三次喫煙評価のための微量分析法の開発

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Determination of Volatile Organic Compounds for a Systematic Evaluation of Third-Hand Smoking

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Abstract:

Third-hand smoking was quantitatively evaluated with a polymer-packed sample preparation needle and subsequent gas chromatography-mass spectroscopy（GC-MS）analysis. The extraction needle was prepared with polymeric particles as the extraction medium, and successful extraction of typical gaseous volatile organic compounds（VOCs）was accomplished with the extraction needle. For an evaluation of this new cigarette hazard, several types of clothing fabrics were exposed to sidestream smoke, and the smoking-related VOCs evaporated from the fabrics to the environmental air were preconcentrated with the extraction needle. Smoking-related VOCs in smokers' breath were also measured using the extraction needle, and the effect of the breath VOCs on third-hand smoking pollution was evaluated.

The results demonstrated that a trace amount of smoking-related VOCs was successfully determined by the proposed method. The adsorption and desorption behaviors of smoking-related VOCs were clearly different for each fabric material, and the time variations of these VOCs concentrations were quantitatively evaluated. The VOCs in the smokers' breath were clearly higher than that of nonsmokers'; however, the results suggested that no significant effect of the smokers' breath on the potential pollution occurred in the typical life space. The method was further applied to the determination of the actual third-hand smoking pollution in an automobile, and a future possibility of the proposed method to the analysis of trace amounts of VOCs in environmental air samples was suggested.

1. Introduction

It has been reported that tobacco smoke contains more than 4000 chemicals containing potential carcinogens[1,2]. The analysis of environmental tobacco smoke (ETS) has been focused on for a systematic evaluation of indoor air pollution, because the evaluation of passive smoking could be important to avoid any risk to nonsmokers' health. In recent years, the expose to passive smoking risk has been reduced by adopting smoke-free areas or smoking rooms; however, a new smoking hazard has been reported, so-called "third-hand smoking"[3].

Third-hand smoking is residual tobacco smoke pollution, that occurs after smoking, and is classified into the following two types: one is in-door air pollution due to tobacco-related volatile organic compounds (VOCs) from in-door surfaces, such as cushions, carpets or curtains. These VOCs are adsorbed on in-door surfaces during smoking, and are then desorbed form the surfaces after smoking, even if the smoke has already been ventilated. Another is exposure to tobacco-related VOCs from a smoker. Although smoking is done outside, tobacco-related VOCs still remain on the surface of the smoker's clothing and also the smoker's breath. Some of these chemical compounds have an unpleasant smell for nonsmokers, and potential health damage has been suspected, especially for children[3].

Gas chromatography (GC) is one of the most promising methods for the analysis of smoking-related VOCs, because of their selectivity, and gas chromatography-mass spectrometry (GC-MS) has been realized as a powerful tool for a sensitive determination of typical VOCs and semi-volatile organic compounds (SVOCs) in tobacco smoke[4,5]. However, a sample preconcentration process should still be needed for accurate and precise determination of these VOCs. Especially, the VOCs concentration related to third-hand smoking could be at a quite low level, and therefore an effective sample preparation process and subsequent separation/determination methods are needed.

Solid-phase microextraction (SPME) is one of the most advanced sampling techniques for typical VOCs analysis in GC[6], and it has several attractive features over traditional sample preparation techniques. Alternative sample preparation techniques have been developed as a needle-type sample preparation device[7-15]. Compared to the conventional SPME, the needle-type sampling device has been regarded to have good mechanical strength and high extraction capacity. In our previous work, a polymer particulate medium based on a copolymer of methacrylic acid (MA) and ethylene glycol dimethacrylate (EDMA) was synthesized, and packed into a specially-designed needle as the extraction medium[9]. This polymer particle-packed extraction needle was successfully applied to the analysis of ETS[11]and human breath[16].

In this paper, a polymer particle-packed extraction needle was applied to the evaluation of a potential risk of third-hand smoking. Smoking-related VOCs adsorbed on several types of fabrics were determined, and the time variation of the VOCs concentration was studied. Smoking-related VOCs in smokers' breath were also measured using the extraction needle, and the effect of the breath VOCs on the third-hand smoking pollution was evaluated. Additionally, the proposed method was applied to the determination of actual third-hand smoking in an automobile.

2. Experimental

2.1. Materials

Benzene, toluene, xylenes and 2, 5-dimethylfurane (2, 5-DMF) were obtained from Tokyo Chemical Industries (Tokyo, Japan). Acetone, pyrrole, limonene and 2-furaldehyde were purchased from Wako Pure Chemical (Osaka, Japan). All of the fabric samples (cotton, linen, silk, acetate and polyester) used in this work were commercially available, and purchased from a local fabric store (Toyohashi, Japan). Breath samples were collected in Tedlar bags (GL Sciences, Tokyo, Japan). A vacuum sampling device and an ammonia gas detection tube were purchased from Komyo Rikagaku Kogyo (Tokyo, Japan).

2.2. Extraction and desorption procedure of VOCs

As the extraction medium, a copolymer of MA and EDMA was synthesized as described previously[9], and copolymer beads having a diameter of between 150 and 180 μm were packed into a section of a specially-prepared needle, 0.5 mm i.d., 0.7 mm o.d., 85 mm length. For the extraction, the needle was attached to a commercially available vacuum sampling device. A gaseous sample was introduced into the extraction needle by manually pulling the handle of the vacuum sampling device, and the analytes were extracted by the polymeric particles therein. The typical sampling volume was 50 mL, and it took about 5 min to complete the sampling.

After extraction, the extraction needle was attached to an injection syringe containing 0.5 mL of N_2 gas. Then, the extraction needle was inserted to a heated GC injection port, and the analytes were injected by the N_2 gas, where the needle was heated for 10 s in the injector before injection. It has been confirmed in preliminary experiments that the pre-heating time could help realize successful desorption of the analytes. The extracted samples could be stored in the needle at room temperature for at least three days.

2.3. A model for evaluating third-hand smoking

In this work, the risk of third-hand smoking was evaluated based on the determination of smoking-related VOCs that adsorbed on several types of fabrics, and that were also contained in the smokers' breath. Figure 1 shows the scheme for the evaluation of smoking-related VOCs desorbed from fabric samples. First, a 10 cm square of fabric sample was placed in a home-made metal box of 18 L volume. Then, tobacco was placed on the bottom of the box. The box had an inlet, as illustrated in Fig. 1, where enough air had been provided during tobacco combustion. During tobacco combustion, the box was filled with sidestream smoke and smoking-related VOCs were adsorbed on the fabric. After 9 min of combustion time, the fabric was transferred to a glass vessel of 4 L volume. Upon completion of the equilibrium time for 30 min in the glass vessel, the extraction needle was inserted into the glass vessel, and then 50 mL of the gaseous sample was extracted, followed by GC-MS analysis. One of the unpleasant odors, ammonia, was measured by using a commercially-available detection tube.

Breath samples of smokers and nonsmokers were collected in a Tedlar bag of 1 L volume, and then extracted with the extraction needle. Tedlar bags were cleaned at least five times with pure N_2 before use.
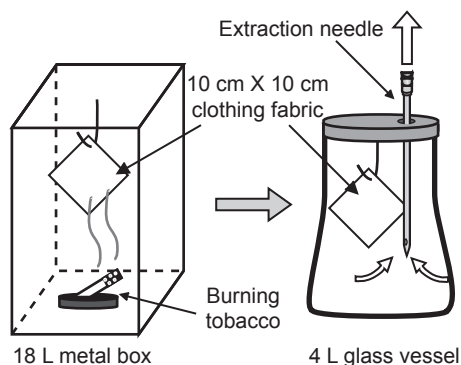

Figure 1 Scheme for the evaluation of smoking-related VOCs level desorbed from fabrics with needle extraction device.

2.4. GC-MS measurements

For all of the GC measurements, an Agilent 6890N gas chromatograph (Yokogawa Analytical Systems, Musashino, Japan) with a split/splitless injection port and a HP 5972A mass selective detector (MSD) was used, and all of the injections were made by a split mode with a ratio of 15:1. GC separation was performed on an HR-17 fused-silica capillary column of 30 m x 0.25 mm i.d. having a film thickness of 0.25 μm (Shinwa Chemical Industries, Kyoto, Japan). As the carrier gas, He was employed at the typical head pressure of the 30 kPa, and the injector was maintained at 200℃. The GC-MS interface temperature and the ionization voltage were set at 250 ℃ and 70 eV, respectively, with electron impact ionization. The column temperature was started at 40℃ for 2.0 min, and then programmed to 240℃ at a rate of 10℃/min. The mass spectrometer was operated in either a total ion monitoring mode (TIM) with a m/z range of 45 to 250, or a selected ion-monitoring mode (SIM). The data collection was made with Chrom NAV (Jasco, Tokyo, Japan) running on a personal computer.

3. Results and Discussion

3.1. Optimization of the evaluation conditions

As an evaluation method for the air pollution generated by the third-hand smoking, the determination of VOCs desorbed from various types of fabrics could be quite valuable. Several experimental conditions, such as the volume of the metal box and the glass desorption vessel, the size of the fabric, and the equilibrium time of tobacco-related VOCs in the glass vessel, were optimized in preliminary experiments to accomplish a reproducible and effective extraction. For all of the evaluations, a 10 cm square of each fabric sample was used, because the physical size of the fabric showed a dominant effect on the amount of the VOCs than that of the weight in the preliminary experiments. This is quite natural that the amounts of desorbed VOCs are more

closely related to the surface area of the fabric samples than the weight [17], and actually the same size of fabric sample should be examined for a more practical evaluation of third-hand smoking in an in-room environment.

Figure 2A shows typical TIM chromatogram for the separation of VOCs related to third-hand smoking. Introducing the TIM mode, a large number of VOCs related to a third-hand smoking have been successfully detected in GC-MS with the sample preconcentration by the extraction needle, although the detected VOCs level was clearly lower than that detected in typical sidestream smoke. In addition, a similar VOCs profile was obtained for several different brands of cigarettes, except for that containing a menthol flavor, where the peak of menthol was clearly observed in the chromatogram. Also, in the sidestream smoke, the peak of nicotine was detected; however, it was not detected in samples related to the third-hand smoking. The above results have a good agreement with phenomena reported previously, where a quite limited desorption, due to the low volatility, of nicotine from the surface of the fabrics was confirmed [18]. For a sensitive determination of VOCs closely related to third-hand smoking, pyrrole, benzene, toluene and 2,5-DMF were chosen as the target compounds, and monitored with a SIM mode of m/z 67, 78, 91 and 96, respectively. A typical SIM chromatogram for the separation of VOCs related to third-hand smoking is summarized in Fig. 2B. The chromatogram was constructed from the sum of these m/zs' responses. The limit of detection (LOD) and the limit of quantification (LOQ) for all these compounds are summarized in Table 1. The RSDs of the peak area were less than 3.0% (n= 5) for all of the standard samples. The extraction/desorption efficiency of the extraction needle was evaluated by comparing the corresponding peak areas for the direct injection of the higher concentration VOCs sample and needle extraction of the lower concentration sample. From this comparison, the sample recovery with the extraction needle was calculated as being more than 99% in the calibration range. The upper limits of the calibration range were more than 500 μ g/L for all VOCs, suggesting that the extraction needle has a satisfactory extraction performance for these VOCs.
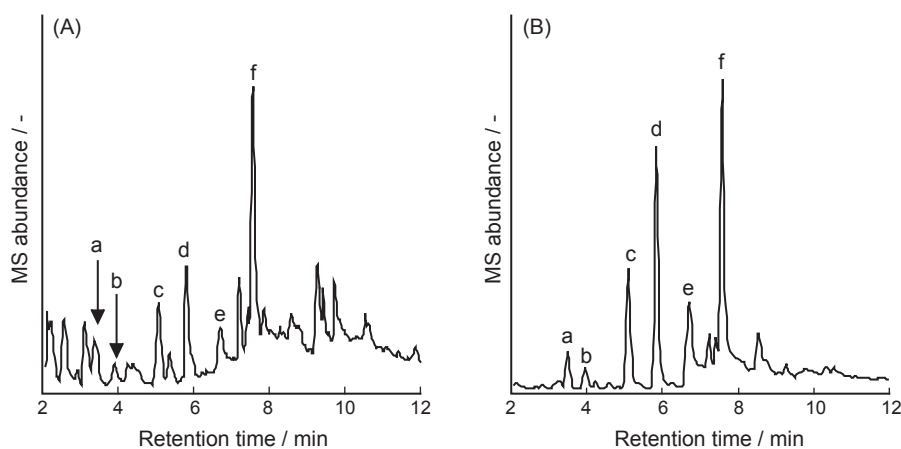

Figure 2 Typical chromatograms of the smoking-related VOCs adsorbed on an acetate fabric. (A) Monitored by TIM mode and (B) monitored by SIM mode. Peaks: (a) benzene; (b) 2,5-DMF; (c) toluene; (d) pyrrole; (e) *o, m*-xylene; and (f) 2-furaldehyde.

Table 1 LOD and LOQ for four typical smoking-related VOCs.

	Benzene	2,5-DMF	Toluene	Pyrrole
LOD (ng/L)	1.0	1.0	0.5	5.0
LOQ (ng/L)	3.0	3.0	1.5	15

The chromatograms were monitored as the sum of the responses at four m/z's : 67, 78, 91 and 96.

3.2. Determination of tobacco-related VOCs adsorbed on different types of fabric

Five different types of fabrics (cotton, linen, silk, acetate and polyester) were exposed to sidestream smoke, and the VOCs related to the third-hand smoking were determined. Figure 3 presents the concentration of the smoking-related VOCs desorbed from the fabric samples in the glass vessel. Significantly higher concentrations for ammonia and 2-furaldehyde (data not shown) were observed for the cotton and linen fabric samples; however, higher concentrations for other smoking-related aromatic VOCs were obtained with the acetate fabric. The results show good
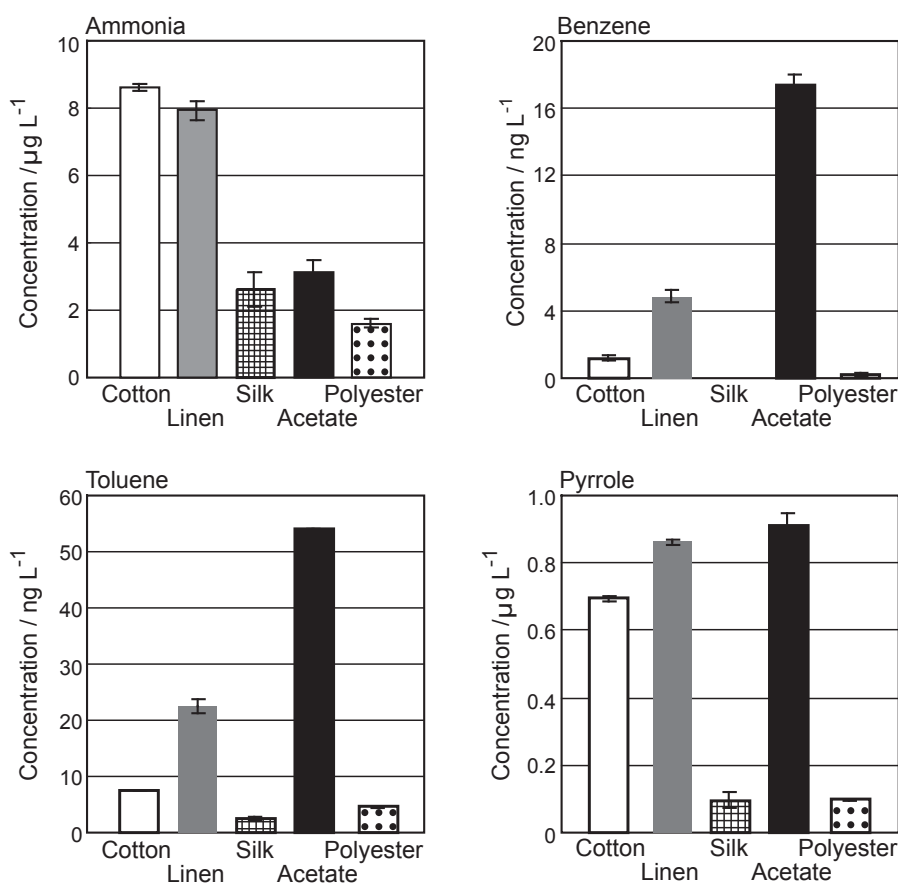

Figure 3 Comparison of smoking-related VOCs adsorbed on each fabric. Concentration of ammonia was determined by a commercially available detection tube. Other compounds were determined by GC-MS in the SIM mode.

agreement with that reported previously [17], where a quite limited adsorption of smoking-related VOCs was observed for the polyester and silk fabric samples. Although a more extensive study, including a consideration for the chemical structure of the fiber, should be needed to reach the final conclusion, these results indicate that the adsorption behavior of VOCs was associated with the chemical structure of the fabric, and that the proposed method could be applied to the development of an evaluation method for preventing third-hand smoking pollution.

In an indoor environment, tobacco-related VOCs are rapidly diffused to indoor air, and adsorbed on various indoor surfaces. The adsorbed VOCs are re-emitted to the indoor air gradually. Therefore, a time-variation profile of the VOCs evaporated from the fabric was determined for an evaluation of third-hand smoking pollution. After the smoking-related VOCs were adsorbed on a fabric in the metal box, the fabric was placed in calm outdoor air for 1 to 10 min. During this period, the adsorbed VOCs were progressively evaporated from the surface of the fabric to ambient air. Then, the fabric was transferred to a glass vessel of 4 L volume, and the VOCs in the vessel were extracted with the extraction needle after 30 min of the equilibration time. The time variations of the typical VOCs level are shown in Fig. 4, where the concentration is plotted against the exposed time of the fabric to the outdoor air. It can be seen that these VOCs were continuously evaporated from the fabric surface for about 10 min, and also that the compounds having high volatility were more rapidly evaporated from the fabric.
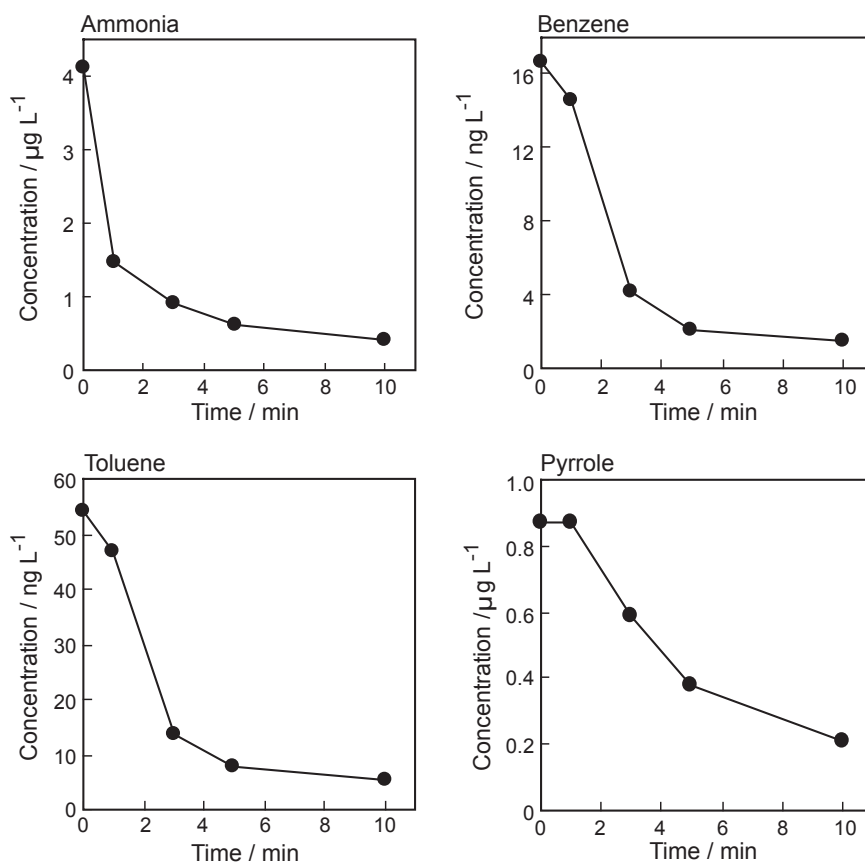

Figure 4　Time variation profile of the concentration of smoking-related VOCs adsorbed on acetate fabric.

3.3. Determination of tobacco-related VOCs in smokers' breath

A large number of tobacco-related VOCs are included in the smokers' breath [19], and these compounds could be one of the origins of third-hand smoking. Figure 5 shows a typical chromatogram of a smoker's breath sample. The breath sample was collected at just after the final puff. The peaks of acetone, benzene and toluene were also detected in nonsmoker's breath samples; however, these concentrations were clearly higher in the smoker's breath. Additionally, many VOCs were only detected in the smokers' breath; especially, 2,5-DMF has been recognized as a tobacco smoke biomarker in the smoker's breath [19,20], and actually detected only in the smokers' breath in this work. For all of the smokers' breath samples, the level of ammonia was below the LOD of the commercially-available detection tube.
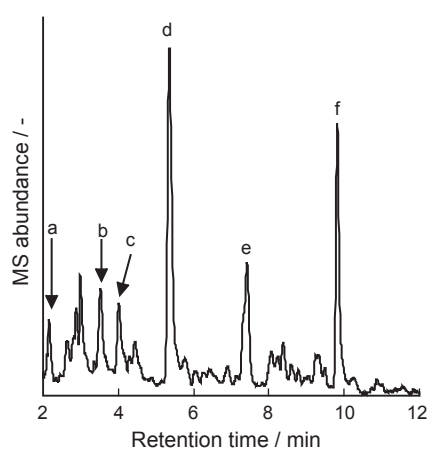

Figure 5 Typical chromatogram of the tobacco-related VOCs in smoker's breath. Peaks: (a) acetone; (b) benzene; (c) 2,5-DMF; (d) toluene; (e) o, m-xylene; and (f) limonene.

The time variations of the tobacco-related VOCs level in smoker's breath are illustrated in Fig. 6, where the concentrations of these VOCs are plotted against the elapsed time from the final puff of the cigarette. It was confirmed that tobacco-related VOCs were continuously expired from the smoker's breath for about 10 min, although the concentrations of these VOCs were significantly higher over the first 5 min.

Using a model case, the effect of the smoker's breath on the third-hand smoking pollution was evaluated. The amount of the expired benzene from the smoker's breath was calculated as 280 ng by the sum of the expired benzene during a period of 10 min, from 0．25 to 10．25 min after smoking, where the typical tidal volume and respiratory rate of healthy adults of 500 mL and 15 times/min, respectively, were used. If a smoker enters into a typical non-smoking room of 22.5 m^3, 3 m x 3 m x 2.5 m, after smoking outside or in a smoking-room, the concentration of benzene could be estimated as 0.012 ng/L in the in-room environment. The above results suggest that any significant contribution of the smokers' breath to the concentrations of smoking-related VOCs in the room was not confirmed by this model. However, tobacco-related VOCs were initially exhausted from the smokers' breath at a relatively high level, and a potential health hazard from the third-hand smoking hazard could be suspected if contact with a smoker immediately after
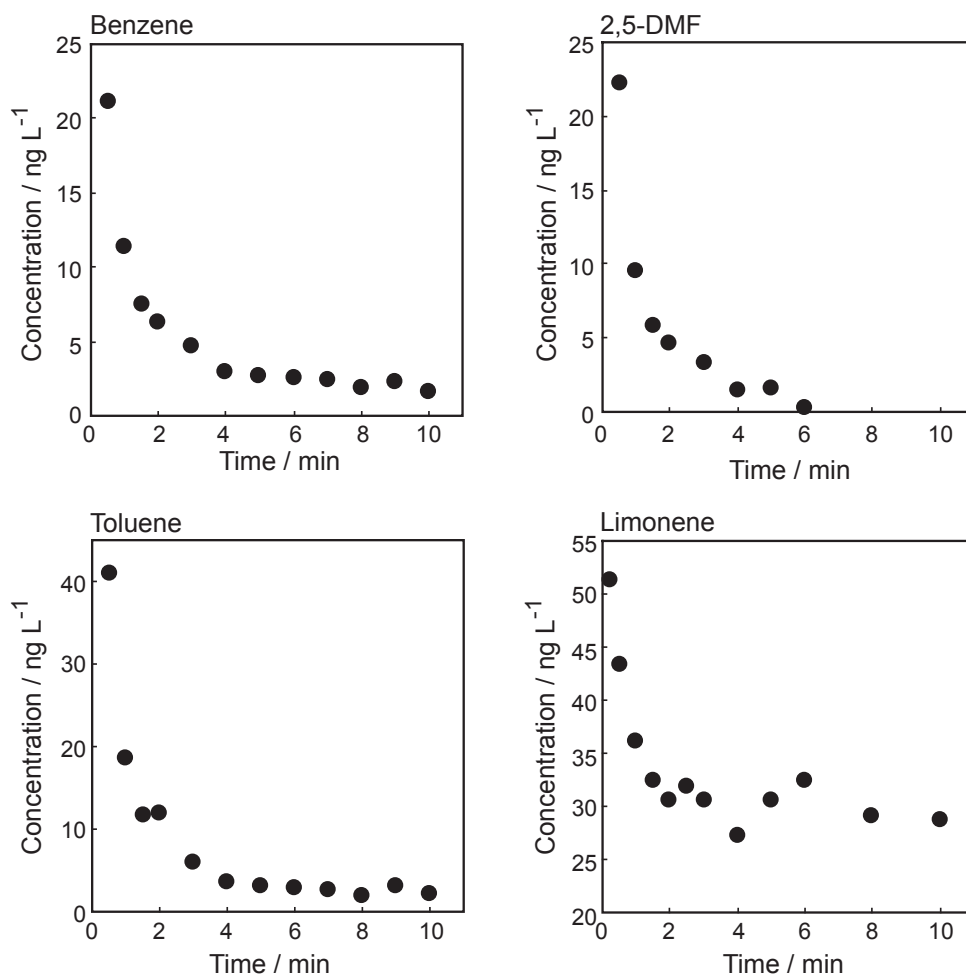
Figure 6 Time variation profiles of the concentration of tobacco-related VOCs in smoker's breath.

his/her smoking. The total amount of the smoking-related VOCs exhausted form a smoker was clearly lower than that in a typical mainstream smoke, suggesting that most of the VOCs in the mainstream smoke were absorbed into the body from the lungs, and only a part of these VOCs were expired as breath.

3.4. Third-hand smoking in the automobile

As described previously, the extraction needle showed a good reproducibility and storage performance for typical VOCs [9], and these features indicated the suitability of the extraction needle to real outdoor sample analysis. The applicability of the present method to actual third-hand smoking evaluation was carried out based on the determination of smoking-related VOCs in a compact automobile having an interior volume of 3.3 m^3. After measurements of the VOCs concentrations, two cigarettes were burned in a car for a period of 9 min, while all the windows and doors were closed. After combustion, these cigarettes were removed from the car and second-hand smoke was maintained for 5 min in the car. Then, all of the doors were opened for 1 min to remove the second-hand smoke from the car completely. Upon completion of air
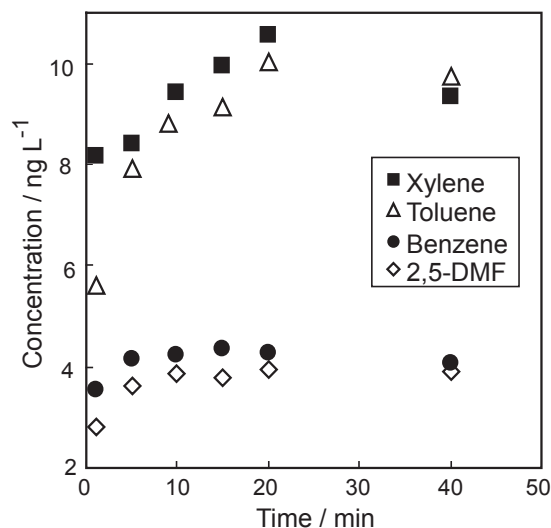
Figure 7 Determination of actual third-hand smoking pollution in a car. The concentration of xylene was determined as m-xylene.

ventilation, all of the doors were closed again, allowing the smoking-related VOCs adsorbed on the indoor surface to re-emit into the air, although a part of the adsorbed VOCs could already be desorbed during the ventilation process. The time variations of these VOCs were monitored using the extraction needle as the sample preparation device. As can be found in Fig. 7, the concentrations of tobacco-related VOCs were gradually increased after closing the doors, suggesting a slow desorption of tobacco-related VOCs from the car interior surface. In this model study, the compounds having a relatively higher volatility, such as benzene and 2,5-DMF, showed an equilibrium concentration within 10 min; however, compounds with a lower volatility, such as toluene and xylenes, needed about 20 min to reach the plateau. Although a more comprehensive study should be scheduled to precisely evaluate the real risk of third-hand smoking, the above results demonstrated a successful application of the extraction needle as a sampling/preconcentration device for the analysis of smoking-related VOCs in air samples, and also suggest the future possibility of the needle device for the trace determinations of other classes of VOCs.

4. Conclusions

Several VOCs potentially related to a third-hand smoking hazard were successfully extracted and determined with a polymer-packed extraction needle. The concentration monitoring of the time variations for these smoking-related VOCs could allow for a more systematic evaluation of any unpleasant odor and the suspected health hazard.

The present method [21] can also be applied to the determination of trace amounts of other VOCs in environment air samples because of their simple and rapid extraction/desorption procedure, along with an excellent repeatability and storage performance.

5. References

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