SAMPLING AND ANALYSIS OF ORGANIC SOLVENT VAPOURS

With Special Reference to Sampling Tubes for a Short Time and for the Working Period

Kazuko NORICHKA†, Shohei KIRA† and Masana OGATA†

常温固体吸着法による有機溶剤蒸気のサンプリングと分析

則 近 和 子*, 吉 良 尚 平*, 緒 方 正 名*

The present paper concerns the sampling and analysis of organic solvent vapours for a short period of time and for the working period.

Porous polymer beads, Porapak Q, was applied to the adsorbent of the sampling tube for mixed vapours of aromatic compounds (benzene, toluene and xylenes). The adsorbent was packed in stainless steel column of a suitable size, and the adsorbed vapours were released by heating in the flasher then analysed by gas chromatography. The concentrations of the mixed vapours could be measured simultaneously with sufficient recoveries at the ordinary concentrations in the working yard.

The sampling conditions by pumps and the practical recoveries were tested. Being sucked with the vacuum pump using a Gastek detection tube (100 ml), the recoveries proved to be almost 100%. Being sucked with portable diaphragmatic pumps at a slow flow rate (22 ml/min), the recoveries were constant with only small variations. At a relatively fast flow rate (220–230 ml/min), the recoveries were not so high as those at the slow flow rate.

These findings indicate that the sampling tube with Porapak Q is useful for aromatic compounds not only as a room air sampler for a short period of time but also as a personal air sampler.

INTRODUCTION

Organic solvents, especially toluene and xylenes, are widely used as the paint thinner, in mixed forms or as pure chemicals. A number of painters are exposed to these vapours. For the health administration of such workers, it is indispensable to measure the exposure levels by the detection tubes, by the personal air sampler or the room air sampler. The detection tubes are very useful for such measurement but cannot be applied to the mixed vapours, because of the interference with each other. Many investigators have reported the

necessity of personal monitoring devices which enable us to measure as well as to analyse the gases by gas chromatography. But the devices used up-to-date have been too bulky to be applied to ordinary working conditions, because of the necessity to carry with refrigerant or some liquid adsorbent¹⁾ to sample and keep in the device. To solve such problem, Cropper *et al.*²⁾ and Novak *et al.*³⁾ suggested the use of column packing materials of gas liquid chromatography and gave theoretical considerations on them. These materials were some types of beads coated with liquid, like silicon rubber or polyethylene glycols. Recently, Myers *et al.*,⁴⁾ Pellizzari *et al.*⁵⁾ and Dietrich *et al.*⁶⁾ showed the performance of porous polymer beads for the vapours as the adsorbents. Now we apply the porous polymer beads, Porapak Q, as an adsorbent of sampling tube for organic solvent vapours at the room temperature. This adsorbent

† Department of Public Health, Okayama University Medical School

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* 岡山大学医学部公衆衛生学教室
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Fig. 1. Schematic diagram of analytical system on the Porapak Q tube.

has an advantage of a highly adsorptive activity and easy desorption by heating for some organic solvents. Thus, a very small amount of the adsorbent can retain the vapours for a long period of time at the room temperature if the adsorbent is sealed in.

The present paper describes the recoveries and usefulness of the adsorbent and discusses the application of the adsorbent to the sampling tube for mixed vapours of aromatic compounds for a short period of time and to the personal air sampler.

MATERIALS AND METHODS

Sampling tube for adsorption

The tube was of stainless steel column, 7.6 cm (1) × 4 mm (id) in size, packed Porapak Q weighing 0.18 g, whose both ends were plugged with glass wool, indicating the direction for adsorption.

Standard vapours of aromatic compounds

Being injected into nitrogen stream at the rate of one l/min, benzene, toluene, *o*- and *m*-xylenes were vaporized and introduced into a Tedler bag of 10 l. Various volumes (0.5–8.0 µg) of these compounds were injected.

Adsorption of vapours

A vacuum pump purchased from Gastek Co. was used in the conventional way for the detection tubes. Portable diaphragmatic pumps were Kimoto Model 902 and Shibata MP-2, which sucked at 22 ml/min for 60–125 min and 220–230 ml/min for 4–8 min respectively.

Desorption of aromatic compounds from the sampling tube

The adsorbed vapours in the sampling tube was

released by heating at 200°C for 1 min in the flasher (Bendix Co. Model H/S 10), then introduced into the gas chromatograph with FID as shown in Fig. 1.

Gas chromatographic condition

Hitachi 063 GC with a flame ionization detector was used; column liquid phases, $\beta\beta'$ -Thiodi-propionitrile 20%; support, chromosorb W(AW); mesh, 60–80; column size, 2 m × 0.3 cm; temperature, 90°C; carrier gas, nitrogen; flow rate, 40 ml/min; chart speed, 10 mm/min.

Calibration

Calibration plots of each compound diluted with carbon disulfide were drawn. Then concentrations of mixed vapours in Tedler bags and desorbed vapours from Porapak Q by the flasher were calculated from this calibration plots.

Retentions of solvents in the sampling tube after the storage

After adsorption of aromatic compounds with Porapak Q by means of a vacuum pump, sampling tubes holding the Porapak Q—both ends of every tube opened—were put into the flask, where 50 g of silica gel powder had been put on the bottom in advance. Twenty five litres of air was introduced into a 500 ml flask through a U tube packed with 100 g of active charcoal, then the flask were sealed by glass stoppers. The sampling tubes were taken out at 10 min from one flask and 20 min from another flask after putting the tubes, and the aromatic compounds adsorbed with Porapak Q were desorbed by the flasher and their amounts were measured by gas chromatography. On the other hand, the tubes, whose both ends were sealed with Parafilm®, were left standing for 2 days and 4

days.

Amounts of aromatic compounds measured by both methods described above were compared with those desorbed immediately and measured.

RESULTS

Gas chromatographic patterns

Figure 2 shows a gas chromatogram of aromatic compounds after adsorption with Porapak Q and desorption by the flasher while heating. It indi-

Fig. 2. Gas chromatogram of aromatic compounds adsorbed in Porapak Q and desorbed by the flasher. A: set the tube and heat, B: change the air way, C: elevate the temp. (from room temp. to 90°C)

cates peaks of benzene, toluene, *m*-xylene and *o*-xylene respectively clearly separated.

Table 2. Recoveries of aromatic compounds adsorbed in Porapak Q (sucked with a portable diaphragmatic pump).

Sampling Volume	Solvent	Concentration ($\mu\text{g/l}$)	Recovery (%)
22 ml/min	Benzene	49.1	117.0
$\times 125$ min	Toluene	37.9	121.9
$= 2750$ ml	<i>m</i> -Xylene	34.3	102.8
	<i>o</i> -Xylene	27.9	109.3
22 ml/min	Benzene	55.3	106.0
$\times 60$ min	Toluene	50.9	99.5
$= 1320$ ml	<i>m</i> -Xylene	38.7	92.8
	<i>o</i> -Xylene	33.6	96.6
230 ml/min	Benzene	50.5	89.9
$\times 8$ min 15 sec	Toluene	38.4	97.3
≈ 1900 ml	<i>m</i> -Xylene	31.9	95.2
	<i>o</i> -Xylene	28.9	90.3
220 ml/min	Benzene	55.3	78.9
$\times 4$ min 10 sec	Toluene	50.9	72.4
$= 900$ ml	<i>m</i> -Xylene	38.7	88.9
	<i>o</i> -Xylene	33.6	92.4

Table 1. Recoveries of aromatic compounds adsorbed in Porapak Q (sucked with a 100 ml-Gastek pump). $N=15$

Solvent	Concentration ($\mu\text{g/l}$)	Recovery (% , $m \pm \text{S.D.}$)	Average (% , $m \pm \text{S.D.}$)
Benzene	25.5	94.1 ± 5.6	102.6 ± 6.2
	55.6	109.7 ± 1.7	
	114.3	102.3 ± 1.8	
	238.3	99.7 ± 5.2	
	493.9	107.1 ± 3.2	
Toluene	22.4	91.1 ± 5.8	106.4 ± 10.8
	48.5	115.6 ± 3.3	
	98.5	103.1 ± 2.7	
	200.5	104.6 ± 5.4	
	443.9	117.8 ± 1.1	
<i>m</i> -Xylene	14.3	101.4 ± 2.4	109.9 ± 19.5
	33.2	143.4 ± 7.2	
	76.5	100.8 ± 4.8	
	166.3	94.5 ± 10.0	
	379.1	109.2 ± 2.7	
<i>o</i> -Xylene	10.7	115.0 ± 8.5	100.4 ± 16.0
	31.1	119.6 ± 5.8	
	73.5	91.4 ± 5.7	
	168.9	83.2 ± 5.8	
	379.6	92.7 ± 1.8	

Table 3. Retention of aromatic compounds in a sampling tube after the storage.

Solvent	Retention in the sampling tubes (%) storage period			
	Unsealed		Sealed	
	10 min	20 min	2 days	4 days
Benzene	88.1	82.7	100.6	103.0
Toluene	89.8	89.8	96.9	98.8
<i>m</i> -Xylene	101.6	96.8	103.6	103.0
<i>o</i> -Xylene	93.8	73.2	102.5	92.8
Minute unknown peak	+	+	—	—

Practical recoveries of the sampling tube

Recoveries of the vapours of benzene, toluene, *m*-xylene and *o*-xylene sucked by both a vacuum pump (100 ml—Gastek pump) and a portable diaphragmatic pump with Porapak Q column are shown in Tables 1 and 2. Recoveries of aromatic compounds using a 100 ml vacuum pump were in the range of 102.6–109.9%, suggesting that the sampling tube could be used as the room air sampler for a short time with these mixed vapours of aromatic compounds (Table 1). In applying the portable diaphragmatic pump as the personal air sampler, as shown in Table 2, the slower flow rate (22 ml/min) attained more satisfactory recoveries than the faster (220–230 ml/min).

Retention of aromatic compounds in the sampling tube after the storage

Being left the tubes without seals after adsorption, decreases were observed in the benzene, toluene, *m*-xylene and *o*-xylene peaks, indicating the desorption within a short period of time and, minute peaks on the gas chromatogram appeared, suggesting additional adsorption from the polluted air. But by sealing both ends of the tube with Parafilm®, the aromatic compounds remain unchanged for a longer period of time.

DISCUSSION

Several researchers proposed silica gel or activated charcoal as the adsorbent, and carbon disulfide or dimethyl sulfoxide as the desorption agent of extraction solvent. Although these procedures are as feasible as the present method and enable us to analyse the same sample extract repeatedly, they require a relatively high concen-

tration or a large volume of the sample in air, because the least part of the sample can be injected into the gas chromatograph at a time. This method enables us to measure the levels of certain aromatics with only a small amount of the air sampler (100 ml) within the range of 10 to 500 $\mu\text{g/l}$. Moreover, this method has an advantage for the analyst in diminishing the danger of exposure to carbon disulfide whose toxicity is very serious if inhaled continuously.

The level of solvent vapours in the work yard should be estimated at least from the following two points of view. One is the time-weight average concentration that can be measured by personal air sampler or room air sampler all through the work time, and the other is the ceiling value of the vapours that can be measured by the detection tube within a few minutes adjusting the work styles. The conventional Kitagawa type detection tube can measure and estimate the ceiling value of only a single solvent vapour immediately, but cannot do it with mixed vapours. The present sampling tube can be applied to only 100 ml of mixed vapour specimens and estimate the levels of its individual components by the use of flasher-gas chromatography system since almost all of the adsorbed gas with Porapak Q was introduced into gas chromatography. Then the estimation of the levels of mixed vapours can be calculated by the equation of the threshold limit value of the mixture documented by ACGIH.

The solvent or thinner of paint at the working yard should be analysed and a suitable column should be selected prior to the analysis. And the use of the integrator for the signals detected by gas chromatography should make the measurement easier if the levels of the vapours are distributed over a wide range. In case of the personal sampler, when the sampling duration is long, the sampling tubes can be used by connecting in series to a short silicon rubber tubing.

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和 文 要 旨

塗装作業などで広く使用されているシンナーには、ト

ルエン、キシレン等、芳香族化合物が多く含まれており、作業者の健康に重大な影響を与えている。現在、有機溶剤蒸気の濃度測定には検知管方式がよくとられているが、この方式では単一の成分しか分析できず、他成分の妨害も著しく受ける場合が多い。そこで最近、注目されている多孔ポリマービーズを吸着剤として充填したステンレス捕集管を使用して採気し、ガスクロマトグラフで分析する方法について、採気量と回収率など基本的な実験を行なった。

多孔ポリマービーズはポラパック Q を用い、脱着には Bendix 社製のフラッシャーを使用した。テドラーバッグ中に調製した、ベンゼン、トルエン、*m*-および *o*-キシレン混合蒸気を、検知管用真空ポンプで 100 ml 吸引してポラパック Q に捕集した場合は、非常によい回収率を示し、短時間における室内サンプラーとして使用可能であることがわかった。また、小型吸引ポンプで採気した場合は、20 ml/min 程度の流速が、回収率の点で満足できる数値を示し、作業場内で数時間採気して個人サンプラーとして使用することができる。なお、採気後の保存試験により、捕集管の両端を密封することで、数日後の分析が可能ながわかった。

Reprint requests to Department of Public Health, Okayama University Medical School, 5-1, Shikata-cho 2-chome, Okayama, 700 Japan (K. Norichika) 著者への通信先：則近和子，〒 700 岡山市鹿田町 2-5-1 岡山大学医学部公衆衛生学教室