Simultaneous Extraction and Determination of Volatile Organic Compounds and Semi-volatile Organic Compounds in Indoor Air Using Multi-bed Solid Phase Extraction Device

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A method for the simultaneous extraction and determination of indoor volatile compounds, including volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), was developed using a multi-bed solid phase extraction (SPE)-type collection device. The collection device was prepared by packing styrene-divinylbenzene polymer particles and activated carbon particles. The collected analytes were completely desorbed by passing 7 mL of acetone, and the solvent was then injected into a gas chromatograph–mass spectrometry without the concentration process. Because the proposed method does not require ultrasonication and a concentration process of eluted solvent, quantitative determination of a relatively volatile compound could be achieved. The total recovery including extraction and elution recoveries for all the investigated analytes were in the range from 91.6 to 109%. The limit of quantification was less than 4.0 ng L^{-1} for all the investigated analytes, and relative standard deviations of the peak area of the analytes in indoor air were less than 12%. The collection device could be reused for over 50 samplings.

Keywords Volatile organic compounds, semi-volatile organic compounds, sick house syndrome, gas chromatography

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Introduction

Volatile organic compounds (VOCs) are organic chemical substances that are emitted into air at room temperature. VOCs are found in indoor air, and exposure to high concentrations VOC or long-term exposure to low levels of VOCs may cause health effects, such as eye irritation and headaches.[1,2] These adverse health effects are called multiple chemical sensitivity or sick building syndrome. To prevent these illnesses, the guidelines and standard measurement methods for VOCs in indoor air have been defined by the relevant agencies as well as the World Health Organization (WHO).[3] In Japan, the Ministry of Health, Labour and Welfare (MHLW) has adopted reference values and standard measurement methods for 13 VOCs in indoor air, such as toluene, ethylbenzene, dibutyl phthalate (DBP), and di-(2-ethylhexyl) phthalate (DEHP).[4] In 2017, the MHLW announced a revision of the reference values and the addition of 2-ethylhexanol (2-EH), 2,2,4-trimethyl-1,3-pentanedion monoisobutyrate (texanol) and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) to the list of regulated substances.[5]

The WHO classifies VOCs with boiling points from 0°C to 50 – 100°C as very volatile organic compounds (VVOCs), 50 – 100°C to 240 – 260°C as VOC, and greater than 250°C as semi-volatile organic compounds (SVOCs). Based on this classification, tetradecane, DBP, DEHP, texanol, and TXIB are categorized as SVOCs, and others are VOCs.

Gas chromatography coupled with mass spectrometry (GC-MS) analysis is mostly used for determination of VOCs. GC-MS shows higher selectivity and sensitivity, although an adequate sample preconcentration process is needed for determining trace VOCs in air. Solid adsorption/thermal desorption (TD) and solid adsorption/solvent extraction are widely employed for the preconcentration of VOCs in air samples, except for formaldehyde and acetaldehyde, and the MHLW also recommends these two sample preparation methods. Formaldehyde and acetaldehyde are typically determined by high-performance liquid chromatography after derivatization with 2,4-dinitrophenylhydrazine due to their high volatility and low detector response.[6,7] The TD method is a solvent-free analytical method, and it has been widely used in recent environmental analysis. However, in most cases an expensive automated TD system is needed, and insufficient desorption from the adsorbent could occur especially for SVOCs.[8,9] To determine a wide variety of volatile compounds (including VOCs and SVOCs), multi-bed-type adsorbents have been employed.[10] In the solvent extraction method, an activated carbon-based porous particle is typically employed as adsorbent,

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Table 1 Analyte VOCs and SVOCs in this study

Compound	Abbreviation	Boiling point/°C	Measured ion (*m/z*)
Toluene	Tol	111	91, 92
Ethylbenzene	EB	136	91, 106
Xylene	Xy	138 – 144	91, 106
Styrene	Sty	145	78, 104
p-Dichlorobenzene	*p*-DCB	174	111, 146
2-Ethyl hexanol	2-EH	184	57, 70
2,2,4-Trimethyl-1,3-pentanedion monoisobutyrate	Texanol	254 – 260	56, 71
Tetradecane	C_{14}	254	57, 71
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	TXIB	280 – 281	56, 71
Dibutyl phthalate	DBP	340	149, 223
Di(2-ethylhexyl) phthalate	DEHP	385	149, 279

and a toxic solvent of carbon disulfide (CS_2) is used as elution solvent. The method requires a long extraction time, and it is thought that there is some evaporation of volatile compounds during the extraction process.

Our research group has developed solid phase extraction (SPE)-type collection devices for extraction of SVOCs in air samples.[11,12] Recently, a device packed with styrene-divinylbenzene (Sty-DVB) polymer particles, Sunpak-H, was developed for precise determination of airborne SVOCs. The Sunpak-H-packed SPE-type collection device exhibited rapid and quantitative elution recovery of collected SVOCs by passing a small amount of organic solvent.[13,14] Because collected analytes can be easily eluted from the adsorbent by just passing an organic solvent, the collection device can be repeatedly used by drying the adsorbent that is packed in a glass cartridge.

In this study, regulated compounds, including VOCs and SVOCs in indoor air, were simultaneously extracted and determined by a novel multi-bed SPE-type collection device as a measure to help prevent sick building syndrome. After the optimization of extraction and elution conditions, the device was applied to the determination of VOCs in real indoor air samples.

Experimental

Chemicals

Toluene, ethylbenzene, xylene, styrene, *p*-dichlorobenzene (*p*-DCB), tetradecane, DBP, DEHP, texanol, and TXIB were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Acetone and 2-EH were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). The abbreviations and boiling points of the investigated analytes are listed in Table 1.

Collection device

The Sunpak-H (50/80 mesh) was prepared by Shinwa Chemical Industries Ltd. (Kyoto, Japan). Carboxen 1000 and Carbopack X were purchased from Sigma-Aldrich Japan (Tokyo, Japan). The specific surface areas of the Sunpak-H, Carboxen 1000, and Carbopack X were 100 – 150, 1200, and 240 $m^2\ g^{-1}$, respectively. First, a stainless steel wire mesh (HORIBA STEC) and a glass filter (15 mm diameter, GA-200, Advantec Tokyo Kaisha, Ltd., Tokyo, Japan) placed in a specially designed glass cartridge (14.9 mm i.d., 60 mm length, HORIBA STEC Co., Ltd., Kyoto, Japan). Then Sunpak-H (0.3 g) and Carboxen 1000 (0.1 g) or Carbopack X (0.1 or 0.2 g) were packed in the cartridge, and fixed by another glass filter and a PTFE O-ring. Packing length of the Sunpak-H and Carboxen 1000 (0.2 g) were 4 and 1 mm, respectively. Figure 1 shows a photograph and an illustration of the developed multi-bed-type collection device. The device was washed with acetone and dried by N_2 flow (5 L min^{-1}) for 10 min before use, and analytes were not detected on the method blank.

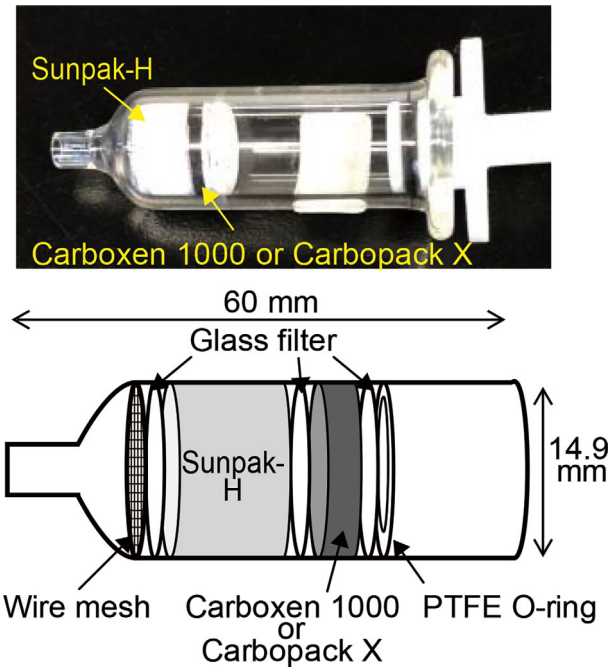

Fig. 1 Photograph and illustration of the multi-bed-type SPE device.

Analytical method

The collection recovery for the investigated analytes using the multi-bed-type collection device was calculated as follows. First, 100 µL of standard solution of the analytes (100 mg L^{-1} each dissolved in acetone) was spiked on the tip side of the device (spiked on the glass filter). Then, another collection device was connected to the first device, and a setting volume of clean air was sampled using a gas sampling pump (HORIBA STEC) through the two devices at 10 L min^{-1}. After the air sampling, the collected analytes were eluted by passing acetone for each respective collection device. The collection recovery was calculated by the ratio of peak area detected on the first collection device (spiked device) and second collection device. When any analytes were detected on the second device, the collection recovery could be calculated to 100%. The elution recovery of the spiked analytes was calculated by sequential solvent elution. When any analytes were detected on the second elution, the elution recovery could be calculated to 100%. The eluted solvent of 2 µL was injected into the GC-MS system without concentration process. The collection device was repeatedly used by drying the adsorbent with N_2 flow (5 L min^{-1}) for 10 min.

GC-MS measurement

A JEOL JMS-Q1000 GCMk-II system (JEOL, Tokyo, Japan) was used for all the GC-MS measurements. Helium (>99.999% purity) was used as the carrier gas at a head pressure of 100 kPa. The injector and interface temperature were set at 300 and 320°C, respectively. Sample solutions (2 µL) were injected by split mode (1:10). A fused silica capillary column of HP-5

Table 2 Elution recovery of the analytes

Solvent volume/ mL	Elution recovery, %											
	Tol	EB	*m*,*p*-Xy	*o*-Xy	Sty	*p*-DCB	2-EH	Texanol	C_{14}	TXIB	DBP	DEHP
6	99.9	99.9	99.9	100	99.8	99.8	100	100	99.7	99.8	100	100
7	99.6	99.8	99.6	99.7	99.3	99.9	100	100	99.4	98.1	100	100
8	100	100	100	100	100	100	100	100	100	100	100	100

Table 3 LOD, LOQ and additional recovery of the proposed method

Compound	LOD/ ng L^{-1}	LOQ/ ng L^{-1}	Reference value/ ng L^{-1}	Additional recovery, %
Tol	0.13	0.40	260	102
EB	0.13	0.40	3800	94.5
m,*p*-Xy	0.67	2.0	200	102
o-Xy	0.67	2.0		91.6
Sty	0.67	2.0	220	97.9
p-DCB	0.67	2.0	240	109
2-EH	1.3	4.0	(130)[a]	94.5
Texanol	1.3	4.0	(240)[a]	102
C_{14}	0.67	2.0	330	105
TXIB	0.13	0.40	(100)[a]	97.4
DBP	1.3	4.0	17	104
DEHP	0.67	2.0	100	94.6

a. Considered guideline values.

Table 4 Quantitative results of VOCs and SVOCs in indoor air samples

Compound	Concentration/ng L^{-1}			
	Teachers room	Laboratory	Clean room	Car
Tol	0.65	40.6	6.36	79.9
EB	0.53	4.54	1.06	4.31
m,*p*-Xy	<LOQ	6.37	2.15	7.50
o-Xy	N.D.	4.40	<LOQ	4.44
Sty	<LOQ	4.37	<LOQ	4.47
p-DCB	<LOQ	2.93	<LOQ	2.91
2-EH	5.30	8.85	8.03	<LOQ
Texanol	N.D.	N.D.	4.40	N.D.
C_{14}	<LOQ	<LOQ	N.D.	<LOQ
TXIB	N.D.	N.D.	N.D.	N.D.
DBP	N.D.	N.D.	N.D.	N.D.
DEHP	<LOQ	N.D.	N.D.	N.D.

N.D.: Not detected.

(30 m × 0.25 mm, 0.25 μm film thickness, Agilent Technologies, Santa Clara, CA, USA) was used for analytes separation. The column temperature was held at 40°C for 3 min, then programmed to 300°C at a rate of 20°C min^{-1}. The mass spectrometer was operated in the selected ion monitoring mode. The selected ions are summarized in Table 1.

Results and Discussion

Evaluation of extraction and elution performances

As investigated in previous studies, SVOCs, including DBP, DEHP, 2-EH, texanol, and TXIB, were successfully extracted on Sunpak-H, and they were completely and quantitatively eluted by passing 7 mL or less of acetone.[14,15] On the other hand, only the Sunpak-H (0.3 g) packed device showed incomplete extraction of toluene, where the extraction recoveries of toluene at air sampling volume of 300 and 600 L were 98.4 and 94.5%, respectively. Therefore, another adsorbent that has higher extraction property than Sunpak-H was introduced on the back side of Sunpak-H. First, Carboxen 1000 (0.1 g) was introduced into the collection device at the back side of Sunpak-H (0.3 g). The Sunpak-H/Carboxen 1000 device showed complete extraction of all the investigated analytes, where any compounds were detected from the second extraction device. However, toluene was not successfully eluted from the device due to strong adsorption onto Carboxen 1000 even if 15 mL of acetone was used. The desorption efficiency for toluene using the Sunpak-H/Carboxen 1000 device was about 98%. Then, Carbopack X was investigated as the second adsorbent. The Sunpak-H (0.3 g)/Carbopack X (0.1 g) packed device demonstrated incomplete extraction efficiency of toluene at a sampling volume of 600 L (60 min). Therefore, the amount of Carbopack X was increased to 0.2 g. The Sunpak-H (0.2 g)/Carbopack X (0.2 g) packed device exhibited complete extraction of all the investigated analytes up to sampling volume of 600 L. In addition, the extracted analytes were completely eluted from the device by passing of acetone. Table 2 shows the elution efficiency of the investigated VOCs and SVOCs using the Sunpak-H (0.2 g)/Carbopack X (0.2 g) packed device. All the investigated analytes were completely and rapidly eluted by using 8 mL of acetone. The elution time was approximately 3 min.

Evaluation of the method

The additional recovery of the proposed method was investigated by comparing the peak area obtained by standard solution to spiked sample. To prepare the standard solution, 100 μL of stock solution, including all the investigated analytes at 100 mg L^{-1} dissolved in acetone, was dissolved in 8 mL of acetone. On the other hand, the same stock solution of 100 μL was spiked onto the Sunpak-H (0.2 g)/Carbopack X (0.2 g) packed device, and then 600 L of clean air was collected (16.7 ng L^{-1} as in air sample). After that, a spiked sample solution was obtained by eluting spiked analytes with 8 mL of acetone. The additional recoveries for all the investigated analytes were in the range from 90.1 to 109% (n = 3) (Table 3). The results clearly showed that all the investigated analytes, including VOCs and SVOCs, were successfully and quantitatively recovered by the proposed method.

The limit of detection (LOD) and the limit of quantification (LOQ) of the proposed method are summarized in Table 3. The LOD was defined as signal to noise ratio of 3.3, and the LOQ was 10. The results showed satisfactory sensitivity of the proposed method for all the investigated analytes. The relative standard deviations (RSDs) of the peak area obtained by measuring the standard solution prepared by spiking 100 μL of stock solution (100 mg L^{-1}) onto the collection device,

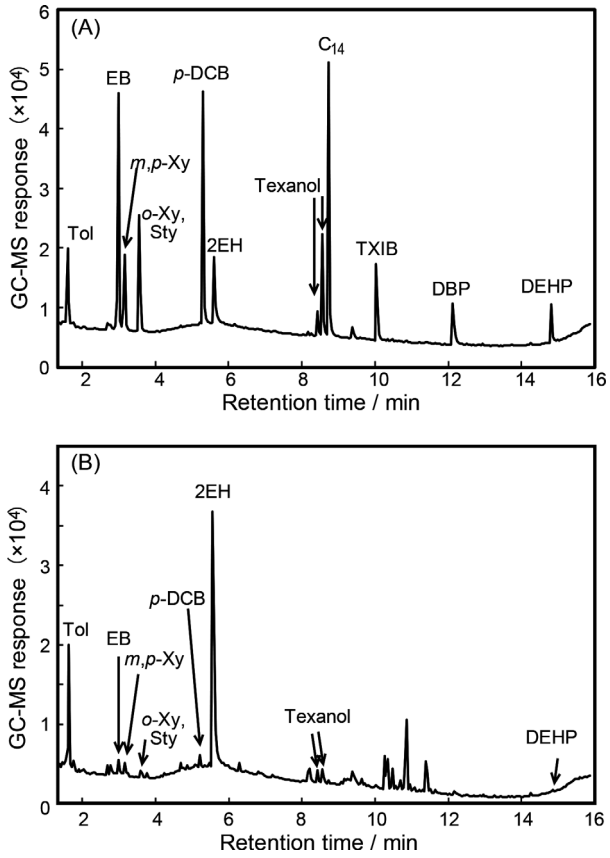

Fig. 2 Chromatogram for the determination of VOCs and SVOCs. (A) Spiked sample (B) clean room air.

collecting 600 L of clean air, and eluting the analytes with 8 mL of acetone were less than 12% for all the analytes.

Since quantitative recovery of the proposed method for all the investigated VOCs and SVOCs was confirmed, the method was applied to the determination of VOCs and SVOCs in indoor air and in-car air samples. The air samples were collected for 600 L (10 L min^{-1} × 60 min) at a height of 1.0 m above the ground at ambient temperature in November 2019. The quantitative results of determined compounds are listed in Table 4. Typical chromatograms for the determination of VOCs and SVOCs spiked with standard solution (100 mg L^{-1} solution 100 μL spiked) and clean room air are shown in Fig. 2(A) and 2(B), respectively. All of the detected analytes were determined without co-eluting compounds, and the results clearly indicated successful determination of trace VOCs and SVOCs in air samples with a simple sample collection method.

Conclusions

A multi-bed SPE-type collection device packed with Sunpak-H and Carbopack X showed quantitative extraction and elution performances for indoor air VOCs and SVOCs. Because the extracted analytes could be completely eluted by passing 8 mL of acetone, the eluted solvent can be directly injected for GC-MS analysis without sample preconcentration with satisfactory sensitivity. In addition, the method does not require use of toxic CS_2 that is typically used as a desorption solvent in solvent extraction for VOC analysis. The developed collection device showed quantitative determination of a wide range of VOCs in air samples. Therefore, the method could be useful for quantification of several types of VOCs in gaseous samples.

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