

Original Paper

## Desorption of Organic Solvents from Activated Charcoal with 2-Hydroxypyridine

Hiromi MICHITSUJI<sup>1)</sup>, Yukio FUJIKI<sup>1)</sup> and Masana OGATA<sup>2)</sup>

*Matsushita Science Center of Industrial Hygiene<sup>1)</sup>*

*Department of Medical Social Work,*

*Faculty of Medical Welfare,*

*Kawasaki University of Medical Welfare<sup>2)</sup>*

*Kurashiki, 701-01, Japan*

*(Accepted October 30, 1995)*

**Key words :** occupational exposure, gas chromatography, organic solvent, activated charcoal, 2-hydroxypyridine.

### Abstract

Gas chromatography has been widely used for analysis of solvent vapor. However, there have been a difficulty that the target solvents were interfered with extraction solvent. A new extraction method of the solvent from activated charcoal with 2-hydroxypyridine was devised. With this procedure, the target solvent was extracted with 2-hydroxypyridine in its liquid state (150°C) from charcoal and after cooling, solvent was liberated into the air from the solid state (20°C) of 2-hydroxypyridine. In the method, solvents in air could be accurately and precisely determined, because carbon disulfide, which interfered with target solvents in gas chromatography, was not used to extract. The recovery rates of common eight organic solvents were examined and high recoveries, more than 90 percent, were obtained in the solvents except acetone and methyl ethyl ketone. Moreover, the mean peak height of seven solvents was 51 times as high as that by the desorption with carbon disulfide by gas chromatography. The present method is considered to be available for the determination of solvent vapor in the workplaces.

### Introduction

The use of a personal sampler for collecting and analyzing organic solvents is an important technique for the assessment of workers' exposures to such solvent.

In the traditional preconcentration of organic solvent vapor prescribed by the National Institute of Occupational Safety and

Health (NIOSH) procedure<sup>1)</sup>, charcoal was used as the adsorbent.

In the sampler first described by Hirayama and Ikeda<sup>2)</sup>, the use of carbon-felt to the dosimetry of solvent vapor mixture, including consistency of results compared with those by direct measurement of air born concentrations. Activated charcoal is also useful for the determination of fluctuating vapor concentra-

tions in the work environment<sup>3)</sup>.

In the extraction of adsorbed solvents from charcoal with carbon disulfide, alcohols and ketones are hardly extracted. Furthermore, the peaks of cyclohexane and acetone, which have a similar retention time to carbon disulfide, are masked by a peak of carbon disulfide on the gas chromatogram.

To overcome these problems, the authors devised a new method in which solvents adsorbed in charcoal are extracted by 2-hydroxypyridine in its liquid state at 150°C and liberated into the air from the solid 2-hydroxypyridine at 20°C.

This paper describes the accuracy and precision of a newly devised method for the determination of solvent vapor concentrations by gas chromatography.

## Materials and Methods

### *Test solutions:*

All reagents used were reagent grade. Eight solvents of n-hexane, acetone, methyl ethyl ketone (2-butanone), benzene, dichloroethane, trichloroethylene, tetrachloroethylene and toluene were diluted 1:10, 1:100 and 1:1000 with carbon disulfide and were used as test solutions.

### *Desorption of solvents from charcoal in sampling tubes with 2-hydroxypyridine:*

The glass tubes used for the personal sam-

pling of solvent vapors had two layers of charcoal with a layer of glass wool between them. One end of the tube was open and the charcoal in the open side weighed 100 mg. The chemical used for the desorption of solvents from charcoal was 2-hydroxypyridine of the reagent grade (Wako Pure Chemical Industries, Osaka).

### *Generation of test atmosphere:*

Test atmospheres for the organic solvents were generated as follows; 0.5 ml of each of the eight kinds of organic solvents were placed into a one cubic meter chamber and left for two hours at 30°C. The vaporized gases were then introduced into a sampling tube.

Headspace - gas chromatographic analyses (HS-GC) of the evaporated gases were carried out by the method described in Table 1.

## Results

### *An examination of the optimal conditions for the desorption of solvents from activated charcoal:*

2-hydroxypyridine powder ranging in weight from zero to one gram was placed in the vials. Two ml of each of the eight test solutions were diluted 10 times with carbon disulfide and placed in activated charcoal. The charcoal was put in the vials containing 2-hydroxypyridine and heated to 150° for 15

Table 1 Analytical conditions of solvents by headspace gas chromatography

Condition for headspace samplers		Condition for gas chromatography	
Sample temperature	80°C	Column Supercowax-10	
Transfer temperature	150°C	90m×0.32I.D. Film 0.5μm	
Thermostatting time	30min	Sprit ratio	6 : 1
Pressurization time	0.5min	Column flow (N <sub>2</sub> )	2.0ml
Injection time	0.08min	Column pressure	26PSI
Withdrawal time	0.2min	Oven temperature	90°C
Vent	- 1	Detector temperature	200°C

PSI=Pond per square inch; 1 PSI=0.070307kg/cm<sup>2</sup>

to 120 minutes. The concentrations of adsorbed solvents were determined by HS-GC.

An analysis of the solvent showed that the desorption efficiency was the highest when 0.1 g of 2-hydroxypyridine was added to 100mg of activated charcoal containing solvents. The efficiency was slightly lower but stable when 0.3 to 0.5 g of 2-hydroxypyridine was added to the charcoal. Therefore, the authors decided that the optimal amount of 2-hydroxypyridine to be applied to 100mg of activated charcoal was 0.3 g.

Similar tests for optimum time requirements indicated that desorption was greatest when heated for 60 minutes; activated charcoal added target solvents was placed in the vials containing 2-hydroxypyridine, which were then heated at 150° for 15 to 120 minutes.

Therefore, the analyses were performed using the optimum conditions of 0.3 gram 2-hydroxypyridine and heated time of 60 minutes.

#### Gas chromatogram:

Chromatograms of eight organic solvents employing carbon disulfide and 2-hydroxypyridine as the desorbents are shown in Fig. 1,

The figure shows that the acetone peak was masked with that of carbon disulfide when carbon disulfide was employed but showed clearly when 2-hydroxypyridine was used. The figure also shows that the peaks of target solvents on the gas chromatograms obtained by the new method are higher than those using carbon disulfide. This is discussed in the section on desorption recovery rates. The retention time of cyclohexane on the gas chromatogram is slightly less than that of carbon disulfide in the new method as shown in Fig. 2.

#### Desorption of solvents from the charcoal:

The analytical procedure for the solvents is shown in Table 2. Two  $\mu\text{L}$  of each solvent

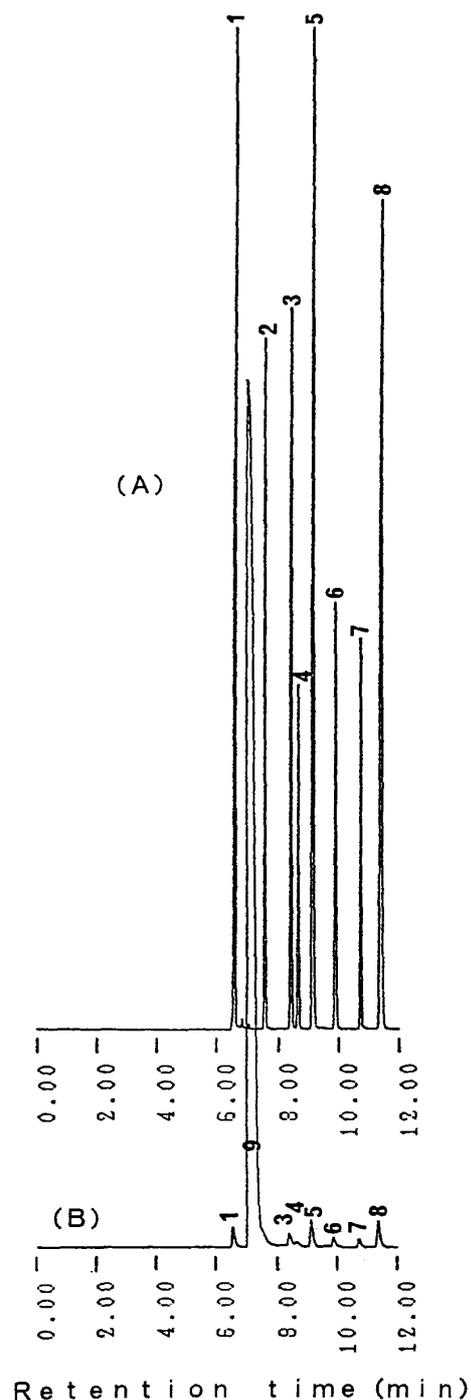


Fig. 1 Typical gas chromatograms of eight solvents and carbon disulfide; comparison of sensitivity between the desorption method with 2-hydroxypyridine (method A) in Fig A. and that with carbon disulfide (method B) in Fig B. Peaks: 1=n-hexane; 2=acetone; 3=methyl ethyl ketone (MEK); 4=dichloromethane; 5=benzene; 6=trichloroethylene; 7=tetrachloroethylene; 8=toluene; 9=carbon disulfide

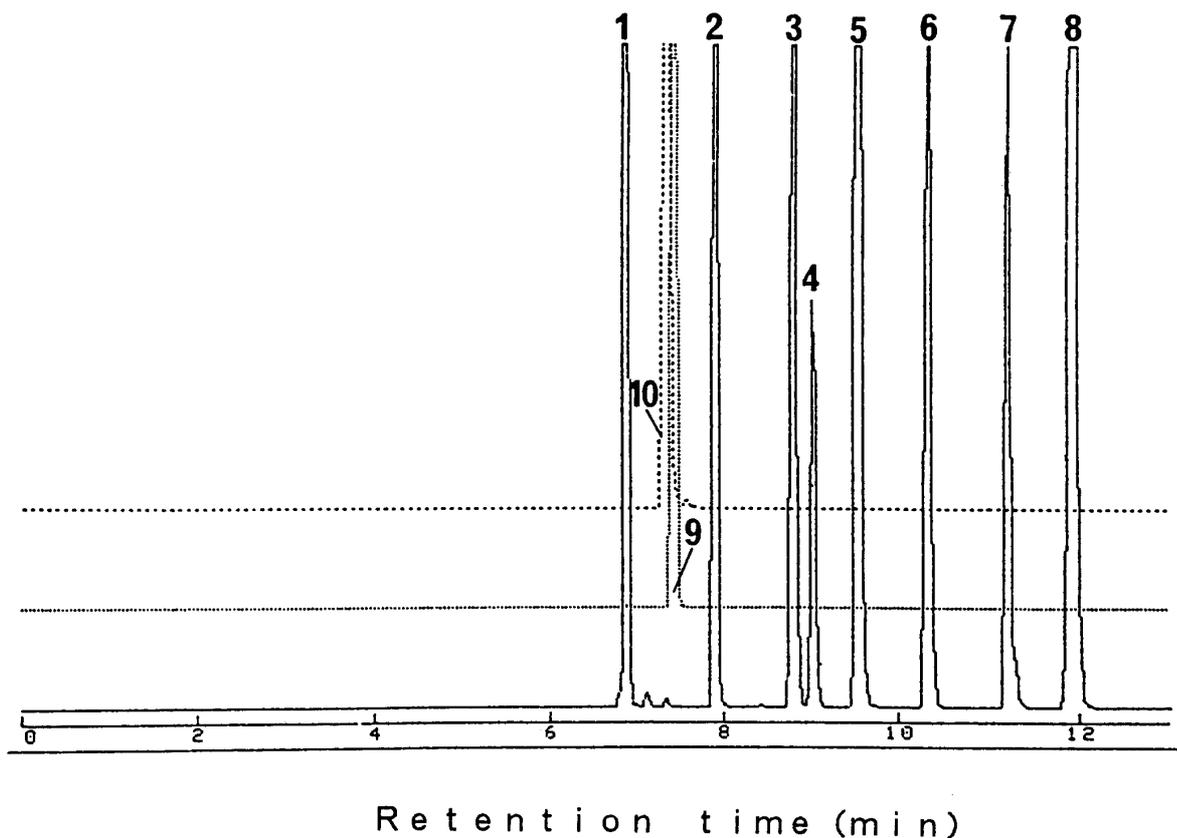


Fig. 2 Typical gas chromatograms of eight solvents by the method A, cyclohexane and carbon disulfide. Solutions ( $2 \mu\text{L}$ ) of cyclohexane and carbon disulfide were put into a 22.5 ml of vial and applied to HS-GC. Numbers of peaks are the same as to those in Fig. 1 and the number 10 peak is the cyclohexane peak.

were diluted 1:100 with carbon disulfide and applied onto the charcoal. Solid 2-hydroxypyridine weighing 0.3 g was put into vials. The charcoal, containing solvents, was placed into the vials. The vials were then sealed and heated in an oven at  $150^\circ\text{C}$  for 60 min. As the 2-hydroxypyridine liquified at high temperature, it extracted the solvents from the charcoal. Then the vials were cooled to  $20^\circ\text{C}$  and the liquid 2-hydroxypyridine was solidified. Then heating the vials at  $80^\circ\text{C}$ , vaporized the solvents and the resultant gases were analyzed by the HS-GS.

The standards for HS-GS were prepared by placing of  $2 \mu\text{L}$  of each solvent, diluted 1:100 with carbon disulfide, were put into vials containing 0.3 g of 2-hydroxypyridine. After heating the vials at  $80^\circ\text{C}$ , gas was applied to HS-GS.

Table 2 Schema of the analytical procedure

Put 0.3 g of 2-hydroxypyridine into a vial
↓
Put 100 mg activated charcoal adsorbed solvents into vial
↓
Seal with a rubber cap lined with Teflon Sheet followed by aluminum cap
↓
Heat vials at $150^\circ\text{C}$ for 60min in an oven
↓
Heating to $80^\circ\text{C}$
↓
Apply solvent gas to HS-GC

*Relationship between concentrations of solvents added to charcoal and peak areas on the gas chromatogram:*

The pure solvents were diluted 1, 10, 100 and 1000 folds with carbon disulfide, and then 2  $\mu\text{L}$  of each solution were applied to charcoal and then desorbed, evaporated and analyzed by HS-GS.

The data obtained from gas chromatography indicated that a linear relationship existed between the common logarithm of solvent concentrations and the common logarithm of the peak areas, in a wide range of solvent concentrations (Fig. 3). The ranges of concentrations of diluted solution described above

corresponded to vapor concentration ranges of 0.0374–37.4 ppm for n-hexane, 0.0668–66.8 ppm for acetone, 0.0548–54.8 ppm for methylethylketone, 0.0764–76.4 ppm for dichloromethane, 0.0547–54.7 ppm for benzene, 0.0545–54.5 ppm for trichloroethylene, 0.0479–47.9 ppm for tetrachloroethylene and 0.04604–46.0 ppm for toluene.

*Desorption recovery and sensitivity:*

Two  $\mu\text{L}$  of solutions diluted 1 : 100 with carbon disulfide were applied to activated charcoal in tubes. Thereafter, the solutions adsorbed in charcoal were desorbed with 2-hydroxypyridine in vials, and the vaporized gases were determined by gas chromatogra-

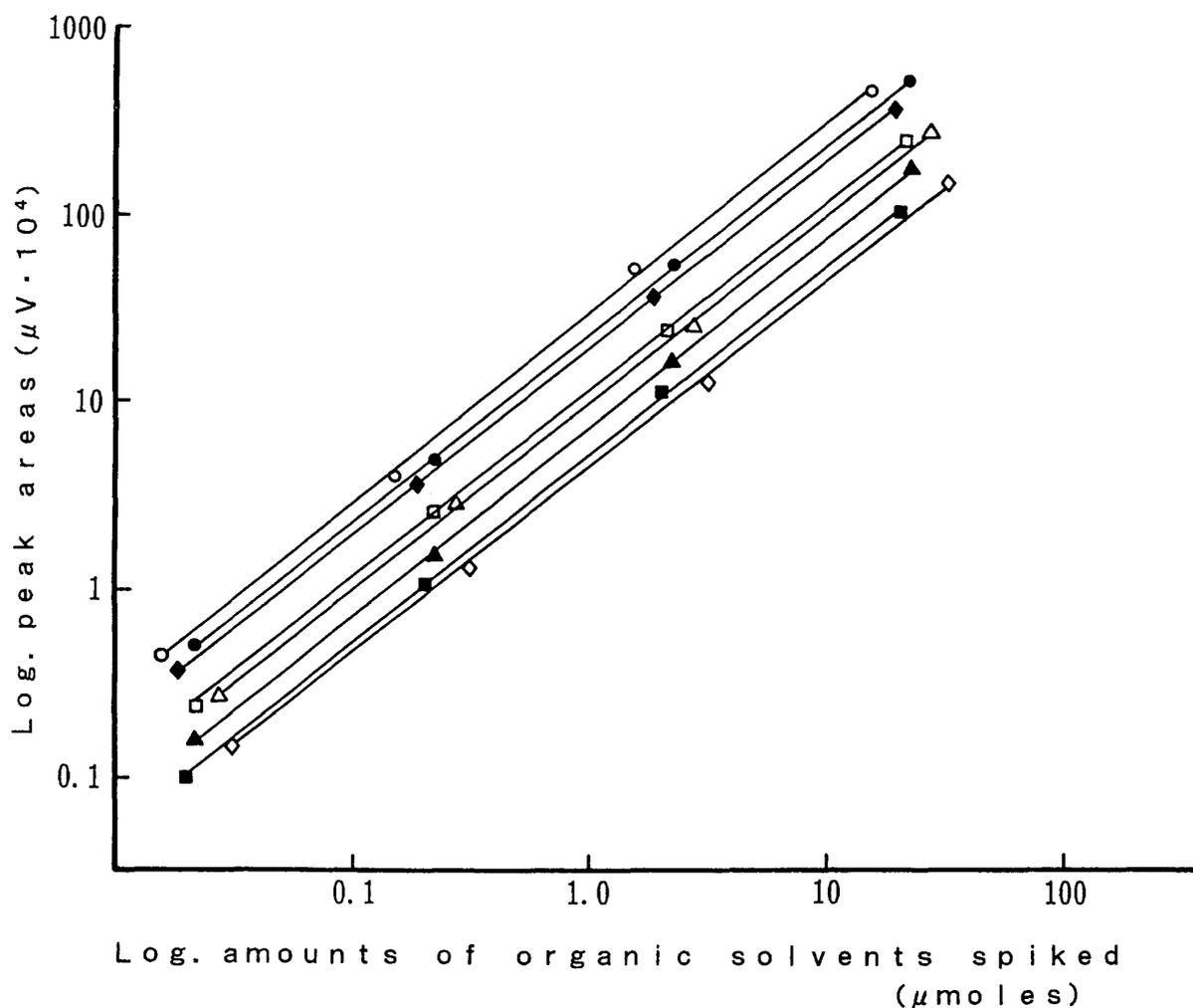


Fig. 3 Calibration graphs for eight solvents in charcoals after application to charcoals and desorption with 2-hydroxypyridine.

Symbols:  $\circ$  = n-hexane;  $\bullet$  = benzene;  $\blacklozenge$  = toluene;  $\square$  = methyl ethyl ketone (MEK);  $\triangle$  = acetone;  $\blacktriangle$  = trichloroethylene;  $\blacksquare$  = tetrachloroethylene;  $\diamond$  = dichloromethane.

phy.

The results are shown in Table 3. The overall recovery rate of eight solvents added to activated charcoal ranged from 74 % to 103 % and corresponding relative standard deviations were 1.3-4.8 % (n=5). The recovery rates for acetone and methyl ethyl ketone were relatively low. To compare the sensitivity of the two methods, the ratios of the peak heights of the target solvents by the desorption of the new method with 2-hydroxy pyridine to the desorption with carbon disulfide in Fig. 1 were calculated. The ratios for n-hexane, methyl ethyl ketone, dichloro-methane, benzene, trichloroethylene, tetrachloroethylene and toluene were 69, 52, 61, 52, 45, 47 and 32, respectively. The average and standard deviations of the ratios of seven solvents were 51.1 and 11.8, respectively. The reason for the above results is the sampling procedure as follows;

In the desorption method using carbon disulfide, 2  $\mu$ L out of 2 mL (1 part out of 1000) carbon disulfide containing solvent were applied to the gas chromatograph and in the method using 2-hydroxypyridine, 1 mL out of 22.5 mL (1 part out of 22.5) solvent vapor was

applied to the gas chromatograph.

The data indicated that the present method has extremely high sensitivity, which means that low concentrations of solvent vapor can be easily detected.

*Comparison of two independent methods:*

Eight kinds of solvents were evaporated in a room and adsorbed by activated charcoal. The concentrations of vapors were determined using both methods. As shown in Table 4, the values obtained with the present

**Table 3** Recovery of organic solvents added to activated charcoals and desorbed by 2-hydroxypyridine

Solvents	Amounts added ( $\mu$ mole)	Recovery (%)	Precision spiked (R.S.D.*, %)
n-hexane	0.153	103	1.5
acetone	0.273	75	2.0
MEK	0.224	74	1.8
DCM	0.312	92	1.3
benzene	0.224	99	2.5
TRI	0.233	90	3.1
TCE	0.196	92	3.4
toluene	0.188	93	4.8

\*R.S.D., relative standard deviation  
MEK; methyl ethyl ketone, DCM; dichloromethane, TRI; trichloroethylene, TCE; tetrachloroethylene

**Table 4** Comparison between ambient concentration obtained by the present method and that obtained by desorption with carbon disulfide.

Solvents	Desorption with carbon disulfide (with CS <sub>2</sub> ) ppm	Desorption with 2-hydroxypyridine (with HOPY) ppm	Ratio HOPY/CS <sub>2</sub>
hexane	18.7	19.5	1.04
acetone	28.6	29.0	1.01
MEK	24.5	24.8	1.01
DCM	34.6	33.5	0.97
benzene	27.2	26.1	0.96
TRI	25.9	25.8	1.00
TCE	22.5	24.0	1.07
toluene	22.1	19.8	0.90

Symbols of solvents are the same as those of Table 3. HOPY ; 2-hydroxypyridine

method were higher than those obtained with the desorption method using carbon disulfide for n-hexane, acetone, methyl ethyl ketone and tetrachloroethylene and lower for dichloromethane, benzene, trichloroethylene, toluene and cyclohexane.

### Discussion

Among pumped and diffusive sampling techniques for the determination of solvents in air, one method widely used is as follows; organic solvents are adsorbed onto activated charcoal, packed into glass tubes and then extracted from the charcoal with carbon disulfide. However, in this procedure, the peaks of some solvents such as acetone and cyclohexane, having similar physicochemical properties to carbon disulfide, are masked by the peak of carbon disulfide on a gas chromatogram. The present method solves this problem and the peaks on a gas chromatogram were not interfered with the peak of carbon disulfide, because the 2-hydroxypyridine used for desorption is not applied to the gas chromatograph. The present method is not only selective but also sensitive. The peak heights on the gas chromatograms were about 50 times higher than those obtained by the desorption method with carbon disulfide, because a larger percentage of the total volume of vaporized gas is applied to the gas chromatograph. Therefore, the present method should prove useful

for the determination of solvent vapors at low concentrations.

Desorption efficiency from charcoal is commonly measured by injecting a known amount of liquid solvent directly onto the charcoal plugged in a tube followed by desorption. A study comparing the method on vapor-dosed charcoal and that on liquid-dosed charcoal showed that there is close agreement between the two methods.<sup>4)</sup> Therefore, the method on liquid-dosed charcoal was used in the present experiment.

The method of thermal desorption of solvents from adsorbed Tenax TA has been used for pumped and diffusive personal sampling of solvents in breathing zone air<sup>5)</sup> as the method other than solvent extraction. Thermal desorption of methyl ethyl ketone from Tenax TA showed recoveries in the range of 94 to 95 % and the recovery rate for toluene was in the 85 to 87 % range<sup>6)</sup>. However, the adsorption efficiency of Tenax TA was lower than that of charcoal.

Finally the present method is safer for examiners than another method using carbon disulfide, because neurotoxic carbon disulfide<sup>7)</sup> is not used in the analyses.

Acknowledgement: This work was partially supported in Grant-in-Aid for Scientific Research (C), (Agency No.07670469), from the Ministry of Education, Science Sport and Culture in Japan.

### References

- 1) National Institute for Occupational Safety and Health (NIOSH) (1977) *Manual of Sampling Data Sheets*. National Institute for Occupational Safety and Health, Cincinnati, pp 77—159.
- 2) Hirayama T and Ikeda M (1979) Application of activated carbon felt to the dosimetry of solvent vapor mixture. *American Industrial Hygiene Association Journal*, **40**, 1091—1096.
- 3) Paul SF and Lonkar ST (1994) Determination of benzene, aniline and nitrobenzene in workplace air: a comparison of active and passive sampling. *Journal of Chromatography*, **688**, 189—199.
- 4) Hori H and Tanaka I (1992) Adsorption characteristics of organic solvent vapor on activated carbon

- under fluctuating vapor concentrations. *American Industrial Hygiene Association Journal*, 347—351.
- 5) Thomas ML and Cohen BS (1995) A simple method for vapor dosing of charcoal sorbent tubes. *American Industrial Hygiene Association Journal*, 70—73.
  - 6) Vahdat N, Swearngen PM and Johnson JS et al. (1995) Adsorption capacity and thermal desorption efficiency of selected adsorbents. *American Industrial Hygiene Association Journal*, 32—38.
  - 7) Patty FA (1962) Carbon disulfide In Patty FA ed. *Industrial hygiene and toxicology*. Vol.II. 2nd edition. pp 901—904.