Quantitative Determination of 2-Ethyl-1-hexanol, Texanol and TXIB in Indoor Air Using a Solid-Phase Extraction-type Collection Device Followed by Gas Chromatography-Mass Spectrometry

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In this study, indoor air semi-volatile organic compounds (SVOCs) including 2-ethyl-1-hexanol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (texanol), and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB), which are scheduled for adding as regulated compounds concerning indoor air reference values in Japan, were quantitatively extracted using a solid-phase extraction-type collection device, followed by sensitively determined by gas chromatography-mass spectrometry. The developed method has shown a good extraction recovery up to an air sampling volume of 900 L. The extracted analytes were quantitatively and rapidly eluted by 7 mL of acetone. The limit of quantification of the analytes were 0.7, 2.1 and 0.2 ng L–1 in air sample at a sampling volume of 300 mL without any concentration of a desorption solvent. The developed method was applied to simultaneous determinations of the investigated target analytes and phthalate esters in real indoor air samples.

Keywords Semi-volatile organic compounds, sick house syndrome, sample preparation, gas chromatography-mass spectrometry

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of VOCs using a needle-type extraction device is an alternative extraction method.\textsuperscript{11–13} In this method, analyte VOCs are adsorbed on the particulate adsorbent that is packed in a stainless steel needle by active sampling of a gaseous sample. Then, the analytes are thermally desorbed by the insertion of an extraction needle into a heated GC injection port. Therefore, this method does not require any expensive instrument or attachment. The method has been successfully applied to the determination of VOCs in both gaseous\textsuperscript{14–17} and aqueous samples.\textsuperscript{18–20} However, the needle extraction method is also a thermal desorption method. Therefore, some semi-volatile organic compounds (SVOCs) are not successfully desorbed from the adsorbent because they are strongly adsorbed on the adsorbent.

In solid adsorption/solvent extraction method, an activated carbon based adsorbent, is typically used. To desorb extracted VOCs from the adsorbent, using carbon disulfide (CS$_2$) is recommended as the standard desorption method; however, CS$_2$ is toxic and odorous. Furthermore, the method shows poor recoveries of VOCs.\textsuperscript{21} Using an alternative adsorbent is admitted by MHLW when the adsorbent has sufficient collection recovery for the analytes.\textsuperscript{3} Because analytical reports for the determination of 2-EH, texanol and TXIB are very limited, the quantitative performances for these compounds by conventional analytical methods have not been demonstrated. Therefore, evaluations of quantitative performances and the development of a reliable analytical method for these compounds could be needed.

Our research group has developed a solid phase extraction (SPE)-type collection device for the collection of gaseous SVOCs, such as poly cyclic aromatic hydrocarbons (PAHs) and sesquiterpenes.\textsuperscript{22–24} Recently we developed a newly developed styrene-divinylbenzene (Sty-DVB) polymer particle of Sunpak-H as the adsorbent of the SPE-type collection device. A Sunpak-H packed collection device showed excellent elution performance, where extracted SVOCs were completely eluted by just passing about 10 mL of an organic solvent.\textsuperscript{25} The Sunpak-H packed collection device was successfully applied to the determination of in-door phthalate esters.\textsuperscript{26}

This manuscript firstly describes the quantitative determination of 2-EH, texanol, and TXIB in air samples using the Sunpak-H packed SPE-type collection device. Several analytical parameters, including extraction and elution recovery, repeatability, were quantitatively evaluated, and the suitability of the proposed method for these newly regulated compounds was confirmed. The method was applied to simultaneous determinations of the analyte compounds and regulated phthalate esters in real in-door air samples.

**Experimental**

**Chemicals**

Texanol and TXIB were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 2-EH, acetone, dichloromethane and methanol were obtained from Kanto Chemical Co. Inc. (Tokyo, Japan). The chemical structures of the analytes are given in Fig. 1. Since texanol has two isomers, two peaks were obtained in the chromatogram. The peak area of texanol was calculated as the sum of both peak areas.

**Collection devices**

Sunpak-H (50/80 mesh; specific surface area, 100 - 150 m$^2$ g$^{-1}$) was prepared by Shinwa Chemical Industries Ltd. (Kyoto, Japan). Sunpak-H (0.3 g) was packed in a specially designed glass cartridge (14.9 mm i.d., 60 mm length, HORIBA STEC Co., Ltd., Kyoto, Japan). The packing length of the adsorbent is approximately 10 mm. The adsorbent was fixed with a stainless-steel wire mesh (HORIBA STEC), glass fiber filters (15 mm diameter GA-200; Advantec Tokyo Kaisha, Ltd, Tokyo, Japan) and a PTFE O-ring. A PTFE adapter (HORIBA STEC) was used to connect the cartridge to a gas sampling pump. The collection device was washed with acetone before use, and analytes were not detected on the method blank.

**Analytical method**

The collection and elution recoveries of the device for the analytes were evaluated using a standard stock solution (100 mg L$^{-1}$ each dissolved in acetone). First, 100 μL of the standard solution was spiked on the collection device (on the glass fiber filter). For evaluating the collection recovery, another collection device was tandemly connected to the device, and clean air was collected via two collection devices at a sampling speed of 10 L min$^{-1}$. The collection recovery of the device for the standard analytes were calculated by the ratio detected on the former collection device to that detected on the former and latter collection devices. When any analytes were detected on the latter device, the collection recovery could be calculated to 100%. The elution recovery was investigated by sequential solvent elution using the same volume; it was calculated by the ratio detected on 1st elution to the total of the 1st and 2nd elutions. When any analytes were detected on the 2nd elution, the elution recovery could be calculated to 100%. In this study, the volume of the elution solvent is the volume obtained on the vial, which was not the same as the solvent volume loaded on the collection device because of absorption of the solvent on the adsorbent. The eluted solvent was concentrated to 1 mL by pure nitrogen stream in a water bath kept at approximately 50 to 60°C, if necessary. The collection device could be reused after drying the adsorbent with an N$_2$ flow (5 L min$^{-1}$) for 10 min.

**GC-MS measurements**

A JEOL JMS-Q1000 GC/MS system (JEOL, Tokyo, Japan) was used for GC-MS measurements. Helium (>99.999% purity) was used as the carrier gas at a head pressure of 100 kPa. The injector and the interface temperatures were set at 300 and 320°C, respectively. Split mode injection at a ratio of 10:1 was carried out. The injection volume was 2 μL. A fused-silica HP-5 capillary column (30 μm x 0.25 mm, 0.25 μm film
On the other hand, for the sensitive determination of texanol and directly injected into GC-MS without concentration process. Hence for the determination of 2-EH, the eluted solvent was due to its lower boiling point. On the other hand, decreased concentration process showed approximately 86% with 6 mL of acetone. The recovery of the analytes with the concentrated to 1 mL by nitrogen flow followed by dilution and another was 7 mL of the standard solution. Where one was 7 mL of the standard solution, where one was 7 mL of the standard solution, and the collection recovery for all investigated analytes up to a sampling volume of 900 L (sampling time of 90 min), where any investigated compounds were shown in the latter collection device. In typical in-door air analysis, the sampling time was 30 or 60 min.

Results and Discussion

Optimization of desorption condition

First, the desorption solvent and solvent volume were optimized by evaluating the desorption recovery of the standard analytes from the Sunpak-H packed collection device. The elution recovery was calculated by spiking 100 μL of the standard solution (100 mg L−1 each) and the collection of 300 L of clean air (10 L min−1). Acetone and dichloromethane showed a better elution recovery than that of methanol. There was no significant difference for the elution recovery between acetone and dichloromethane. Therefore, acetone was chosen as the elution solvent by taking into account health risk. The elution recovery values of analytes with different volumes of acetone are summarized in Table 2. As shown in the table, the investigated analytes were completely desorbed from the collection device by simply passing 7 mL of acetone. Therefore, the desorption solvent volume was determined to be 7 mL. The desorption time using 7 mL of acetone was less than 3 min.

The concentration of the eluted solution by nitrogen flow has been widely used to increase the sensitivity of the analytes. On the other hand, the loss of analytes should be avoided during the concentration process. The loss of the three analytes during nitrogen flow concentration was investigated by comparing two standard solutions, where one was 7 mL of the standard solution, and another was 7 mL of the standard solution that once concentrated to 1 mL by nitrogen flow followed by dilution with 6 mL of acetone. The recovery of the analytes with the concentration process showed approximately 86 ± 7% for 2-EH due to its lower boiling point. On the other hand, decreased recoveries were not obtained for texanol and TXIB (n = 5).

Hence for the determination of 2-EH, the eluted solvent was directly injected into GC-MS without concentration process. On the other hand, for the sensitive determination of texanol and TXIB, the eluted solvent was analyzed after concentrating the solvent to 1 mL.

The extraction recovery of the analytes was investigated at different air sampling volumes. Two collection devices were tandemly connected, and the standard solution was spiked on the former device. Then, clean air was collected through two collection devices. The air was collected at a temperature of over 30°C. After air sampling, the analytes collected on each device were eluted by passing 7 mL of acetone, and determined, respectively. The collection device showed a satisfactory collection recovery for all investigated analytes up to a sampling volume of 900 L (sampling time of 90 min), where any investigated compounds were shown in the latter collection device. In typical in-door air analysis, the sampling time was 30 or 60 min.

Method evaluation

The whole recoveries of the method for the target analytes were investigated. First, 100 μL of the standard solution (100 mg L−1) was dissolved in 6.9 mL of acetone (1.4 mg L−1 standard solution). Next, 100 μL of the standard solution was spiked on the collection device, and 300 L of clean air was collected at 10 L min−1. After that the spiked analytes were eluted by 7 mL of acetone (ideally 1.4 mg L−1 eluted solution). The whole recoveries were calculated by comparing the analyte peak areas obtained for the standard solution and the eluted solution (n = 3). The results showed that whole recoveries in the rage of 95 – 104% for the investigated analytes, and the quantitative recovery of the proposed method for 2-EH, texanol, and TXIB were demonstrated.

The limit of quantifications (LOQs) of the proposed method for the investigated analytes was evaluated. LOQs were determined to signal-to-noise ratio of 10. The LOQs of the proposed method at the air sampling volume of 300 L (10 L min−1 × 30 min) are summarized in Table 3. The LOQs obtained at without solvent concentration are quite satisfactory for determining the analytes at the considered guide line levels. As described above, 2-EH was not quantitatively determined after nitrogen flow concentration, although further sensitive determinations for texanol and TXIB could be obtained by solvent concentration with nitrogen flow. The relative standard deviations of the peak areas for analyzing five standard solutions (five consecutive spike, air sampling and solvent extraction) were less than 10%. The extraction and elution recoveries were not decreased upon consecutive procedures using the collection device at least 50 times.

Real sample analysis

Based on a quantitative evaluation of the proposed method, it was applied to the determination of 2-EH, texanol, and TXIB in real air samples. In real sample analysis, phthalate esters were simultaneously extracted and determined based on our previous study. For indoor air quality reference values published by MHLW, DBP and DEHP are included. The reference values of these phthalate esters are 17 and 100 ng L−1, and these boiling

### Table 1

| Compound | Quantitative ion (m/z) | Confirmation ion (m/z) |
|----------|------------------------|------------------------|
| 2-EH     | 57                     | 70                     |
| Texanol  | 71                     | 56                     |
| TXIB     | 71                     | 56                     |

### Table 2

| Acetone volume/ mL | Elution recovery, % |
|--------------------|---------------------|
|                    | 2-EH    | Texanol | TXIB   |
| 5                  | 100     | 100     | 99.5   |
| 6                  | 100     | 100     | 99.8   |
| 7                  | 100     | 100     | 100    |

### Table 3

| Solvent volume/ mL | 2-EH   | Texanol | TXIB |
|--------------------|--------|---------|------|
| 7                  | 0.7    | 2.1     | 0.2  |
| 1                  | —      | 0.3     | 0.03 |
First, indoor-air samples in a building were determined. This building was under recovering of the outer wall from July, 2018 to September, 2018. The quantitative results of the investigated analytes are listed in Table 4. The relatively higher concentration of 2-EH was determined in this building. This could be due to the use of 2-EH as the solvent of an adhesive or paint. Figure 2 shows a typical chromatogram for the determination of three investigated analytes and phthalate esters in room C. As shown in the chromatogram, TXIB and DEP were co-eluted, although they were quantified separately using a respective quantify ion.

In-door air samples taken from a newly-build house were also determined. In this newly build house, any furniture was present. The quantitative results of the investigated analytes are given in Table 5. 2-EH were not detected in this house, and the concentrations of texanol, TXIB, and phthalate esters were also sufficiently low.

**Conclusions**

In this work, a quantitative and reliable determination of 2-EH, texanol, and TXIB in indoor air was reported with the Sunpak-H packed SPE-type collection device. The proposed method provided simple and sensitive analysis for the investigated compounds without an expensive and specific instrument. Because the extracted analytes were successfully eluted from the collection device with a small amount of acetone, the analytes could be sensitively determined in GC-MS without concentrating the eluted solvent. The method applicability was confirmed by determining the investigated compounds in real air samples. In addition, phthalate esters including DBP and DEHP were simultaneously determined in real sample analysis. Simultaneous quantitative analysis of VOCs and SVOCs by the solvent extraction method without CS2 could be a clear advantage for in-door air analysis. Further applications of the device could be expected for the quantitative determinations of SVOCs or VOCs in air samples.

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