed at a constant concentration of VHHs. All glaswares such as chamber, desiccators, flasks and tubing



IC : insertion cork
 MP : mini pump
 PH : propeller homogenizer
 ACF : activated charcoal filter(4mm i. d.×10cm l.)
 IP : injection port
 PV : pressure valve
 SVC : standard evaporation cylinder

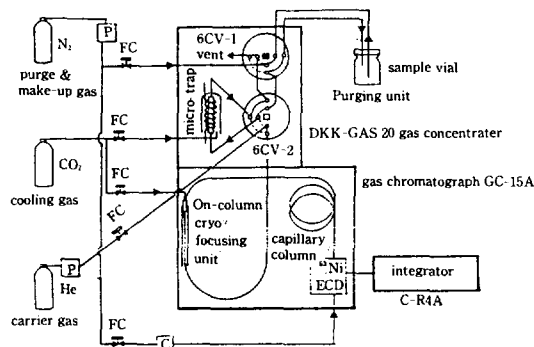
Fig. 2. Diagram of Exposure Chamber Assembly.

was washed and dried to exclude any possible contamination of VHHs. The VHHs free air was constantly supplied into the exposure chamber by minipump(MP-2N, Shibata, Japan)

2.4 ANALYTICAL INSTRUMENTATION

Chromatography was performed using a Shimadzu GC-15A gas chromatograph equipped with ⁶³Ni-electron capture detector and fitted with a 30 m×0.32mm id Quadrex Halomatic^R 624 capillary column coated with a 3.0 μ m film of a chemically bonded cyanomethyl phenyl silicone. The data were integrated by Shimadzu C-R4A.

A modified DKK-GAS 20(DKK, Japan) gas concentrator was used as gas trap unit. Micro-trap of a stainless steel(40mm length x 1/8" o.d.)packed with Tenax[®] GC(beads of polymeric 2,6-diphenylphenylene oxide, 35/60 mesh) was hand-made. The schematic diagram of analytical instrumentation assemblies is illustrated in Figure 3.

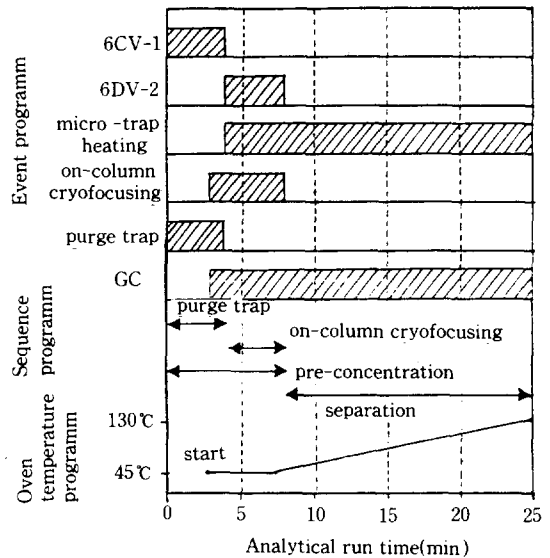


6CV : 6-port chromatographic valves (Supelco, ■ on/ □ off)
 P : gas purifiers
 FC : flow controller
 PG : pressure gauge
 C : charcoal filter

Fig. 3. Schematic Diagram of Analytical Instrumentation for VHHs.

2.5 METHODS

The VHHs levels in gaseous phase were measured by two different methods and the results were compared to each other. Direct suction-purge trap/on-column cryofocusing method was as follows : The gaseous sample in indoor air was collected by direct suction as the authors previously reported elsewhere(Fujita et al, 1991). The other method using a personal sampler was as follows : a personal sampler was exposed to indoor air or exposure chamber containing the air of constant levels of VHHs. After the exposure, the activated charcoal as an adsorbent was taken out and trapped VHHs were extracted with solvent and spiked into a sample vial. The injected analytes are purged(20ml/min × 4min) and trapped to cryofocused to Tenax[®] GC micro trap. Then the 6 port chromatographic valves are switched and trapped VHHs are thermally desorbed by heating at 150°C and introduced to capillary column and on-column cryofocused at



6CV : 6-port chromatographic valves □ on/off

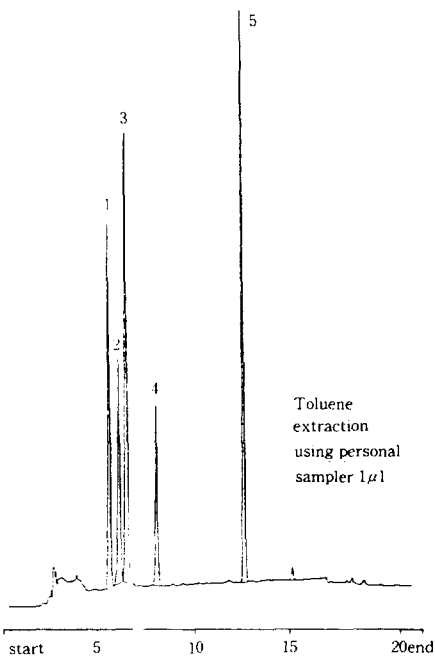
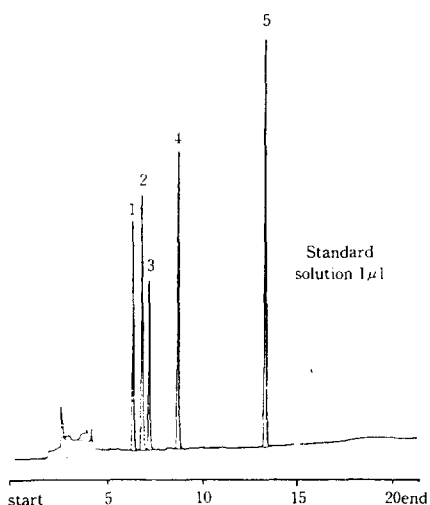
Fig. 4. Time Program of Analytical Sequence.

-60°C for 4 min. And GC oven program was initiated. The time program of analytical sequence is shown in Figure 4.

3. RESULTS AND DISCUSSION

3.1 TYPICAL CHROMATOGRAM OF VHHs OBTAINED BY SOL-VENT EXTRACT USING PERSONAL SAMPLER

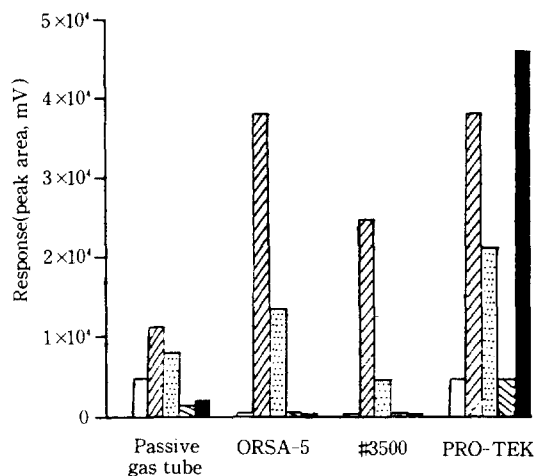
To evaluate the possibility of application of passive diffusion for determining the VHHs in gaseous samples, a personal sampler was opened and exposed in indoor air for 24hours. The indoor air of a laboratory in Japanese National Institute of Public Health was tested. The institute is located in a residential area of Minato, Tokyo where is surrounded no industrial VHHs source. After the exposure, the adsorbent was taken out and trapped VHHs are extracted with 1.5ml toluene. This extracted solvent 1 μl was injected to be analyzed. Figure 5 shows a typical chromatogram of VHHs obtained by this method. Enough recoveries of VHHs are obtained and the peaks of VHHs which have very closed boiling points are clearly separated by the method. This result enable personal sampler applicable to determine VHHs in gaseous phase.



- 1 : chloroform
- 2 : 1,1,1-trichloroethane
- 3 : carbon tetrachloride
- 4 : 1,1,2-trichloroethylene
- 5 : 1,1,2,2-tetrachloroethylene

Personal sampler (passive gas tube, Shibata) was exposed in indoor air of a laboratory in National Institute of Public Health (Tokyo, Japan) for 24hrs

Fig. 5. Typical Chromatograms Obtained from Personal Sampler Following Solvent Extraction.



- chloroform
- ▨ 1,1,1-trichloroethane
- ▩ carbon tetrachloride
- ▧ 1,1,2-trichloroethylene
- 1,1,2,2-tetrachloroethylene

Fig. 6. Background Levels of VHHs in Various Personal Samplers.

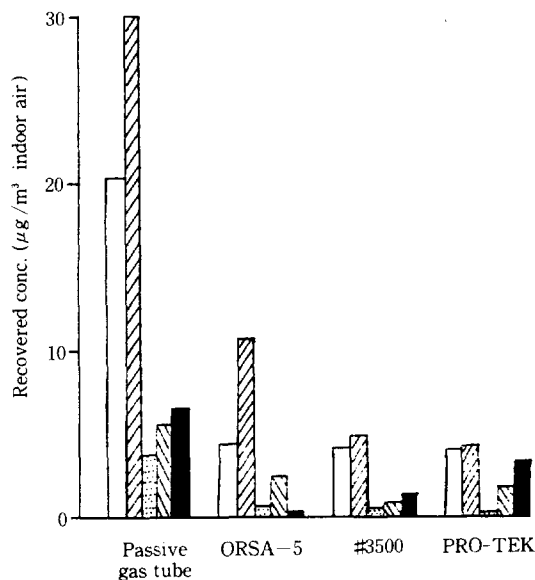


Fig. 7. Comparison on the Adsorbed Amount of VHHs by Various Personal Samplers. (See legend of Figure 6.)

3.2 BACKGROUNDS OF VHHS IN PERSONAL SAMPLERS

Four kinds of commercially available personal samplers have been frequently used to determine organic compounds in gaseous samplers. To choose the most appropriate one to determine VHHS in indoor air, self-containing VHHS levels of 4 kinds personal samplers were compared. The adsorbent in samplers were extracted with 1.5ml of toluene and analyzed. The result indicated that passive gas tube contained the least amount of VHHS among the investigated samplers, as shown in Figure 6.

3.3 VHHS ABSORBING ABILITIES OF PERSONAL SAMPLERS

In an identical condition of indoor air, samplers were exposed for the same period to compare the total trapped amounts of VHHS. The absolute amount of recovered VHHS obtained by passive gas tube showed the highest values as shown in Figure 7.

Based upon these results, passive gas tube was adopted as the appropriate material for adsorption of VHHS in indoor air.

3.4 SOLVENT EXTRACTION OF ADSORBENT

Trapped VHHS in adsorbent of personal samplers were thought to be extracted with different recoveries according to solvent. n-Hexane and toluene were compared to each other in this study. The personal samplers are exposed in an identical condition and the adsorbent was extracted by n-hexane and toluene, respectively. When the recoveries of n-hexane were set as 100%, the relative recoveries of toluene extraction were about 6 times higher than those of n-hexane except 93% of carbon tetrachloride, as shown in Figure 8. According to this result, toluene was adopted as solvent for extraction. The recoveries of n-hexane were set as 100%

3.5 THE CALCULATION OF VHHS CONCENTRATION

One μl of extraction solvent containing total trapped VHHS was injected to be analyzed. The total amounts of trapped VHHS was calculated

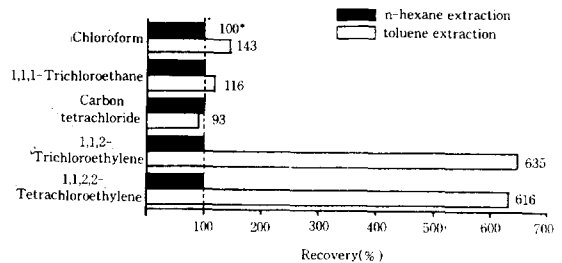


Fig. 8. Recoveries of VHHS by n-Hexane and Toluene Extraction.

as follows;

$$M_s(g) = M_1 \times V(\text{ml}) \times 10^3$$

where, M_s : total amounts of VHHS trapped to sampler

M_1 : amounts of VHHS included in $1 \mu\text{l}$ of extraction solvent

V : total volume of extraction solvent

Then, the concentration of VHHS were converted by following equation :

$$C(\text{ppm}) = \frac{M_s \times 10^6 (\mu\text{g})}{\text{sampling rate} (\mu\text{g}/\text{ppm} \cdot \text{min}) \times \text{sampling time} (\text{min})}$$

The sampling rate of VHHS were investigated and reported elsewhere by Ashida et al, as chloroform 0.241, 1,1,1-trichloroethane 0.269, carbon tetrachloride 0.288, 1,1,2-trichloroethylene 0.238 and 1,1,2,2-tetrachloroethylene 0.304 with repeatabilities between 6.0-7.1% of C.V.

3.6 LEVELS OF VHHS IN EXPOSURE CHAMBER

The VHHS changes in indoor air determined by direct suction-purge trap/on-column cryofocusing method were fluctuated very widely in a day. To make the gas sample contain a constant levels of VHHS, an exposure chamber was used. 1,1,2-Trichloroethylene standard solution was vaporized and introduced into the chamber. The concentration of VHHS in the chamber was monitored by injecting the gas using purge trap/on-column cryofocusing method. The time-series analysis gave the result that 1,1,2-trichloroethylene level rise to the maximum in 2 hours after the start of evaporation and became stationary

after 22 hours as shown in Figure 9. So, personal samplers were started to expose from at least 24 hours after the start. And when samplers were exposed in chamber, the level of VHHs was checked every 2 hours by purge trap/on-column cryofocusing method.

3.7 LINEARITY BETWEEN EXPOSED TIME AND RECOVERED AMOUNT OF VHHs OBTAINED BY PERSONAL SAMPLERS

Quantitative linearity between exposed time of sampler and recovered amount of VHHs is essential for the application of passive diffusion samplers to determine VHHs at proper levels. Figure 10 shows the relationship between exposure time and recovered amount. 1,1,2-Trichloroethylene showed linear calibration curve, which meant quantitative analysis with personal sampler was possible.

3.8 RELATIVE RECOVERIES OF VHHs BY PERSONAL SAMPLERS FOLLOWING SOLVENT EXTRACTION

The found amounts of VHHs determined by direct suction-purge trap/on-column cryofocusing method and by personal sampler following toluene extraction were compared to each other. As shown in Table II about 66~119% of VHHs except 1,1,2,2-tetrachloroethylene were recovered by personal sampler method. 1,1,2,2-tetrachloroethylene showed relatively worse recovery of 52.5%, which might be due to low existing level of itself in indoor air.

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3.9 VHHs DETERMINATION IN INDOOR AIR BY PERSONAL SAMPLER

The diurnal changes of VHHs in indoor air were monitored using personal samplers. Personal sampler (passive gas tube) was exposed for 2 hours in indoor air. The extracting solvent was toluene. 1,1,1-Trichloroethane showed relatively higher value of 100~5,000 $\mu\text{g}/\text{m}^3$ variation in a day. Other VHHs were varied from below 10 to 1,400 $\mu\text{g}/\text{m}^3$ in a day as shown in Figure 11.

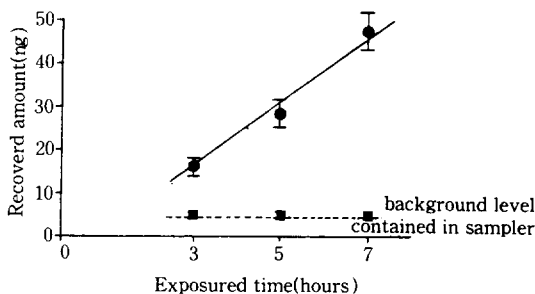


Fig. 10. Linearity between Exposure Time and Accumulative Amount of 1,1,2-Trichloroethylene.

4. CONCLUSION

As a simple and convenient method to determine the VHHs in indoor air, personal sampler using passive diffusion-solvent extraction-gas chromatography with electron capture detector was developed. The peaks of VHHs obtained by personal sampler were separated clearly. Among the investigated 4 kinds of personal samplers, passive tube was considered as the most suitable material for gaseous VHHs, because it contained the relatively least VHHs backgrounds and it showed the relatively large adsorbing abilities for vhh. For solvent extraction procedure, toluene was selected because it showed 6 times higher extraction abilities for VHHs than n-Hexane. When the personal sampler was exposed to constant level of VHHs in exposure chamber, the linearity between total recovered amount of VHHs

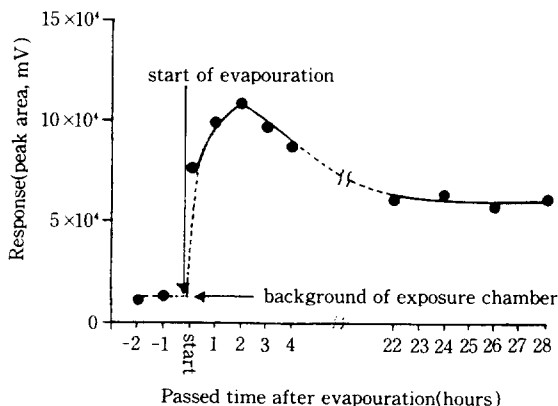


Fig. 9. Fluctuation of 1,1,2-Trichloroethylene Level Contained in Gaseous Phase in Exposure Chamber.

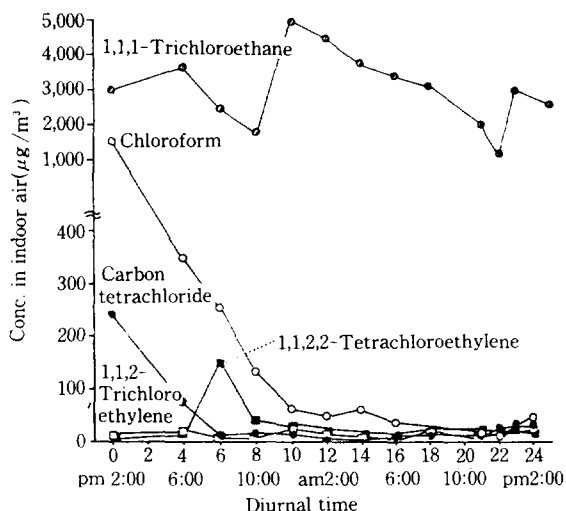


Fig. 11. Diurnal Changes of VHHs Levels Determined by Personal Sampler.

and exposure time was shown, which enabled the personal sampler applicable for VHHs determination. Comparing to direct analysis purge-trap/on-column cryofocusing method, the recoveries obtained by personal sampler were 66-119% except 52.5% for 1,1,1-trichloroethane. The approximately same levels with differences not exceeding $20\mu\text{g}/\text{m}^3$ were obtained by the developed method. With this method, VHHs concentrations in indoor air were measured by 2 hours to trace the diurnal variations of VHHs. 1,1,1-Trichloroethane showed the value range of 1,000-5,000 $\mu\text{g}/\text{m}^3$. While others showed the value below $10\mu\text{g}/\text{m}^3$ except the maximum $1,400\mu\text{g}/\text{m}^3$ of chloroform.

Table II. Comparative Recoveries of VHHs Determined by Personal Sampler Following with Solvent Extract.

| Compounds | found($\mu\text{g}/\text{m}^3$) | | recovery B/A(%) |
|-----------------------------|-----------------------------------|---------------------|--------------------|
| | DS-PT/OC*(A) | personal sampler(B) | |
| Chloroform | 49.5 ± 0.0 | 59.1 ± 0.1 | 119.3 |
| 1,1,1-Trichloroethane | 409.5 ± 14.4 | 391.8 ± 38.2 | 95.5 |
| Carbon tetrachloride | 45.0 ± 0.1 | 52.5 ± 0.5 | 116.6 |
| 1,1,2-Trichloroethylene | 42.5 ± 2.1 | 28.1 ± 0.4 | 66.1 |
| 1,1,2,2-Tetrachloroethylene | 13.5 ± 0.1 | 7.1 ± 0.0 | 52.5 |

* Direct suction-purge trap/on-column cryofocusing method

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REFERENCES

- Ashida T., T. Shibata S. Koike and K. Ohmori (1986) Passive Gas Sampler for Organic Vapors. *Jpn.J.Industr.Health*, 28 pp 362-363
- Cothern C. R., W. A Conglio. and W. L. Marcus (1986) Estimating Risk to Human Health. *Environ. Sci. Technol.*, 20(2) pp111-116
- Fujita M., W. T. Jung H. Tatematsu D. H. Sohn and T. Meada (1991) Automated Analysis of Volatile Halogenated Hydrocarbons in Rainwater and Ambient Air by Purge Trap Capillary Gas Chromatography, *High Resol. Chromatogr.*, 14(2) pp83-90
- Heikes D. L. and M. L. Hopper M. L. (1987) Pesticides and Industrial Chemical Residues. *J. Assoc. Off. Anal. Chem.* 70(2) pp215-226
- Hirobumi H. (1988) Fine Water Attracted the Pollution. *Gagaku Asahi* 11, pp116-121
- Hobara T., H. Kobayashi E. Higashihara T. Kuwamoto and S. Iwamoto (1983) Changes in Hematologic Parameters with Acute Exposure to 1,1,2-Trichloroethylene. *Indu-*

- str. Health*, 21, pp255-261
- Jung W. T. and M. Fujita (1991a) Optimal Conditions of Purge Trap/On-column Cryofocusing Method with Capillary Gas Chromatography for Determination of Volatile Halogenated Hydrocarbons in Aqueous Samples, *Jpn. J. of Environ. Toxicol. Health*, 37(5) pp395-400
- Jung W. T. and M. Fujita (1991b) Application of Double Cryofocusing Method with GC-ECD to Determining Volatile Halogenated Hydrocarbons in Gaseous Samples. *Bull. Inst. Pub. Health*, 40 (2) pp135-140
- Jung W. T., M. Fujita and D. H. Sohn (1992a) Levels of Volatile Halogenated Hydrocarbons in Tokyo Rain and Their Seasonal, Time-series Changes. *Jpn. J. of Environ. Toxicol. Health*, 38(6) pp490-496
- Jung W. T. and D. H. Sohn (1992b) Biological Monitoring of Human Exposure to Volatile Halogenated Hydrocarbons Using Urinalysis with Capillary GC-ECD, *Arch. Pharm. Res.* 15(2) pp109-114
- Kimbrough R. D., F. L. Micheli and V. N. Houk (1985) Trichloroethylene : An Update data. *J. Toxicol. Environ. Health*, 15, pp369-383
- Noy T., P. Fabian R. Rocers F. Janssen C. Cramers and J. Rijks (1987) Trace Analysis of Halogenated Hydrocarbons in Gaseous Samples by On-line Enrichment in Air Adsorption Trap On-column Cold Trapping and Gas Chromatography. *J. Chromatogr.*, 393 pp343-345
- Ohta T., M. Morita and I. Mizoguti (1976) Local Distribution of Chlorinated Hydrocarbons in the Ambient Air in Tokyo, *Atmos. Environ.*, 10 pp 550-557
- Scott B. C.(1988) In Atmospheric Pollutants in Natural Waters, Eisenreich, Ann Arbor, pp3-21
- Sohn D. H., W. T. Jung and M. Fujita (1992) Determination of Volatile Organochlorine Compounds in Environmental Samples of Seoul. *Atmos.Chem. Critical Issue in the Global Environment vol2* IU15.09
- Tanada S., S. Shinoda and T. Nakamura T. Harada and J. Ohtsu (1992) Studies on the Adsorption Characteristics of Trichloroethylene onto Activated Carbon Fiber in Gaseous Phase. *Jpn. J. of Environ. Toxicol. Health*, 38(1) pp93-98