Development of Novel Analytical Techniques for Evaluating In-room Air Environment

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Mitsuru Inoue

Toyohashi University of Technology

Summary

Precise determination of volatile organic compounds (VOCs) in in-room air has been increasingly focused in recent years due to the requirement of more accurate and systematic analysis of in-room environment. As the analytical tool of VOCs in air samples, gas chromatography (GC) is one of the most promising methods because of the excellent separation selectivity and the availability as commercial instruments, and gas chromatography-mass spectrometry (GC-MS) has been realized as a powerful tool for a sensitive determination of typical VOCs in air samples. However, the concentration of VOCs in air samples is relatively low in most cases, and the direct determination of these compounds is still quite challenging. In this thesis, novel analytical techniques for the analysis of in-room air environment are described including the development of extraction medium and separation medium. Applications of the developed techniques to the real in-room environmental analysis are also described.

In Chapter 1, general introduction of this thesis including the aims and scope of the study is described along with the background of this work.

In Chapter 2, novel packed-capillary columns for gas chromatography were developed with a thin-wall stainless steel capillary having typical internal diameter of 1.0 mm. After a fundamental evaluation of the compatibility of these packed capillary columns with typical temperature-programmed

separations, rapid temperature-programmed separations were also conducted on the basis of mathematical analysis of the retentions in the preliminary temperature-programmed runs. The results suggest that the new packed capillary columns provide a good separation performance comparable with that of the conventional particle-packed columns. The performance of rapid temperature-programmed operations with the developed packed-capillary columns could be quite satisfactory for almost all separations currently performed in typical analytical laboratories.

For a systematic evaluation of indoor air environments in school facilities, a rapid on-site air-sampling technique was developed with a miniaturized needle-type sample preparation device in Chapter 3. The in-needle extraction device was prepared with particles of activated carbon and divinylbenzene polymer, and various types of volatile organic compounds (VOCs) were successfully extracted with the developed needle extraction device. The results clearly showed that the levels of VOCs in most rooms sampled in school facilities could be successfully determined, allowing a systematic analysis of in-room air environment in schools. The developed needle device can be widely applied to indoor air analysis in other types of facilities such as rooms in hospitals and hotels.

In order to evaluate the adsorption performance for typical organic pollutants, a novel cross-linked chitosan phase was synthesized and the

interaction between the chitosan phase and aromatic compounds was studied in Chapter 4. The chitosan phase was prepared with a novel cross-linking reagent having both aliphatic and aromatic functionalities, and employed as the stationary phase in liquid chromatography. As the model sample probes, a group of polycyclic aromatic hydrocarbons was introduced, and the retention behavior was compared with that obtained from several commercially available stationary phases including monomeric and polymeric octadecylsilicas (ODSs). The results clearly demonstrate a potential applicability of the newly synthesized chitosan phase as the stationary phase in chromatographic methods and as novel wall paint or wallpaper materials for reducing VOCs in indoor air environments.

Introducing a novel polyimide material as the extraction medium of the miniaturized sample preparation device for air samples, the preconcentration of VOCs was simultaneously carried out at the time of the sampling as described in Chapter 5. Spherical polyimide particles having a typical diameter of 5 μm were packed into a microscale sample preparation tube, and used for the sample preparation of typical VOCs existed in-room environment. Taking advantage of a good stability of the polyimide material to organic solvent, the developed polyimide-packed tube showed a good performance as the sample preparation medium with an effective and quick desorption by a typical organic solvent.

Finally, the overall conclusion of this thesis is summarized in Chapter 6.

Contents

Chapter 1

General Introduction

1.1 **General Introduction**

As a powerful and convenient separation technique for volatile organic compounds (VOCs), gas chromatography has been employed in various research fields. In the past decades, many types of stationary phases have been developed and commercialized along with numerous number of applications [1-3]. Among these, open-tubular capillary columns have been successfully employed, especially for high-resolution and rapid analyses. On the other hand, owing to their unique selectivity as a GC stationary phase, conventional packed-type columns are still employed for routine separations of specific classes of compounds that cannot be easily achieved with the typical liquid stationary phase of conventional open-tubular columns. However, those conventional particle-packed columns attain only a limited column efficiency compared with that theoretically possible with open-tubular columns. Furthermore, the conventional packed columns are normally not perfectly compatible with rapid temperature-programmed rates as typically employed for modern open-tubular columns.

Introducing polymer-coated fine fibrous materials as the stationary phase in GC, a significant miniaturization of the column has been achieved [4-7]. This is quite similar to the development of microscale sample preparation devices in which filaments are packed into a short polymeric tubing, such as polyetheretherketone (PEEK) or polytetrafluoroethylene (PTFE), to prepare

capillary-based extraction cartridges [8-10]. Packing a short capillary with a bundle of filaments coated with a polymeric material enables a parallel alignment of the filaments, and the resulting polymer-coated fiber-packed columns show satisfactory GC separation performance with fast temperature-programmed rates [11,12]. Miniaturization of the packed column also enables a successful use of the resulting miniaturized fiber-packed columns in modern capillary GC systems without any special modification to the GC instruments already employed world-wide. However, the compatibility of the packed column with temperature-programmed operations should be still considered more. Although many studies have reported theoretical predictions of retention in GC, only a few publications have comprehensively compared the compatibility of packed columns having different internal diameters with rapid temperature programming in modern GC systems.

In chapter 1, novel packed capillary columns were developed from a thin-wall capillary of stainless steel. Using a numerical integration process, the compatibility of these columns with fast temperature-programmed separations was investigated on the basis of theoretical predictions of the retention of model analytes. In order to confirm the compatibility between the developed packed capillary columns and the temperature program, observed retention data for a standard analytes at different temperature-programmed ramps were

systematically compared with corresponding theoretical retention values predicted from a set of retention data obtained at each column temperature in the corresponding preliminary experiments.

In Chapter 2, a double-bed sorbent consisting of divinylbenzene (DVB) and activated carbon (AC) particles was introduced as the extraction medium in the needle device for analysis of indoor air in school facilities. On the basis of recent studies, human health is now known to be adversely affected by indoor air pollution, such as sick building syndrome (SBS) and multiple chemical sensitivity. Especially, children are quite sensitive to toxic chemical compounds, and therefore, precise determinations of the presence of VOCs in educational facilities could be regarded as one of the important research objectives in the area of in-room air analysis.

In 2002, the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan established guidelines for concentrations of formaldehyde and other VOCs including toluene, xylene, and p-dichlorobenzene in air environments of school facilities. The MEXT guidelines are based on reference values by the Ministry of Health, Labour and Welfare (MHLW) of Japan [13,14]. The regulatory limits for ethylbenzene and styrene were added

to the guidelines in 2004. To avoid exposure to excessive amounts of these VOCs, not only the detection of these regulated compounds but also the sensitive determinations of other VOCs might be necessary[15,16]. For accurate and precise determinations of these VOCs, a sample preconcentration process should be performed before the analysis. Especially, VOC concentrations in school facilities could be at quite low levels [17,18], and therefore, an effective sample preparation process and subsequent separation/determination methods are required for a systematic analysis of the in-room environment. Introducing a needle-type sample preparation device, the analysis of in-room air environment in school facilities was carried out, With the needle extraction device, concentrations of VOCs in rooms of extensively renovated and newly built primary schools were successfully measured. In addition, temporal profiles of typical VOCs found in these school facilities were monitored.

Development of novel extraction/separation materials designed for air sample analysis was studied in Chapters 4 and 5. With a cross-linked chitosan phase, novel separation medium in liquid phase separation was developed in Chapter 4. Chitosan is synthesized by the deacetylation of acetylamino

functional groups in chitin, a natural polymer occurring in the cell walls of crustaceans such as crab and shrimp. On the basis of their characteristic chemical structure and unique characteristics, such as biocompatibility and biodegradability, many studies have investigated the chemical modifications of chitosan molecules and subsequent applications such as an adsorbent for metal ions [19-23] and dyes [24] and as a stationary phase in LC [25-27]. However, most reported chemical modifications were conducted by chemical derivatization of amino groups in the chitosan molecule.

Introducing a crosslinking reaction, the stability of the resulting chitosan materials can be dramatically improved without losing the adsorption power for metal ions [28-31] and dyes [32-36]. Results also suggest possible applications of cross-linked chitosan as a novel stationary phase in LC. On the basis of previous publications [37-39], novel cross-linked chitosan material was synthesized with a cross-linking reagent having aromatic and aliphatic functionality, and the resulting cross-linked chitosan material was evaluated as a LC stationary phase in Chapter 4.

Spherical polyimide particles was also introduced as a novel sample preparation medium in Chapter 5, where a miniaturized extraction tube was

prepared for the sampling and preconcentration of typical VOCs in in-room air samples. The polyimide particles was prepared with pyromellitic dianhydride (PMDA) and 4,4'-diamino diphenyl ether (ODA) as the starting materials, and the resulting spherical polyimide particles were evaluated as an extraction medium for the sample preparation of typical gaseous VOCs followed by the analysis in capillary GC.

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Chapter 2

Rapid Temperature-Programmed Separation and Retention Prediction on a Novel Packed-Capillary Column in Gas Chromatography

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Modified from *Analytical Sciences*, **26**, 687-691 (2010).

2.1 **Abstract**

Novel metal packed-capillary columns for gas chromatography (GC) were developed with a thin-wall stainless-steel capillary of 1.0 mm i.d.; and rapid temperature-programmed separations have been carried out after a fundamental evaluation concerning the compatibility of these columns to the temperature programmed operation. With a numerical integration method, the retention of several test analytes during temperature-programmed elution was successfully estimated. To confirm the suitability of the packed-capillary columns to relatively fast temperature programming operation up to 40ºC/min, the theoretically predicted retention data with the numerical integration method were compared with that actually measured. The results suggested a good separation performance of the newly developed packed-capillary columns as a particle-packed column conventionally used today. In addition, the compatibility to a rapid temperature-programmed operation was quite satisfactory for almost all of the separations currently carried out in typical analytical laboratories.

2.2 **Introduction**

As one of the most powerful and convenient separation techniques for wide variety of volatile organic compounds (VOCs), gas chromatography (GC) has been used in various research fields of science, and many types of stationary phases have been developed and commercialized in the past several decades along with a large number of applications [1–3]. In these columns developed, open-tubular capillary columns have been successfully introduced especially for high-resolution analysis, although conventional packed columns are still used for a certain types of routine separations of some types of compounds due to a unique selectivity that could not be easily obtained with the typical liquid stationary phase of conventional open-tubular columns. In contrast to the unique selectivity of the conventional particle-packed columns, however, only a limited number of column efficiency could be obtained, as expected from a theoretical comparison with open-tubular columns, and also from a difficultly in using a rapid temperature-programming rate.

Introducing polymer-coated fine fibrous materials as a stationary phase in GC, a significant downsizing of the column was reported [4–7], as similar to the development of miniaturized sample preparation devices. The filaments were packed into a short polymeric tubing, such as polyetheretherketone (PEEK) or polytetrafluoroethylene (PTFE) to prepare

capillary-based extraction cartridges [8–10]. Packed with a bundle of filaments having a polymeric coating material thereon, a parallel alignment of these filaments was established in a short capillary. The resulting polymer-coated fiber-packed columns offered a satisfactory separation performance with a relatively quick temperature-programming rate in GC [11,12]. It has been demonstrated that the use of a narrower capillary allows these columns to be operated at a fast temperature-programming rate, as compared with conventional particle-packed columns.

Miniaturization of the packed column also enables the employment of the resulting downsized packed column in a modern capillary GC instrument without any special modification to the system, although the compatibility of the packed column to the temperature-programmed operation should be considered as typically reported in several publications dealing with the theoretical prediction of the retention time for the separation with temperature programming [13–21]. In contrast to a large number of papers for a theoretical prediction of the retention in GC, a comprehensive comparison of the compatibility of packed columns having different internal diameters to a rapid temperature program in a modern GC instrument had been somewhat limited [21–23].

In this chapter, novel packed-capillary columns have been developed with a short thin-wall capillary of stainless-steel, and the compatibility to a fast

temperature-programmed separation was studied on the basis of a theoretical prediction of the retention of the analytes by a numerical-integration method. In order to confirm the compatibility of the developed packed-capillary columns to the temperature-programmed operation, the observed retention data of a standard analytes at different temperature-programming rates were compared with the corresponding theoretically predicted value on the basis of a set of retention data at each column temperature.

2.3 Experimental

Materials

All of the chemical reagents and solvents were of analytical reagent grade, and obtained from either Kishida Chemical (Osaka, Japan), Tokyo Kasei Industries (Tokyo, Japan) or Wako Pure Chemical (Osaka, Japan). All of the gas samples were purchased from GL Sciences (Tokyo, Japan) as a small desktop gas cylinder. To prepare gaseous sample mixtures from corresponding liquid analytes, either a Tedlar Bag (GL Sciences) or an aluminum bag (GL Sciences) was used along with a glass gas vessel of 1.0 L internal volume (GL Sciences) for preparing initial standard gas samples, as described previously [24–26]. To the inlet of the gas sampling bags, a section polymeric tube, TYGON tube (Saint-Gobain, Tokyo, Japan), of 5 mm i.d., 7 mm o.d., and 30 mm length, was attached, where the other end of the tube was capped with a silicon septum, and a syringe needle was inserted into the gas sampling bag through the silicon septum. All of the sampling bags were cleaned at least five times by pure N_2 before use, and the successful completion of the complete cleaning process was well confirmed in preliminary experiments. Glass gastight syringes, micro-syringes and other miscellaneous items were all commercially available and purchased from a corresponding local distributor.

GC measurements

All GC measurements were made with a Shimadzu GC-2014 gas chromatograph (Kyoto, Japan). As the detector, either a thermal conductivity detector (TCD) or a flame ionization detector (FID) was employed, depending on the target compounds. For capillary column separation, a split/splitless injection port was used, while a conventional glass-packed column of 3.2 mm i.d. and a stainless-steel-packed column of 3.0 mm i.d. was installed to the corresponding injector designed for conventional packed column connection. As the carrier gas, either N_2 or He was used depending on the detector employed, and the carrier gas and air were supplied from the respective gas cylinders through the cartridge packed with a molecular sieve.

Packed-capillary columns were prepared in a conventional method, as described previously [11] except for the use of a stainless-steel capillary of 1.0 mm i.d., 1.27 mm o.d., 1.0 m length and a packing material having a relatively smaller particle diameter, as described below. With a careful packing, the resulting column efficiency per unit length was almost the same as that of the typical conventional particle-packed columns. A pair of stainless-steel capillaries of 0.3 mm i.d., 0.52 mm o.d., 0.5 m length were attached to the inlet and outlet of the packed-capillary column, thus allowing easy installation of the packed-capillary column to a conventional GC injection port designed for conventional capillary column connection.

For preparing the packing material, a Shimalite W, white diatomaceous earth, acid washed and subsequent dimethylchlorosilane (DMCS) treated (Shinwa Chemical Industries), was introduced as a support material. The spherical porous particles of between 100 and 80 mesh size, corresponding to about 150 and 180 μm in diameter, respectively, were sieved, and the specific surface area (SSA) of the material was about 0.7 m^2/g. Among various types of liquid phases for packed columns, one of the most popular liquid phases, Silicone SE-30, was employed as the liquid phase. For the coating onto the support material, a hexane solution of SE-30 was used, where the weight of the SE-30 was set at 5%-weight of the support material. The resulting packing material was packed into the stainless-steel capillary described above. The same packing material was packed into both a conventional glass column of 3.2 mm i.d. × 1.1 m (Shinwa Chemical Industries) and a conventional stainless-steel column of 3.0 mm i.d. × 1.0 m (Shinwa Chemical Industries) for a comparison. These columns were treated with an appropriate preconditioning typically at 300ºC for 60 h before use, and no significant bleeding was found in the temperature range up to 300ºC after the above preconditioning procedure.

For typical separation, injection and detection temperatures were set at 300ºC unless otherwise specified. The other separation conditions, such as the carrier-gas flowrate, column head pressure, and temperature programs

were determined on the basis of preliminary experiments for each sample. The sample loading capacity of the developed packed-capillary column was quite comparable to that expected from the conventional packed capillary having a larger internal diameter. All GC measurements were conducted at least five times, and the relative standard deviations (RSDs) for the retention times were less than 1.0%. The data collection was made with ChromNAV data handling/analysis software (Jasco, Tokyo, Japan) running on a personal computer, while the calculation for retention prediction was carried out with a laboratory-made retention prediction program using an integration equation described below.

2.4 Results and Discussion

Retention prediction

Before a mathematical calculation for the retention prediction, the retention data of several test analytes were systematically measured at different column temperatures in the range between 50 and 200ºC. In this measurement, methane was employed as the dead-time marker. A good linear relationship was clearly confirmed in the resulting van't Hoff plots, where the logarithmic retention factor (*ln k*) was plotted against the reciprocal absolute column temperature with a correlation coefficient of more than 0.995.

The retention factor of the analyte at a constant column temperature could be estimated from the linear plot, allowing for an estimation of the distance traveled by the analyte per unit time. Therefore, the infinitesimal distance traveled by the analyte along the column during "a minute time period" in a temperature-programmed elution could be calculated based on an assumption that the column temperature is constant during a short moment. Integrating the above infinitesimal distance to reach the total column length over the time interval from the injection to the elution time with the Eq. (1), where the column length is normalized to be unity, it can be obtained that the elution time with a particular temperature-programmed run similar to that reported previously [27–29]:

$$\int_0^{t_R} \frac{dt}{t_0\left\{1 + k_1 e^{\frac{k_2}{T_0 + k_3 t}}\right\}} = 1 . \qquad (1)$$

In Eq. (1), t_R is the elution time of the target analyte as a function of the absolute column temperature, t_0 is the elution time of the unretained analyte as a function of the absolute column temperature, T_0 is the initial column temperature, and $k_1 = e^{\frac{\Delta S}{R} + \ln \Phi} = \Phi e^{\frac{\Delta S}{R}}$ is the entropic term, $k_2 = -\frac{\Delta H}{R}$ is the enthalpic term, k_3 is the temperature-programming rate, where Φ is the phase ratio.

From the van't Hoff plot, where *ln k* is plotted against 1/T, –ΔH/R and Φexp(ΔS/R) could be obtained as the slope and the intercept, respectively. In this work, a Gaussian integration (number of data points: 5), shown by Eq. (1), was employed to calculate the retention time, because a more accurate retention prediction could be obtained when compared to other numerical integrations, such as the trapezoidal method or the Simpson method.

Figure 2-1 shows the estimated retention time based on the above calculation at various temperature-program rates, where the retention data actually measured are also plotted in the figure for a comparison. For the packed-capillary column developed in this work, the

temperature-programmed elution was investigated at a rate from 10 to 40ºC/min with octane as the sample analyte. A good compatibility of the packed-capillary column to a relatively rapid temperature-programming rate could be confirmed. In order to compare the compatibility to a quick temperature program, conventional glass and stainless-steel columns packed with the same stationary phase were also studied in the same conditions. For this comparison, the relative delay (RD, %) of the observed retention time from the estimated value, as defined as Eq. (2), is introduced in Figure 2-2 as:

$$\mathrm{RD}(\%) = \frac{(\text{measured retention time}) - (\text{estimated retention time})}{(\text{estimated retention time})} \times 100. \qquad (2)$$

Compared to the conventional glass and stainless-steel columns having a larger internal diameter and a thick tube wall, the developed packed-capillary column shows a significantly short delay from the expected retention time, especially at a fast temperature-programming rate, such as 40ºC/min, clearly indicating an excellent compatibility of the packed-capillary column to the fast temperature program.

As can be expected, conventional columns made of both glass and stainless-steel showed a significant delay from the temperature program with

increasing the program rate, and a larger delay was also observed at a higher linear velocity of the carrier gas. Taking into account other miscellaneous parameters that could also affect the variance of the retention time, such as the linear velocity of the carrier gas, the observed delay of the retention time on the packed-capillary column, less than 4.6%, can be quite acceptable as a GC column. The result can clearly suggest a good performance of the developed packed-capillary column to the temperature-programmed separation of complex mixtures, especially when using a rapid temperature programming rate.

Compatibility of packed-capillary columns to rapid temperature-programmed elution

On the basis of successful confirmation of the compatibility of the packed-capillary column to temperature-programmed elution, an alkane mixture was separated with a different temperature program. Typical chromatograms for the separation of a mixture containing nine alkanes from decane to octadecane are illustrated in Figure 2-3, where all of the conditions except for the temperature-programming rate are the same in these chromatograms. A similar rapid separation of seven alkylbenzenes, containing from butylbenzene to decylbenzene, was also confirmed in Figure 2-4. These results demonstrate that rapid temperature-programmed

separations at 40ºC/min could be possible with the developed packed-capillary column, where a satisfactory separation performance is maintained with a short analysis time without significantly reducing the sample loading capacity as a packed column.

To confirm the advantageous feature of a packed-capillary column for rapid separation with rapid temperature-programming rates, another stationary phase was introduced. After a set of the same preliminary experiments and a subsequent retention prediction procedure as the SE-30 phase described earlier, applications to the rapid temperature-programmed separation were studied on another capillary column packed with a Shincarbon ST (Shinwa Chemical Industries). Before the column preparation, spherical particles of between 100 and 80 mesh, corresponding to about 150 and 180 μm in diameter, respectively, were sieved.

Introducing a rapid temperature program to the packed-capillary column, as shown in Figure 2-5A, a complete separation of oxygen, nitrogen, carbon monoxide and carbon dioxide was obtained along with the simultaneous separation of methane, ethylene and ethane, where the detection was conducted with the TCD set at 350ºC. Figure 2-5B illustrates typical separation of several VOCs on the developed packed-capillary column at a high temperature-programming rate, clearly suggesting the bright future possibility of this stationary phase to the applications in gas and

petrochemical industries along with other research fields, such as environmental analysis and biological gas analysis.

2.5 Conclusions

Further discussions should be needed to reach the final conclusion of an acceptable delay from the temperature program on a packed GC column having a well-characteristic selectivity over a conventional open-tubular capillary column. However, the packed-capillary columns developed in this work demonstrate an excellent compatibility to rapid temperature-programmed elution as a packed column. The advantageous features of the packed-capillary column, such as a unique selectivity and a good sample loading capacity, could make itself to be an attractive novel separation medium for the high-throughput analysis of various complex mixtures consisting of many components.

The developed packed-capillary columns in this work can be installed to a conventional capillary GC system without any modifications and adapters, allowing for an easy introduction of the packed-capillary columns to most of the modern GC system widely employed with an open-tubular capillary column. A more comprehensive study for a precise interpretation of the effect of rapid temperature programming on the separation, including the temperature ununiformity in the packed column and resulting peak shape [30], should be scheduled.

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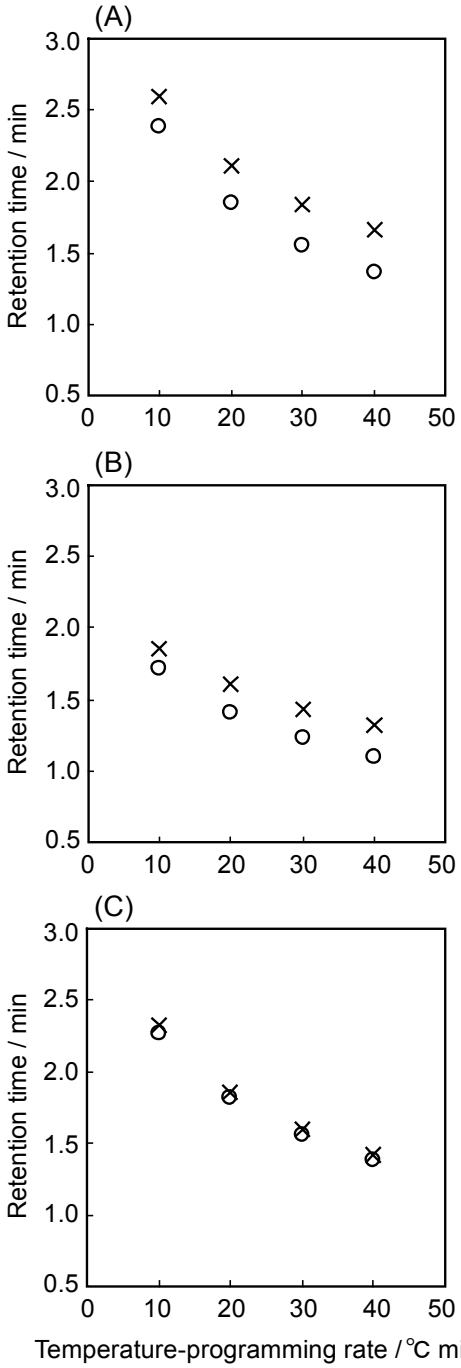

Figure 2-1 Comparison of the measured (cross) retention data with that estimated (open circle) for three types of packed columns using temperature-programmed analyses at different ramp rates.
Column: (A) glass column of 3.2 mm i.d. x 1.1 m, (B) stainless-steel column of 3.0 mm i.d. x 1.0 m, (C) packed-capillary column of 1.0 mm i.d. x 1.0 m. Conditions: initial column temperature, 75°C; carrier gas liner velocity, 7.5 cm/s. Other conditions are in the text.

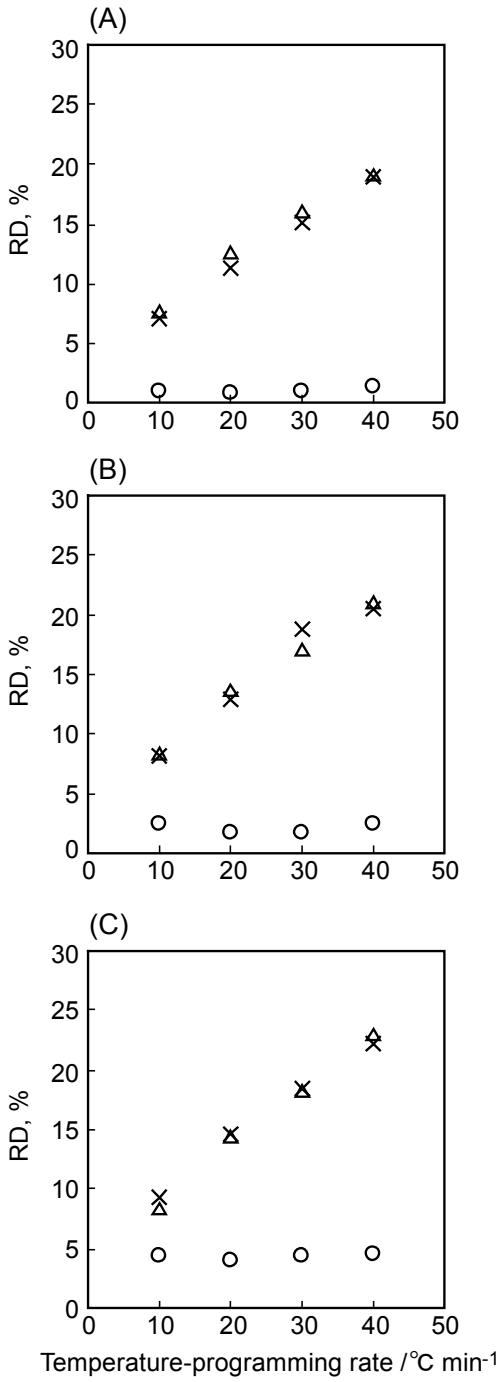

Figure 2-2 Relative delay of the actual retention time from that estimated for various separation conditions.

Carrier gas liner velocity: (A) 5.0, (B) 7.5, (C) 10.0 cm/s. Column: glass column of 3.2 mm i.d. x 1.1 m (cross), stainless-steel column of 3.0 mm i.d. x 1.0 m (triangle) and packed-capillary column of 1.0 mm i.d. x 1.0 m (open circle). Other conditions are the same as in Figure. 2-1.

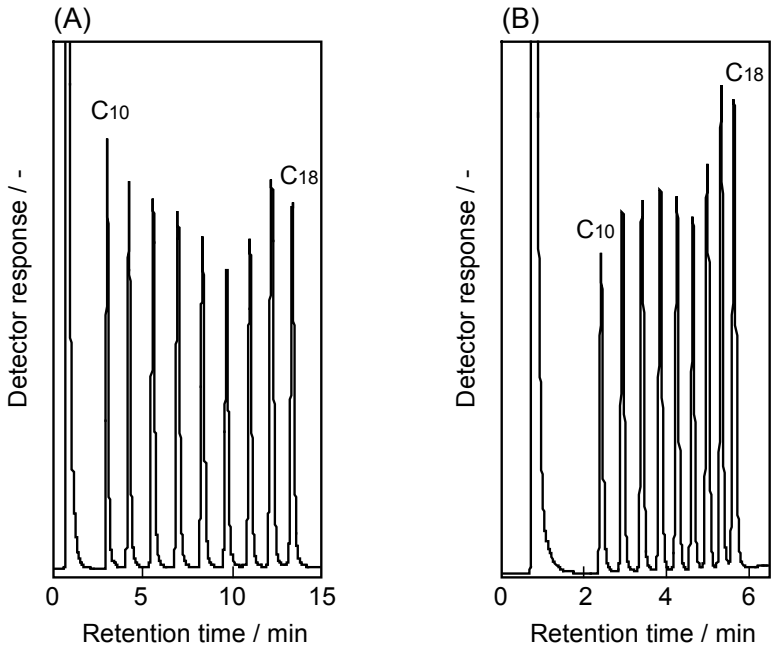

Figure 2-3 Chromatograms for the separation of alkanes on the developed packed-capillary column at different temperature programs.
Temperature program: (A) 100°C (1 min) to 240°C at a rate of 10°C/min; (B) 100 °C (1 min) to 300°C at a rate of 40°C/min. Detector, FID at 300°C; column head pressure, 70 kPa; injection, splitless injection of 1.0 L; sample, alkane mixture containing 1.0% each of nine alkanes from decane to octadecane in hexane as the solvent.

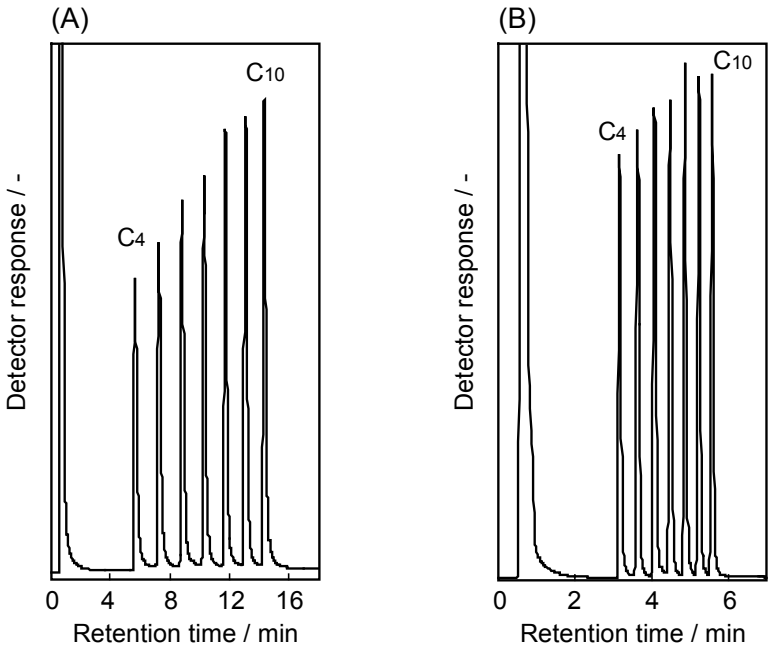

Figure 2-4 Typical chromatograms for the separation of seven alkylbenzenes from butylbenzene (C4) to decylbenzene (C10) on the packed-capillary column.

Temperature program: (A) 50°C (1 min) to 210°C at a rate of 10°C/min; (B) 40°C (1 min) to 260°C at a rate of 40°C/min. Column head pressure, 150 kPa; injection, splitless injection of 1.0 L; sample, alkylbenzene mixture containing 1.0% each of seven alkylbenzenes in hexane as the solvent.

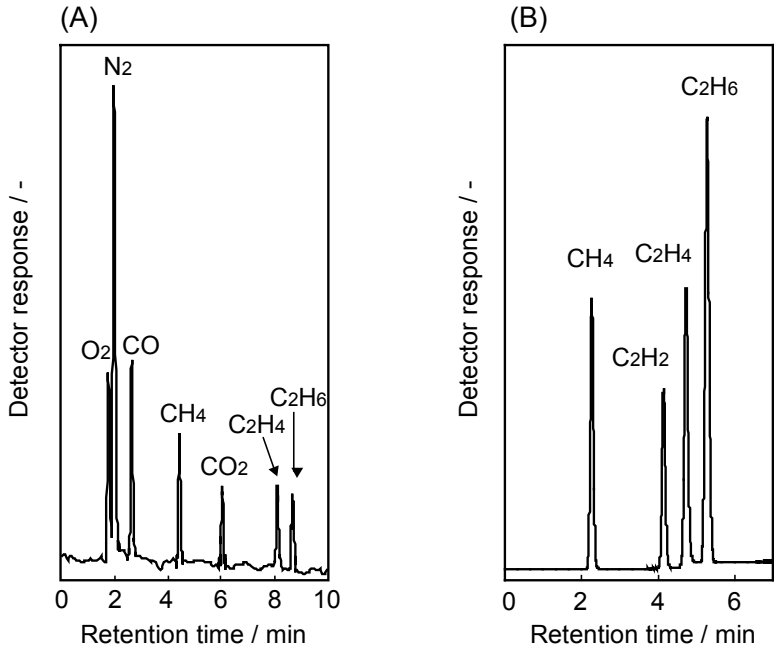

Figure 2-5 Rapid temperature-programmed separations on the packed-capillary column. Stationary phase, Shincarbon ST; column size, 1.0 mm i.d. x 2.0 m length.

Temperature program: (A) 20°C (2 min) to 300°C at a rate of 40°C/min; (B) 130°C to 350°C at a rate of 40°C/min. Detector, (A) TCD at 310°C and (B) FID at 350°C; carrier gas, (A) He and (B) N_2; column head pressure, 150 kPa; injection, splitless injection (150 L) of standard gas samples. All other conditions are given in the text.

Chapter 3

Rapid On-site Air Sampling with a Needle Extraction Device for Evaluating the Indoor Air Environment in School Facilities

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Modified from *Analytical Sciences*, **29**, 519-525 (2013).

3.1 Abstract

A rapid on-site air sampling/preconcentration technique was developed with a miniaturized needle-type sample preparation device for a systematic analysis of the indoor air environments in school facilities. Introducing the in-needle extraction device packed with a polymer particle of divinylbenzene (DVB) and activated carbon (AC) particles, various types of volatile organic compounds (VOCs) were successfully extracted.

For evaluating the indoor air environments in school facilities, air samples in renovated rooms using organic solvent as a thinner of the paint were analyzed along with measurements of several VOCs in indoor air samples taken in newly built primary schools mainly using low-VOCs materials. After periodical renovation and/or maintenance, the time-variation profile of typical VOCs found in the school facilities has also been systematically monitored.

From the results, it could be observed that the VOCs in most of the rooms in these primary schools were at a quite low level, while a relatively higher concentration of VOCs was found in some specially-designed rooms, such as music rooms. In addition, some non-regulated volatile compounds, including benzyl alcohol and branched alkanes, were additionally detected in these primary schools. The results clearly showed a good applicability of the needle device to indoor air analysis in schools, suggesting a wide range of future applications of the needle device, especially for indoor air analysis in other types

of facilities and rooms including hospitals and hotels.

3.2 Introduction

Recently, indoor air pollution, such as sick building syndrome (SBS) and multiple chemical sensitivity, have been increasingly focused on its undesirable effect on human health [1–3]. Particularly, children are most sensitive to these toxic chemical compounds in indoor air, and therefore, precise determinations of volatile organic compounds (VOCs) in educational facilities could also be a quite important objective in environmental analysis. In 2002, the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan established an official guideline for the indoor concentration of formaldehyde and other VOCs, including toluene, xylene and *p*-dichlorobenzene, in school facilities, based on reference values by the Ministry of Health, Labour and Welfare (MHLW) of Japan [4,5]. The regulation value of ethyl benzene and styrene were additionally listed in the guideline in 2004. In order to avoid any exposure to excessive chemical compounds, not only the detection of these regulated compounds, but also a sensitive/precise determination of other VOCs might be needed.

Gas chromatography (GC) is one of the most promising modern analytical methods for the separation and determination of VOCs, and gas chromatography-mass spectrometry (GC-MS) has been realized as a more powerful tool for a sensitive determination of typical VOCs and semi-volatile organic compounds (SVOCs) in air samples [6,7]. In order to realize the

accurate and precise determinations of these VOCs, a sample preconcentration process should still be performed prior to the analysis. Especially, the VOCs concentration related to school facilities could be at a quite low level [8,9], and therefore, an effective sample preparation process and subsequent analytical methods are necessary. As the sample preparation of VOCs in air samples, the use of a classic extraction cartridge, containing silica-gel or charcoal particles, is still accepted, however, these conventional methods often require the use of a hazardous solvent or a special desorption device. A time-consuming analytical process with these conventional sample preparation techniques could be another disadvantage, especially when a large number of sampling points must be necessary for a systematic indoor air analysis.

During past several years, our research group has developed novel needle-type extraction devices, designed for the GC analysis of typical VOCs in various gaseous samples [10-13], including organic solvents often used in chemical laboratories [14], ethylene oxide [15], aldehydes and ketones [16] and smoking-related compounds [17,18], along with the applications to real on-site sampling, such as fire scene investigation [19] and breath analysis of diabetic patients [20]. These results clearly suggest a possibility of needle-type extraction to the indoor air analysis, although the extraction medium packed in the needle should be further optimized to the corresponding particular analysis.

In this chapter, double-bed-type sorbent consisting of divinylbenzene

(DVB) and activated carbon (AC) particles [21] has been introduced as the extraction medium in the needle device for the analysis of indoor air in school facilities. Introducing the needle extraction device, VOCs in rooms of extensively renovated and newly-built primary schools were successfully determined. In addition, the time-variation profiles of typical VOCs found in these school facilities were systematically monitored.

3.3 Experimental

Materials

Toluene, ethylbenzene, xylene, styrene and *p*-dichlorobenzene (*p*-DCB) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). The nitrogen gas (>99.99% purity) used for the desorption of the extracted analytes and for the preparation of standard gas samples was purified by passage through a gas filter packed with molecular sieves (0.5 nm) to remove any undesirable organic contaminations. Smart Bag PA gas sampling bags were obtained from GL Sciences (Tokyo, Japan). A formaldehyde gas detector tube was purchased from Komyo Rikagaku Kogyo (Tokyo, Japan).

Preparation of standard gas samples

Standard VOC samples having desired concentrations were prepared as follows. First, an appropriate amount of the analyte was injected into a 1.0 L-vacuum glass vessel and evaporated therein. Then, 1.0 L of pure N_2 gas was supplied to the glass vessel. Next, a few milliliters of the above-mentioned gas sample were injected into a gas sampling bag and diluted with pure N_2. As a result, a standard gas sample of a few hundreds of ng/L was prepared in the gas sampling bag. To prepare standard samples having lower concentrations, a similar dilution process was repeated once more.

Extraction and desorption procedure of VOCs

In this work, a double-bed-type of extraction medium consisting of a polymer particle of DVB (25 mm packed section) as the first sorbent and an AC particle of Shincarbon ST (5 mm packed section) as the second sorbent were employed [21]. In a previous study, this extraction needle showed successful extraction and desorption performances for typical VOCs in indoor air samples, where relatively low-volatile compounds were extracted on the DVB sorbent, and high-volatile compounds were extracted on the AC sorbent. Although these sorbents were not specially designed for the extraction of specific compounds based on such as molecular shape recognition, relatively less-volatile compounds could be well-trapped on the DVB, and highly volatile compounds could be successfully trapped on the AC [21]. These sorbents particles 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 with a tip hole.

For the sampling of indoor air samples, the extraction needle was attached to a commercially available vacuum sampling device (Komyo Rikagaku Kogyo, Tokyo, Japan), unless otherwise specified. Typical sampling volume was 50 mL, and it took about 3 min to complete the sampling with the vacuum sampling device. Additionally, at some of the sampling points, parallel sampling with a commercially available gas sampling pump (GSP-300FT-2, Gastec, Kanagawa, Japan) was also made, where a gaseous sample was introduced

into the extraction needle at a flow rate of 20 mL/min for 30 min. All indoor sampling was carried out as follows: first, the room air was well-ventilated for 30 min, where all of the windows and doors were opened; next, all of the windows and doors were closed for 5 h before air sampling. All air samples were collected at a height of 80 cm from the floor. Sampling was done for at least 5 points in all of the rooms. All the quantitative results shown in this study were the corresponding mean value of 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, without any heating time in the injector before injection. It has been confirmed in preliminary experiments that the pre-heating time causes insufficient desorption of the extracted analytes, because of a backflow of the thermally desorbed analytes from the DVB layer to AC layer [21]. The extracted samples could be stored in the needle at room temperature for at least three days. Formaldehyde was detected by a detector tube, where 1000 mL air samples were collected with a gas-sampling pump.

GC measurements

A JEOL JMS-Q1000GC Mk-II GC-MS instrument (JEOL, Tokyo, Japan) with a split/splitless injection port and a Shimadzu GC-2010 gas

chromatography-flame ionization detector (GC-FID) (Kyoto, Japan) were used, and all of the injections were made by a split mode with a ratio of 5:1. GC separation was performed on an HR-5 fused-silica capillary column of 30 m × 0.25 mm i.d. having a film thickness of 0.25 μm (J&W Scientific, Folsom, CA). As the carrier gas, He was employed at a typical head pressure of 50 kPa; and injector was typically maintained at 250°C. The GC-MS interface temperature and the ionization voltage were set at 250°C and 70 eV, respectively, with electron impact ionization. The FID temperature was set at 250°C. The column temperature was started at 40°C for 2.0 min, and then programmed to 140°C at a rate of 20°C/min for a GC-MS measurement, and started at 50°C (1.0 min hold time), and then programmed to 190°C at a rate of 20°C/min for a GC-FID measurement. The mass spectrometer was operated in a total ion monitoring mode (TIM) with a *m*/*z* range of 45 to 250.

3.4 Results and Discussion

Determination of VOCs using a needle-type extraction device

In our previous study, good extraction and desorption performances of DVB/AC-packed extraction needle were confirmed along with a satisfactory sample storage performance at room temperature [21], where the sampling volume was 600 mL at a flow rate of 20 mL/min using a sampling pump on the basis of the guideline stated by MHLW [5]. In this study, a sampling volume of 50 mL with a vacuum sampler was investigated using a DVB/AC-packed needle for rapid on-site air sampling.

The limit of quantifications (LOQs) of typical VOCs were less than 1 ng/L with a sampling volume of 50 mL. This result clearly indicates adequate sensitivities of the method, because of a satisfactory sensitivity for VOCs in school facilities, as tabulated in Table 3-1. In addition, there were no significant differences between these sample collection methods for the extraction performances, and the corresponding quantitative results in real indoor air samples. Therefore, the vacuum gas sampler was good enough to get satisfactory detectability for the VOCs in this work, however, to further improve the detectability, of course, the gas sampling pump could be introduced to increase the volume of the air sampling. The relative standard deviations (RSDs) of the peak areas were less than 5.0% (n = 5) for real indoor air samples.

Determination of VOCs in renovated rooms

After a systematic optimization of the experimental conditions, indoor air samples taken from three small meeting rooms (in school A) were analyzed. The rooms (26 m^2, 3.0 m height) were renovated by replacing with new ceiling boards, and also by painting all of the walls. Figure 3-1 shows typical chromatograms for the separation of VOCs in air samples collected three days after completing the renovation. In all three rooms, significantly high concentrations of branched alkanes having carbon numbers of 10 and 11 were detected, probably because of using an organic solvent-based thinner for the paint. At this stage, however, these compounds were not yet regulated in the guidelines stated by MEXT and MHLW. Due to security reasons, all of the windows and doors in rooms B and C could be only opened during the day time, approximately from 9 a.m. to 5 p.m., while those in room A had to remain closed at all times. As can be expected in advance, the level of VOCs in room A1 was significantly higher than those in rooms A2 and A3, although all of these chromatographic profiles are quite similar as found in Figure 3-1.

The time variations were monitored for up to 35 days after completing the renovation, as illustrated in Figure 3-2. The amount of one of the branched alkanes (appeared at 5.2 min in Figure 3-1) was plotted, where the amount was estimated as decane. It is clearly found from the plots that the ventilation was quite effective to reduce the amount of VOCs; however, at the same time, more

than several weeks should be necessary to reduce the level by about two orders of magnitudes, even with the ventilation normally carried out in this type of school facility renovation.

VOCs in school rooms after a large renovation

Indoor VOCs level after a large renovation in a primary school (school B) was investigated. All 16 rooms listed in Table 3-2 were renovated as three groups, where each renovation was finished in June, September and December 2011. During the period of these renovations, all of the ceiling boards, floor panel and wall paper were thoroughly replaced with new materials. As can be found in Table 3-2, the first sampling was made just 3 days after completing the second renovation work in September, 2011. At that time, about 3 months had passed from completion of the first renovation in June, 2011, and third renovation was still in progress at that time. The indoor air samples in third renovation area were collected 3 days after the completion of renovation in December, 2011. Because these three sections were located in different buildings, no effect of VOCs coming from other section was observed when monitoring outdoor air samples surrounding each building.

In Table 3-2, it is clearly found that the concentrations of all the regulated VOCs were lower than the corresponding reference values in all of the measured rooms in this school. The concentration of formaldehyde was less

than 61 ng/L (50 ppm), and *p*-dichlorobenzene was not detected in all of the rooms. In the music rooms, relatively higher concentrations of VOCs were detected, and some terpene compounds were also detected, as can be found in Figure 3-3A. This is probably because these compounds were evaporated from specially-designed soundproofing materials used for the walls and ceiling of the room. Relatively higher concentrations of VOCs were also observed in the art and craft room, as illustrated in Figure 3-3B. This could be associated with educational items, such as paints and adhesives. Some alkanes and alkyl benzenes were detected in a small gymnasium (Figure 3-3C). These compounds might be generated from floor wax. The concentrations of these compounds were measured at three different height levels, *i.e*. at 2, 80 and 180 cm from the floor; however, no significant difference was found in all of the rooms measured. In addition, a relatively higher concentration of benzyl alcohol was detected in most of rooms, especially in class rooms B1 to B3. The low concentrations of benzyl alcohol in class rooms B4 to B6 could be attributed to a lower temperature of the sampling rooms.

Time-variation profiles of the concentrations of the VOCs in class room B3 were plotted in Figure 3-4. As can be expected, all of the compounds decreased with the time, however, at the same time, it was confirmed that all of the concentrations of these VOCs reached a plateau, at about 2 months from completion of the repair, suggesting extensive air ventilation for at least several

weeks should be necessary to minimize the exposure to these VOCs.

Monitoring the Long-term concentration profile in newly-built school facility

Because of recent increasing attention to the SBS, the use of paint and other miscellaneous materials with less VOCs emission have become popular. A school facility (school C) was built of the above-mentioned low VOCs materials. Table 3 summarizes the quantitative results of the VOCs in this newly-built school facility, where the air samples were collected in March, 2012. At the time of the sampling, about 7 months had already passed from completion of the construction.

In this school facility, quite low concentrations of the regulated VOCs were observed, while *α*-pinene and *d*-limonene (data not shown) were detected because of the employment of wood materials in interior materials. In this school, the library and computer room are connected by wood stairs, and this is probably the reason for a high concentration of *α*-pinene in both rooms, as shown in Table 3-3. In addition, decane and some branched alkanes having a carbon number of about 10 were only detected in the gymnasium (data not shown), and the total concentration of decane and these branched alkane in the gymnasium is approximately 200 ng/L as decane. The source of these alkanes could also be attributed to the floor wax used in periodical maintenance in the gymnasium. Since all of the materials used in the renovation were carefully

chosen not to have a high emission of formaldehyde, as expected, the concentration of formaldehyde was less than 61 ng/L (corresponds to 50 ppm) in all the rooms.

Five months after the first sampling, air samples in this newly-built school facility were measured again (August 2012). Comparisons of the detected VOCs in March and August are shown in Table 3-4. Comparing the samples collected in March and August, the concentrations of most of the compounds were almost the same. However, the concentration of *α*-pinene was significantly increased in the library and computer room. In addition, a higher level of styrene in these rooms was also found in August, 2012. This is probably due to evaporation during high temperatures in the summer, although a clear identification of the source of styrene is not established at this stage.

3.5 Conclusions

A needle-type extraction device was successfully introduced to the GC-MS determination of VOCs in indoor air samples taken from school facilities. The results showed that the needle extraction technique could be one of the suitable sample collection/extraction techniques for indoor air analysis. The results also demonstrated that the VOCs levels in most of the schoolrooms were thoroughly low level, although a relatively higher concentration of VOCs may be found in some room specially-designed for education purposes, and some non-regulated VOCs may also be found in school facilities.

Taking advantage of the storage performance up to three days after the sampling at room temperature, multipoint sampling at several rooms could be easily carried out. The developed technique will be a powerful tool for more systematic assessment of indoor air analysis, especially in newly build facilities and houses.

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Table 3-1 Reference values of VOCs in a school facility by MEXT.

	Reference value (ng L^{-1})
Formaldehyde	100
Toluene	260
Ethylbenzene	3800
p-Dichlorobenzene	240
Xylene	870
Styrene	220

Table 3-2 Concentration of VOCs in indoor air in a renovated primary school.

Room	Concentration (ng L^{-1})				
	Toluene	Ethyl benzene	Xylene	Styrene	Benzyl alcohol
Broadcasting room [a]	37.4	75.5	28.8	191	7.6
Music room (B1) [a]	117	73.1	32.6	159	82.1
Music room (B2) [a]	125	45.2	22.8	65.2	87.6
Library [a]	62.2	< 1	< 1	60.9	< 1
Computer room [a]	< 1	< 1	< 1	27	< 1
Art and craft room [a]	62.8	196	153	250	32.5
Science room [a]	14.8	10.1	< 1	< 1	N.D.
Small gymnasium [a]	41.7	26	< 1	< 1	< 1
Gymnasium [a]	9.3	< 1	< 1	< 1	< 1
Class room (B1) [b]	39.4	3.1	< 1	16.3	193
Class room (B2) [b]	60.6	39.1	16.6	127	259
Class room (B3) [b]	58.7	76.1	36.2	369	480
Class room (B4) [c]	46.4	8.8	17.1	< 1	82.1
Class room (B5) [c]	47.5	18.5	17.9	< 1	66.6
Class room (B6) [c]	32.7	17.6	17.1	< 1	62.4

N.D.: Not detected.

[a] Sampling was made after 3 months from the completion of the repair in September.

[b] Sampling was made after 3 days from the completion of the repair in September.

[c] Sampling was made after 3 days from the completion of the repair in December.

Table 3-3 VOCs found in a newly built primary school.

Room	Concentration (ng L^{-1})				
	Toluene	Ethyl benzene	Xylene	Styrene	α-Pinene
Class room (C1)	11.9	20.7	18.1	6.6	13.4
Class room (C2)	14.8	7.5	11.9	12.6	21.8
Class room (C3)	11.5	10.0	14.9	6.9	23.1
Class room (C4)	8.5	14.2	14.2	8.5	31.9
Class room (C5)	6.4	8.6	12.3	5.6	104
Class room (C6)	6.9	10.8	11.2	15.7	87.3
Class room (C7)	8.7	11.4	19.7	10.8	24.6
Class room (C8)	< 1	7.1	12.4	7.2	25.8
Student council room	8.3	8.4	11.5	21.8	22.1
Infirmary room	8.7	< 1	8.1	8.3	N.D.
Broadcasting room	< 1	< 1	< 1	8.3	N.D.
Music room	7.2	< 1	7.1	< 1	4.4
Music instrument room	10.8	6.0	10.2	20.4	14.5
Library	10.0	6.5	12.0	9.8	499
Computer room	8.4	6.5	12.2	9.1	506
Art and craft room	8.5	5.7	10.9	7.4	70.0
Home economics room	< 1	< 1	12.1	< 1	N.D.
Printing room	8.2	11.7	14.0	10.7	N.D.
Science room	17.7	24.3	15.0	< 1	14.6
Small gymnasium	9.6	9.6	11.7	16.8	15.9
Gymnasium	2.2	2.6	< 1	10.0	N.D.

N.D.: Not detected.

Table 3-4 Long-term variation of the concentration of VOCs in a newly built school.

Room	Measure period	Concentration (ng L^{-1})				
		Toluene	Ethyl benzene	Xylene	Styrene	α-Pinene
Class room (C6)	March	6.9	10.8	11.2	15.7	87.3
	August	5.5	< 1	2.9	28.9	214
Gymnasium	March	2.2	2.6	< 1	10.0	N.D.
	August	3.9	4.3	< 1	12.1	85.4
Music room	March	7.2	< 1	7.1	< 1	4.4
	August	7.5	2.3	< 1	11.2	87.4
Library	March	10.0	6.5	12.0	9.8	499
	August	17.2	8.4	13.8	165	3253
Computer room	March	8.4	6.5	12.2	9.1	506
	August	16.7	8.1	13.9	168	3252
Science room	March	17.7	24.3	15.0	< 1	14.6
	August	13.5	7.6	20.0	48.4	73.8

Average room temperature: March, 11.2 ± 1.1ºC; August, 33.5 ± 3.0ºC.

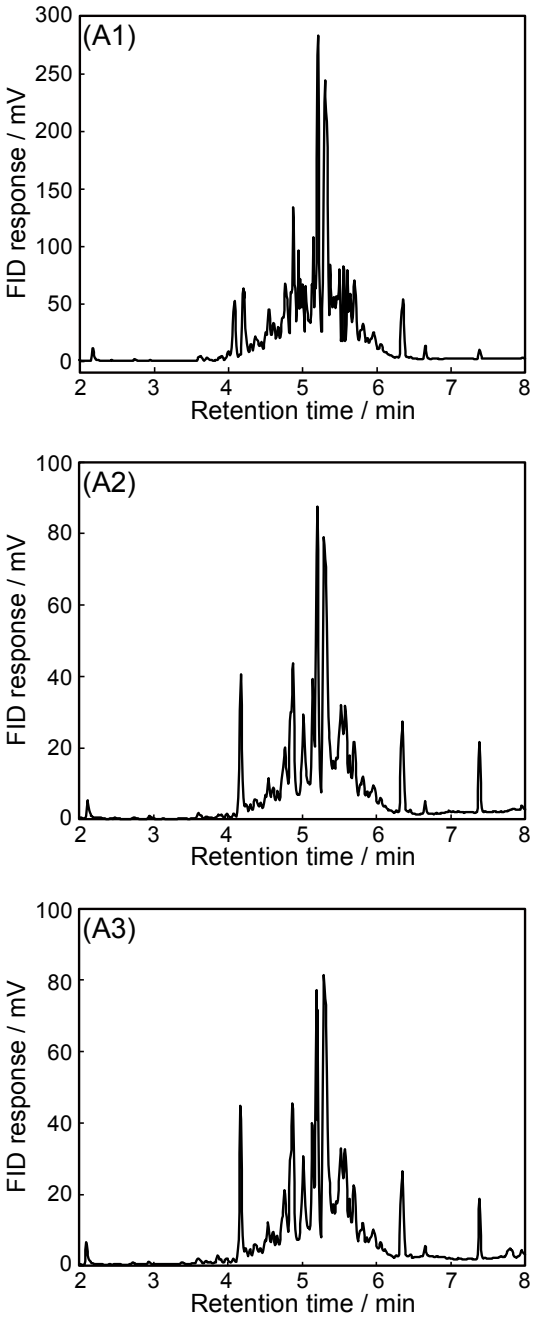

Figure 3-1 Chromatograms for the separation of branched alkanes observed in three small teachers' rooms after a renovation in school A.

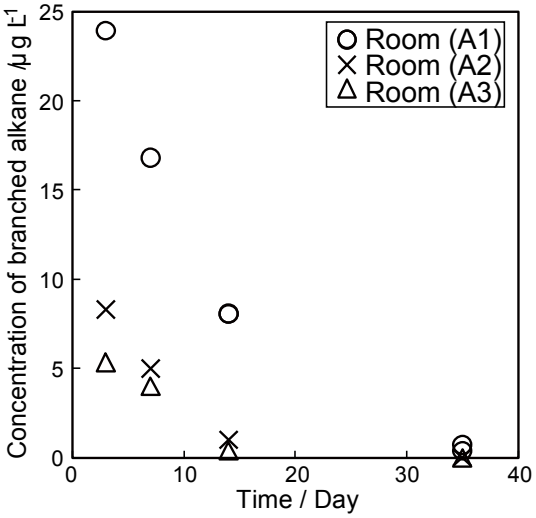

Figure 3-2 Time profile of a branched alkane found in in-room air samples after a renovation in school A.

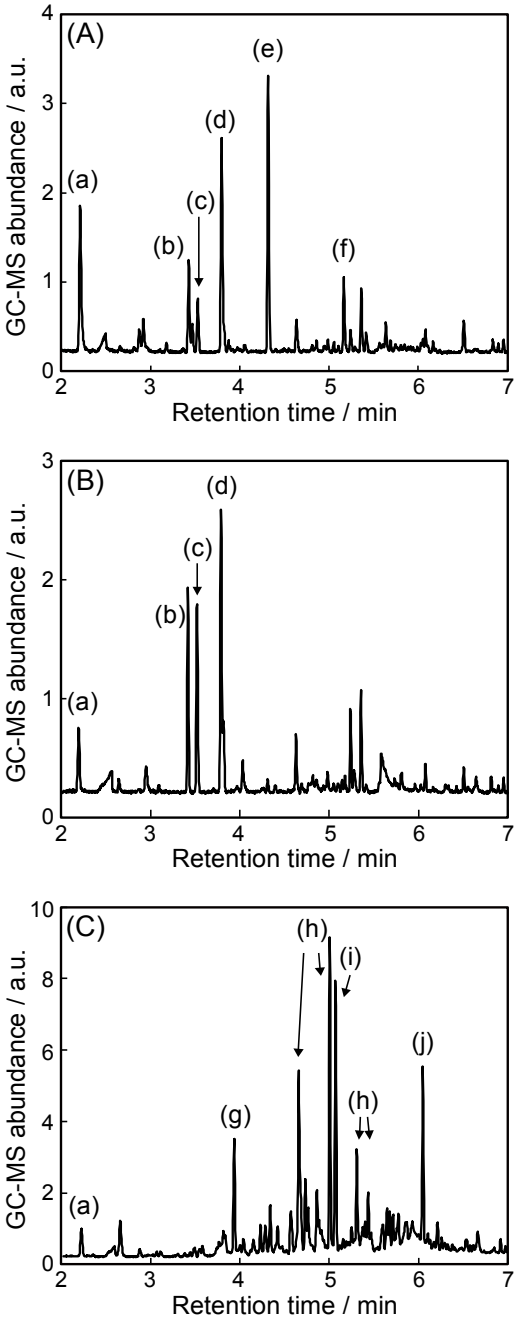

Figure 3-3 Typical chromatograms for the separation of VOCs found in large-scale repaired school facilities (school B).
(A) Music room, (B) art and craft room and (C) small gymnasium. Peaks: (a) toluene, (b) ethylbenzene, (c) *m*, *p*-xylene, (d) styrene, (e) *α*-pinene, (f) 3-carene, (g) nonane, (h) alkylbenzenes, (i) decane, (j) undecane.

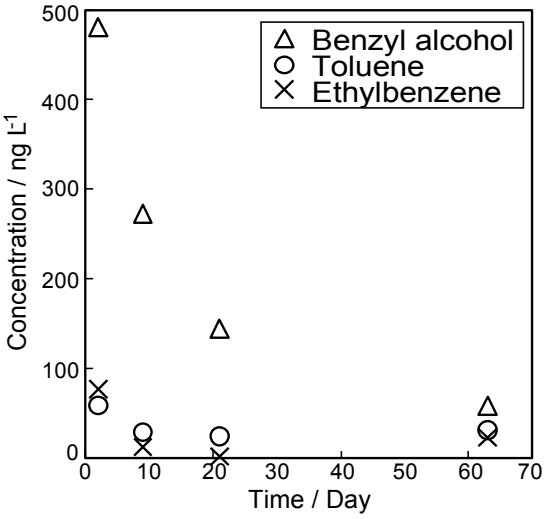

Figure 3-4 Time variations of three VOCs after a large-scale repair in class room B3.

Chapter 4

Retention Behavior of Aromatic Hydrocarbons on a Novel Chitosan-based Stationary Phase Synthesized with a Bifunctional Crosslinking Reagent Having Aliphatic and Aromatic Functionalities

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Modified from *Chromatography*, **35**, 111-116 (2014).

4.1 Abstract

A novel cross-linked chitosan stationary phase was synthesized with a new cross linking reagent having both aliphatic and aromatic functionalities in the molecular structure. Retention behaviors for polycyclic aromatic hydrocarbons (PAHs) were compared with that obtained on several commercially available stationary phases including monomeric and polymeric octadecylsilicas (ODSs) in microcolumn liquid chromatography (LC). The results clearly demonstrated the applicability of the newly-synthesized chitosan phase as the stationary phase in LC, especially for the separation of PAHs having different planarities, and also as novel wall-paint or wall-paper materials for reducing volatile organic compounds in indoor air environment.

4.2 Introduction

In liquid chromatography (LC), polycyclic aromatic hydrocarbons (PAHs) have been widely employed as the sample probes to systematically analyze the retention behavior of various stationary phases, especially focused on the molecular shape recognition mechanism [1-7]. Because of the unique molecular shape and structure, and the availability of many critical pairs having quite similar molecular structures, which are quite valuable for analyzing the interaction mechanism between the solutes and the ligands of stationary phases, a group of PAHs can be considered to be one of the essential probes to evaluate a novel stationary phase in LC [7-9].

On the other hand, chitosan is synthesized by the deacetylation of the acetylamino functional groups in chitin, which is a natural polymer in the cell walls of crustaceans, such as crabs and shrimps. On the basis of the characteristic chemical structure and the unique characteristics such as the biocompatibility and biodegradability, a number of reports have been published for the chemical modification of chitosan molecules and a wide range of applications for example, an adsorbent material for metal ions [10-14] and dyes [15], and as a stationary phase in LC [16-18]. In contrast to numerous number of applications, most of the reported chemical modifications were carried out by the chemical derivatization of the amino groups in the chitosan molecule, therefore, the resulting chemically-modified chitosan materials only show a

limited stability as the stationary phase, although the increased selectivities, such as chiral selectivities, could be obtained by the derivatization of the amino functionalities with various ligands.

Introducing an appropriate crosslinking reaction, it has been shown that the stability of the resulting chitosan materials could be dramatically improved without losing the adsorption power for metal ions [19-22] and dyes [23-27]. The results also suggest the possible applications of the crosslinked chitosan as a novel stationary phase in LC. Crosslinked with an appropriate reaction, a novel stationary phase having both a unique selectivity and sufficient stability for the operation under a conventional LC conditions could be synthesized.

As an extension of our previous publications [26-29], in this chapter, novel crosslinked chitosan material was synthesized with a crosslinking reagent having aromatic and aliphatic functionality in the structure, and the resulting cross-linked chitosan materials was evaluated as a stationary phase in microcolumn LC. With two phenyl groups in the crosslinker, an enhanced retentivity to typical aromatic compound. Taking advantage of the wide availability of the sample probes with the closely-related molecular structure, several pair of the PAHs have been employed as the solutes for the study on the systematic retention behavior. Commercially available monomeric and polymeric octadecylsilica (ODS) stationary phases were also used for comparison.

4.3 Experimental

Materials and reagents

Chitosan was obtained from Koyo Chemical Co., Osaka, Japan and the reagent for crosslinking reaction, 8,9-diphenylhexadecanoic diacid diglycidyl (DPHG) was supplied from Okamura Oil Mill Ltd., Kashiwara, Japan. The chemical structure of the DPHG is illustrated in Figure 4-1. All solvents were of analytical grade and obtained from Kishida Chemical, Osaka, Japan, and all PAHs and aromatic sample probes (Figure 4-2) were purchased from Tokyo Chemical Industries, Tokyo, Japan. Fused-silica capillaries for microcolumns were obtained from Shinwa Chemical Industries Ltd., Kyoto, Japan. Water was purified by a Milli-Q Water Purification System (Millipore, Tokyo, Japan). For comparison, two types of ODS phase, Develosil ODS-UG-5 (monomeric-type; Nomura Chemical, Seto, Japan) and Vydac 201 TPB-5 (polymeric-type; Separations Group, Hesperia, CA, USA) were also used.

Micro-LC system

Micro-LC was consisted of an Ultra-Plus II Capillary LC pumping system (Micro-Tech Scientific Inc., Vista, CA, USA), a UV/Vis absorption detector (Model 875-UV, Jasco, Tokyo, Japan) with a home-made flow-cell of about 0.3-μL volume. The detection wavelength was typically set at 254 nm unless otherwise specified. As the injector, a Model 7520 micro-injector (Rheodyne,

Cotati, CA, USA) with a sample loop volume of 0.2 μL was employed. A laboratory-made packed capillary column (fused-silica of 150 mm x 0.32 mm I.D.) was prepared with a slurry packing method.

Data processing

As the data acquisition and processing, Borwin Chromatography Data Handling Software (Jasco) running on a personal computer was used. All chromatographic measurements were carried out at least three times and the relative standard deviations (RSDs) for retention time were less than 3% for all runs.

4.4 Results and Discussion

Synthesis of crosslinked chitosan stationary phase

The crosslinking reaction (Figure 4-1) was carried out by a similar procedure as described previously [25,26]. First, chitosan (2.50 g) was dissolved in 100 mL of 5% acetic acid and diluted with methanol (100 mL). To the solution, 100 mL of methanol solution containing DPHG was added dropwise under stirring for 30 minutes at 65ºC, and then, the temperature was maintained for 48 hours. Changing the amount of DPHG for the reaction, three types of DPHG-crosslinked chitosan phases (DCCs), having different molar ratios for the epoxy- and amino-functionalities, were prepared as shown in Table 4-1.

After the reaction, the solution was neutralized by an aqueous solution of 5% potassium hydroxide. Then the contents were poured into 500 mL of acetone. The precipitate was filtrated, and sequentially washed with acetone and ether, and finally dried in *vacuo*. Other synthetic conditions were determined by the preliminary experiments to ensure the successful reaction between the chitosan and the crosslinking reagent.

With the infrared spectroscopic analysis and the solubility measurements in aqueous acetic acid solution (10%), the formation of the crosslinked structure was confirmed as a similar way as described previously [24,25]. By the elemental analysis of the resulting DCCs, it was also confirmed that about 30% of amino groups in chitosan were reacted with DPHG when the

reaction was carried out using the epoxy/amino-ratio of 2.00 (DCC-1). However, at the same time, the other two crosslinked chitosan materials (DCC-2 and DCC-3) showed quite low reactivities, suggesting a limited retentivity, as similarly found in our previous work, when employed as a stationary phase in LC [24,28,29]. Therefore, DCC-1 was used in the following experiments to ensure that the evaluation of the effect of DPHG-crosslinking on the retention behavior. Before the LC column preparation, the solid of DCC-1 was ground to powder with a mean diameter of about 10-20 μm and packed into a laboratory-made fused-silica capillary column as described elsewhere [30].

Retention behavior of PAHs on the crosslinked chitosan phase

To evaluate basic retentivity of DCC-1 as the stationary phase in LC, three typical PAHs, naphthalene, anthracene and pyrene, were separated. Figure 4-3 shows the representative chromatogram obtained with a packed-capillary column of 150-mm length. Although the efficiency is not comparable to that of commercially available ODS phases, a good separation was obtained, suggesting the practical retentivity as a novel stationary phase in LC.

Comparing the retentivity for these analytes on DCC-1 to that observed on other crosslinked chitosan phases reported earlier [28], a contribution of aromatic functional groups in the crosslinker was clearly found. The retentivity

on DCC-1 was quite comparable to that on a crosslinked chitosan phases synthesized by the crosslinker with a similar aliphatic group but without aromatic group in the structure, in which about 50% of amino groups in chitosan were reacted with the crosslinker. Therefore, the increased retentivity for the various aromatic analytes tested in this work can be at least partially attributed to the interaction between the aromatic functional group and the solute, since only about 30% of the amino groups were reacted in DCC-1.

With the sample probes shown in Figure 4-2, further evaluation of the molecular size and shape selectivities for PAHs, having different molecular size and shape, on the cross-linked chitosan phase was carried out. As a molecular size descriptor for PAHs, *F*-number was introduced. The descriptor, *F*, is defined by Hurtubise *et al.* [31] as follows: *F* = (number of double bonds) + (number of primary and secondary carbons) - 0.5 x (number of non-aromatic rings).

A high linear correlation between logarithmic retention factor and *F*-number was reported for the retention behavior of PAHs with monomeric ODS phases in aqueous reversed-phase (RP) LC [7]. The logarithmic retention data for various PAHs were plotted against their *F*-number in Figure 4-4. The plot clearly indicates a linear correlation between *log k* and *F*-number for planar PAHs, where the linear correlation coefficient for planar analytes was 0.996. The results demonstrate that DCC-1 stationary phase has a selectivity based on

the F-number for planar PAH molecules, that means, the planar solutes were mainly separated according to these molecular size on DCC-1 phase.

In contrast to a high linear correlation for planar solutes, however, a negative deviation from the line was observed for all the non-planar solutes such as diphenylmethane, triphenylmethane and *o*-terphenyl. Introducing three pairs of PAHs, having a similar molecular size and a different planarity, such as triphenylene and *o*-terphenyl, further evaluation of the planarity recognition was carried out. The selectivities for planar/non-planar solute pairs are summarized in Table 4-2, where the data on commercially available monomeric and polymeric ODSs are also tabulated for comparison. Among these selectivities, especially the selectivity for triphenylene/*o*-terphenyl has been well confirmed by Tanaka *et al.* [32] and Jinno *et al.* [1] as a good indicator of the planarity recognition power of the stationary phases in RPLC.

Figure 4-5 shows typical chromatograms for the separation of *o*-terphenyl and triphenylene on DCC-1 phase. In general, typical polymeric ODS phases give a value of about 2.0-3.0, where typical monomeric phases show the value about 1.0-2.0 in RPLC conditions. Taking into account these typical value for the selectivity and also the data for ODS phases, it can be found that DCC-1 phase has an excellent molecular planarity recognition ability over typical polymeric ODS phases. The selectivity for triphenylene/*o*-terphenyl on DCC-1 phase was even higher than a crosslinked chitosan phase previously

developed [28]. Because DCC-1 phase is assumed to be three-dimensionally bridged by DPHG-crosslinker, the intervals between chitosan backbones linked together should be similar, resulting a uniform ordered phase having a certain size of space for interaction with aromatic functionalities therein.

As reported in our previous studies [28,29], the excellent molecular planarity recognition power of the DCC-1 phase can be explained by the *"slot-model"* proposed by Wise *et al.* [1-3]. They proposed a *"slot-like"* structure to interpret the strong molecular shape recognition capabilities of polymeric ODS phases, in which the bonded ligands were partially cross-linked together on the surface of the silica gel. For the present crosslinked chitosan phase, a similar model can be proposed, because the cross-linked chitosan phase should form a kind of three dimensional network structure having deep *"slot-like"* space for the interaction with planar PAHs.

4.5 Conclusions

Introducing a crosslinking compound having aromatic and aliphatic functionality in the structure, novel crosslinked chitosan phase was synthesized, and the resulting cross-linked chitosan materials was evaluated as a stationary phase in micro-LC. The newly synthesized cross-linked chitosan stationary phase possessed a strong molecular planarity recognition power over typical ODS stationary phases. The contribution of aromatic functionality in the cross-linking reagent to the retention has been clearly confirmed.

The results also suggest that the molecular shape selectivity can be tuned by changing the chemical structure of the cross-linking reagent and that the further development of chitosan-based stationary phases can be expected in various separation techniques such as an extraction medium in sample preparation [33-37] and a stationary phase in gas chromatography [38,39]. Taking advantage of the biocompatibility and the characteristic adsorption behavior, a further applications to develop a more "human-friendly" wall-paint or wall-paper materials for reducing volatile organic compounds [36,37] in indoor air could be expected as well.

4.6 References

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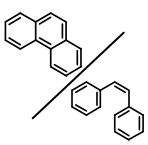
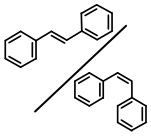
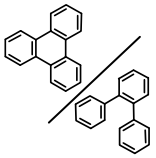
Table 4-1 Three types of crosslinked chitosan phases synthesized in this work.

Crosslinked chitosan phase	Amount used for the crosslinking reaction		Epoxy/ amino ratio [a]	Reactivity [b] (%)
	Chitosan (g)	DPHG (g)		
DCC-1	2.5	8.23	2.00	31.3
DCC-2	2.5	4.13	1.00	13.5
DCC-3	2.5	2.07	0.50	10.6

[a] Calculated from the amount of chitosan and DPHG for the crosslinking reaction.

[b] Determined by the elemental analysis after the crosslinking reaction.

Table 4-2 Comparison of molecular shape selectivity of cross-linked chitosan phase (DCC-1) and commercially available monomeric and polymeric ODS phases.

Stationary phase	Mobile phase (methanol/ water)	α (k_{planar} / $k_{non\text{-}planar}$) 		
Cross-linked	90/10	2.24	1.83	4.43
chitosan	80/20	2.27	1.79	3.78
Develosil	90/10	0.96	1.13	1.72
ODS-UG-5 [a]	80/20	0.98	1.16	1.51
Vydac 201	90/10	1.56	1.47	2.86
TPB-5 [b]	80/20	1.46	1.51	2.73

[a] Monomeric ODS.

[b] Polymeric ODS.

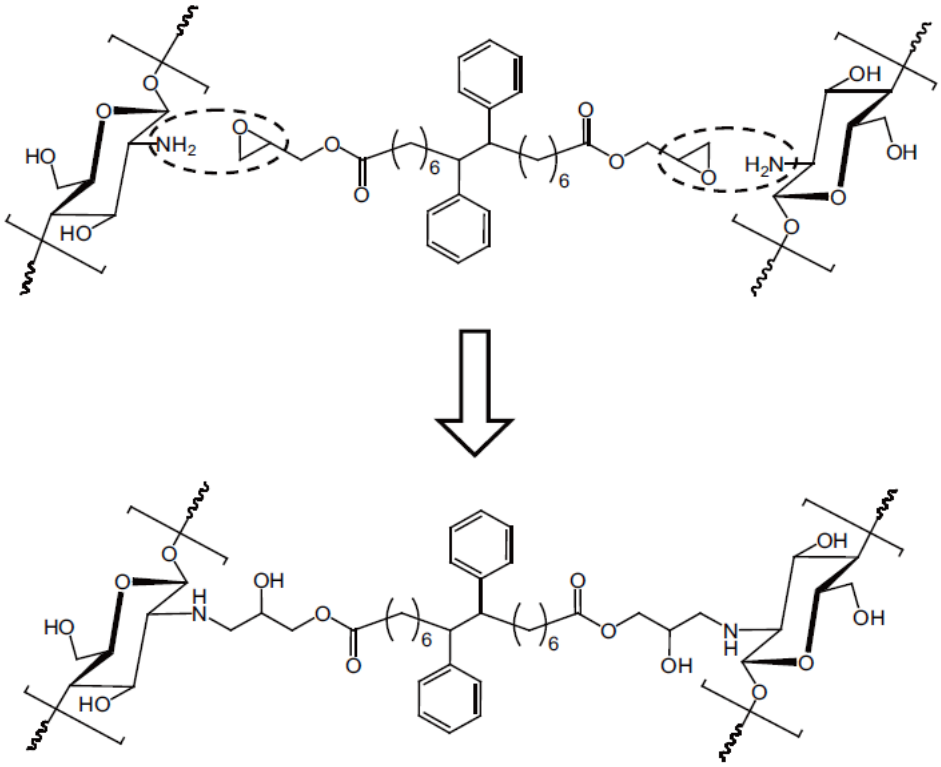


Figure 4-1 Synthetic scheme of crosslinked chitosan stationary phase.

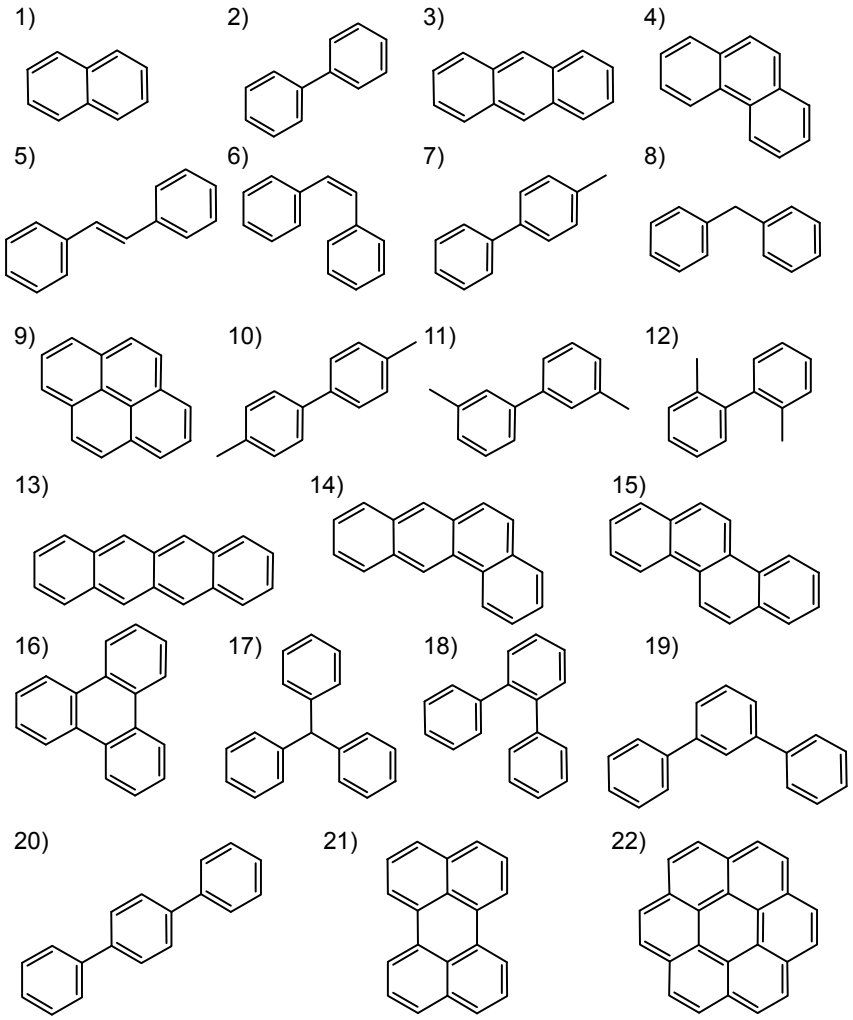


Figure 4-2 Chemical structures of PAHs employed as sample probes in this study. 1) naphthalene; 2) biphenyl; 3) anthracene; 4) phenanthrene; 5) *trans*-stilbene; 6) *cis*-stilbene; 7) 4-methylbiphenyl; 8) diphenylmethane; 9) pyrene; 10) 4,4'-dimethylbiphenyl; (11) 3,3'-dimethylbiphenyl; 12) 2,2'-dimethylbiphenyl; 13) naphthacene; 14) benz[*a*]anthracene; 15) chrysene; 16) triphenylene; 17) triphenylmethane; 18) *o*-terphenyl; 19) *m*-terphenyl; 20) *p*-terphenyl; 21) perylene; 22) coronene.

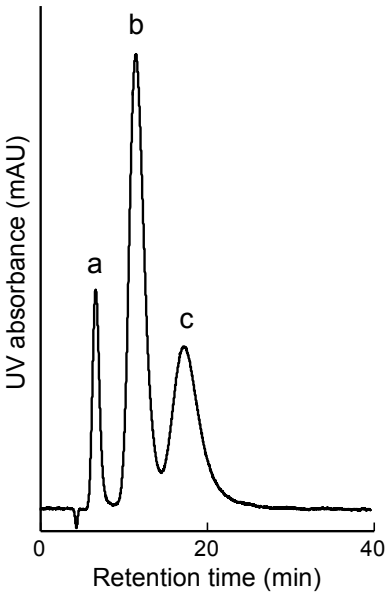


Figure 4-3 Typical chromatogram of PAHs on the crosslinked chitosan stationary phase (DCC-1). Conditions: mobile phase, methanol/water = (80/20); detection wavelength, 254 nm. Other conditions are found in the text. Peaks: (a) naphthalene; (b) anthracene; (c) pyrene.

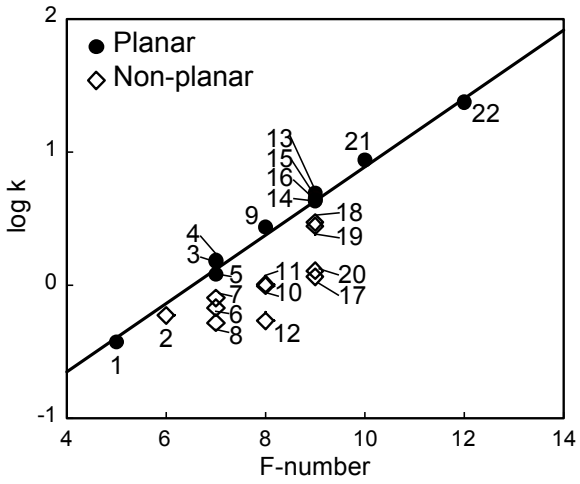


Figure 4-4 Relationship between logarithmic retention factor (*log k*) and *F*-number for various PAHs with the crosslinked chitosan phase (DCC-1). Conditions are the same as in Figure 3, except for the detection wavelength for perylene and coronene at 300 nm. All the solute assignments are the same as in Figure 2.

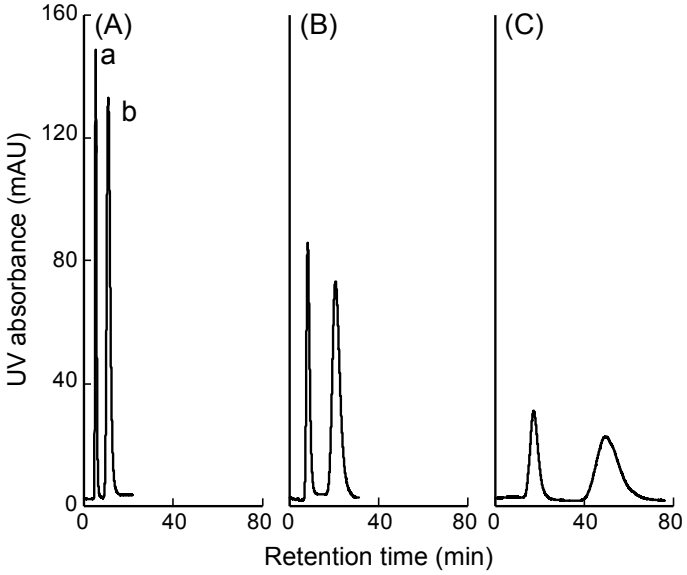


Figure 4-5 Separation of o-terphenyl and triphenylene on the crosslinked chitosan phase (DCC-1) with different mobile phase compositions. Mobile phase composition (methanol/water): (A) 90/10; (B) 80/20; and (C) 70/30. Other conditions are in the text. Peaks: (a) o-terphenyl; (b) triphenylene.

Chapter 5

Sample Preparation of Volatile Organic Compounds in Air Samples with a Novel Polyimide-packed Cartridge Designed for the Subsequent Analysis in Capillary Gas Chromatography

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Modified from *Chromatography*, **36**, 33-37 (2015).

5.1 Abstract

Spherical polyimide particles have been synthesized as an extraction medium of volatile organic compounds (VOCs) in air samples. The polyimide was prepared with the stating materials of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (4,4’-oxydianiline, ODA), resulting a spherical particles having an average diameter of about 5 μm. Packed into a laboratory made mini-extraction tube, the synthesized PMDA-ODA particles were employed as the adsorbent for the subsequent analysis in capillary gas chromatography. The results clearly showed a good adsorption ability of the PMDA-ODA particles to typical VOCs frequently found in indoor environments, suggesting a future possibility to develop a more miniaturized sample preparation device specially-designed for on-site sampling of indoor air samples.

5.2 Introduction

Volatile organic compounds (VOCs), such as organic solvents emitted from adhesives or paints for room interior finishing, can be regarded as one of the priority pollutants in indoor air environment [1-3]. A wide variety of sample preparation techniques for liquid sample matrix, especially designed for the subsequent analysis in liquid chromatography (LC), have been recently developed, however, the developed sample preparation techniques for inroom air samples are somewhat limited to several classic and time-consuming methods [4]. Furthermore, most of those conventional sample preparation techniques for gaseous sample matrix often require a multi-step procedure by a skilled analyst.

Miniaturization of sample preparation techniques enables more sophisticated analytical process along with simple, quick and economical analysis [5-7]. Introducing fine polymeric filaments as the extraction medium, miniaturized sample preparation devices have been developed [6-8]. Various types of filaments were longitudinally packed into a needle-shaped capillary, where appropriate derivatization reactions could be also employed; the resulting sample preparation device demonstrated an effective simultaneous derivatization/extraction of target analytes such as formaldehyde and ethylene oxide [9,10] for subsequent sensitive analysis in gas chromatography (GC). In addition, particle-packed sample preparation devices were developed [11-15]

typically with a copolymer of methacrylic acid (MA) and ethyleneglycol dimethacrylate (EDMA) [16,17].

As an extension of our previous publications [18-20], novel polyimide particles was prepared with pyromellitic dianhydride (PMDA) and 4,4'-diamino diphenyl ether (ODA) as the starting materials, and the resulting spherical polyimide particles were evaluated as an extraction medium for the sample preparation of typical gaseous VOCs followed by the analysis in capillary GC.

5.3 Experimental

Materials and reagents

All chemicals and solvents were of analytical grade and obtained from either Kishida Chemical, Osaka, Japan or Tokyo Chemical Industries, Tokyo, Japan, unless otherwise specified. Several types of tubing made with polytetrafluoroethylene (PTFE) and polyetheretherketone (PEEK) were obtained from GL Sciences, Tokyo, Japan.

Vacuum gas sampler for gas sample collection was purchased from Shinwa Chemical Industries, Kyoto, Japan. Water was purified by a Milli-Q Water Purification System (Millipore, Tokyo, Japan). Capillary column for GC separation employed was HR-1 (0.25 mm i.d., 30 m length, df: 0.25 μm) was purchased from Shinwa Chemical Industries.

For the evaluation of extraction capacity of the polyimide-packed extraction tube, needle-type extraction device (NeedlEx, Shinwa Chemical Industries, Kyoto, Japan) [9,10] was also used as described below.

Preparation of polyimide particles

Polyimide particles with starting materials of PDMA and ODA were synthesized on the basis of conventional procedure as shown in Figure 5-1. Details of the synthesis could be found elsewhere [21,22]. As can be seen in the SEM image of the particles (Figure 5-2), the resulting polyimide particles

have a spherical shape with an average diameter of about 5 μm.

GC system

GC separation was carried out using Model 6890 Gas Chromatograph (Agilent, Palo Alto, CA, USA) equipped a split/splitless injector and flame ionization detector (FID). Injector temperature was set at 250^{o}C, while detector was maintained at and 300^{o}C, unless otherwise specified. The split ratio was typically set at 15:1.

Data processing

As the data acquisition and processing, ChromNAV Chromatography Data Handling Software (Jasco, Tokyo, Japan) running on a personal computer was used. All chromatographic measurements were carried out at least three times and the relative standard deviations (RSDs) for retention time were less than 3% for all runs.

5.4 Results and Discussion

Static adsorption of VOCs to polyimide particles

In order to evaluate the adsorption of VOCs by the polyimide particles, gaseous standard VOCs were prepared in sample vials of 20 mL volume. 100 mg of polyimide particles were placed into the vial and the time profile of the concentration of each VOC was monitored by analyzing the head space concentration in GC, where no agitation was carried out in the vial. The time profile was also monitored without the polyimide particles for comparison.

As expected, all the VOCs levels remaining in the head space were gradually decreased without the polyimide particles in the vial (Figure 5-3), mainly due to the surface adsorption to the glass wall of the vial along with the silicon septum of the cap. Taking into account the boiling points of these VOCs, a relatively quick decrease of toluene level than other compounds could be interpreted. At the same time, a remarkable adsorption onto the polyimide particles in the vial was also confirmed in Figure 5-3. The amount of adsorbed VOCs on the polyimide particles could be estimated from the plots.

The results clearly demonstrated a good possibility of the polyimide particles to the extraction medium for typical VOCs in air samples. This is because a satisfactory adsorption ability could be found in the above experiment without any mechanical agitation of the polyimide and gaseous VOCs in the vial, suggesting a more efficient adsorption could be expected by a dynamic contact

of the polyimide particles with the VOCs.

Miniaturized extraction tube for dynamic adsorption VOCs to polyimide particles

Upon confirmation of the adsorption of VOCs to the polyimide particles in a static condition as described above, a miniaturized extraction tube designed for the dynamic adsorption of VOCs was prepared. The polyimide particles were packed in a section of a PTFE tube having 1.6 mm i.d., 10 mm length (amount of packed particulate PDMA-ODA: about 7.5 mg) as depicted in Figure 5-4.

With the vacuum gas sampler, standard gas sample was transferred from the gas sampling bag via the polyimide-packed tube to a commercially available needle extraction device that could collect the overflowed VOC molecules from the polyimide-packed tube. The operation of vacuum gas sampler was continuously repeated several times until the overflowed VOC molecules could be detected in the needle extraction device, allowing the determination of the maximum adsorption capacity of the polyimide-packed tube, as summarized in Table 5-1. These data showed a satisfactory dynamic extraction performance of the polyimide-packed tube.

A successful desorption of the extracted VOCs from the polyimide-packed tube was also confirmed, where a glass gas tight syringe containing 100 μL of acetonitrile (ACN) and 0.5 mL of nitrogen was attached at

the top of the tube during the GC injection, as reported previously for the desorption from a needle extraction device [9]. More than about 95% of the extracted VOCs could be desorbed with a flow of ACN and N_2 at room temperature as summarized in Table 5-2.

The developed extraction tube could be repeatedly used for more than 100 times without any significant decrease in the extraction performance. If in case, slight carry-over is observed when accidentally extract a non-volatile compounds, the extraction tube could be washed with pumping a relatively strong organic solvent such as tetrahydrofuran. Taking advantage of the excellent stability to typical organic solvent, the reconditioning process is simple and easy to be carried out.

5.5 Conclusions

Packed into a miniaturized extraction tube, the polyimide particles could adsorb typical VOCs found in in-room environment, where an effective desorption of the extracted analytes from the particles could be obtained at room temperature. The potential applicability of spherical polyimide particles to a novel sample preparation medium for gaseous VOCs was suggested in this preliminary work, although a further downsizing of the extraction tube should be done for more effective preconcentration and quick analysis that will be the advantageous features for the analysis of in-room environment.

The molecular shape selectivity can be tuned by changing the chemical structure of the polyimide, and the further development of polyimide-based stationary phases can be expected in various separation techniques including as an extraction medium in sample preparation [23], a stationary phase in LC [24,25] and GC [26,27]. Although more investigations should be scheduled on the basis of a systematic analysis of the correlation between the chemical structures of the polymeric extraction medium and the selectivity to specific target compounds being extracted [28], taking advantage of the excellent heat resistant property, some additional applications of the polyimide micro-particles can be additionally expected.

5.6 References

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Table 5-1 Extraction capacity for typical VOCs.

Analyte	Extraction Capacity (μmol/g)
Acetone	0.42
Hexane	0.24
Toluene	0.78

Table 5-2 Recovery obtained with solvent desorption.

Analyte	Recovery (%)
Acetone	94.7
Hexane	95.9
Toluene	95.1

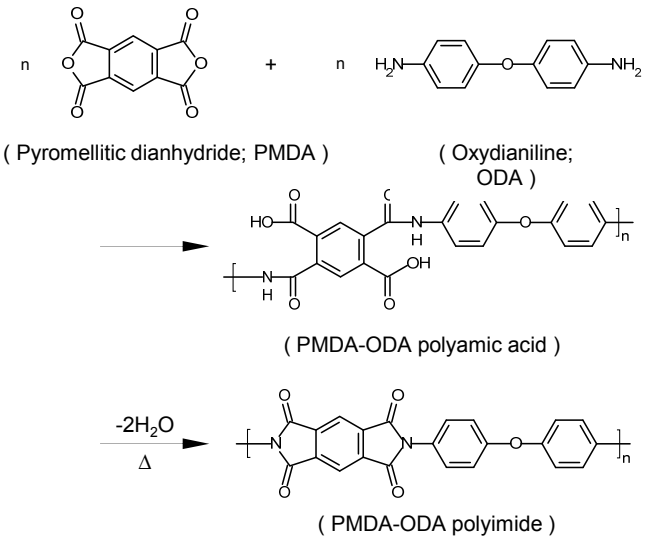

Figure 5-1 Synthetic scheme of PMDA-ODA.

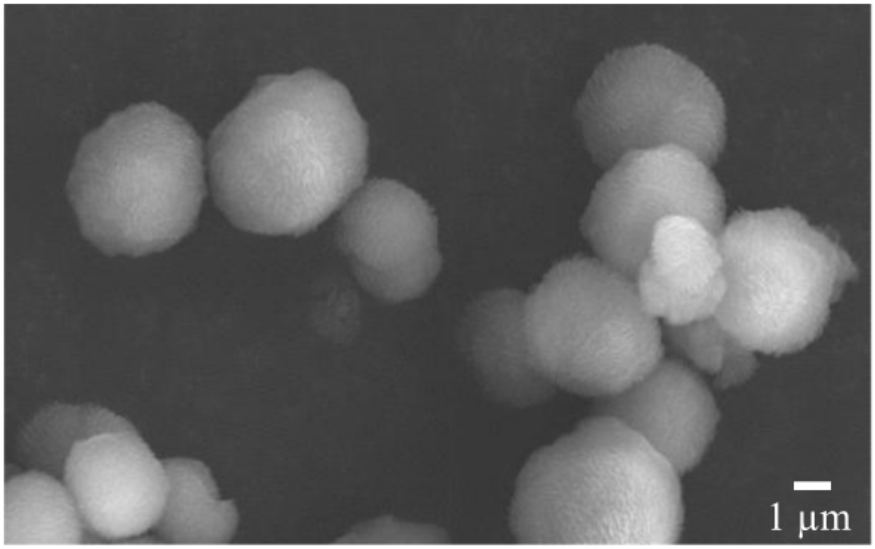

Figure 5-2 SEM image of the PMDA-ODA particles.

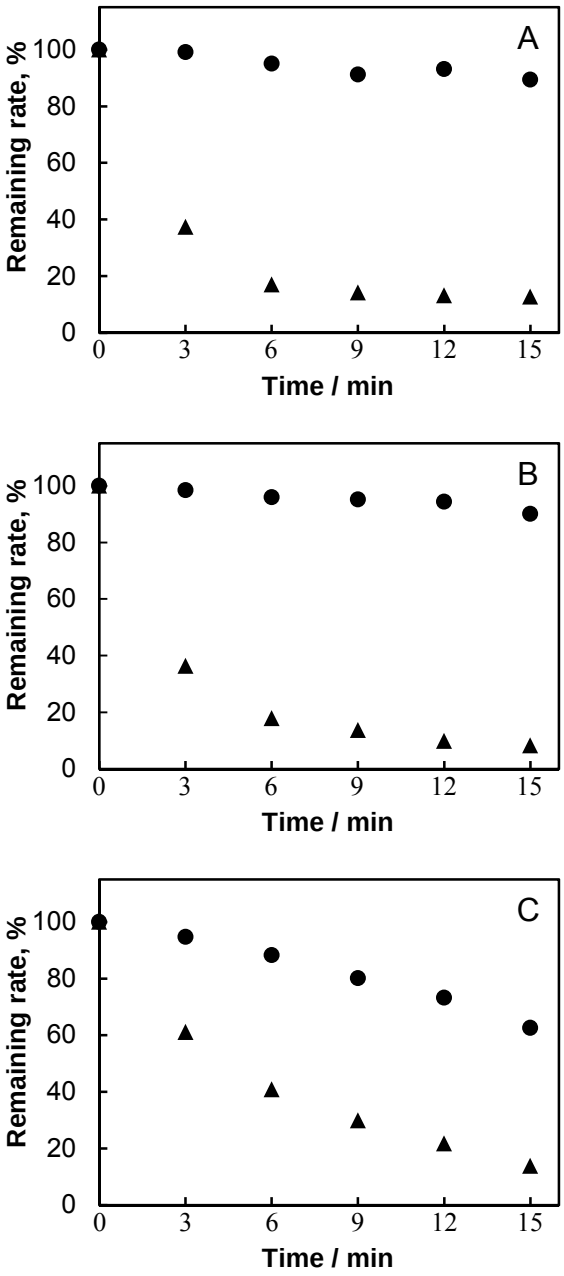

Figure 5-3 Time profile of VOCs concentration in the sample vial with (triangle) and without (circle) polyimide particles. (A) acetone, (B) hexane and (C) toluene.

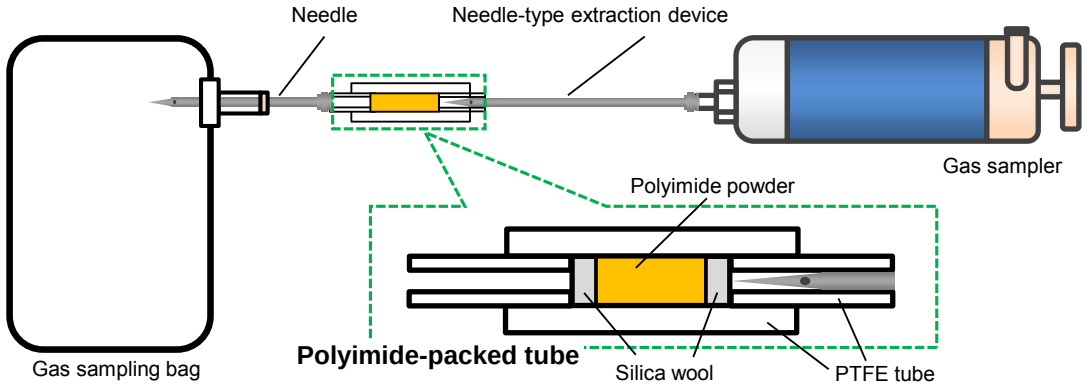

Figure 5-4 Illustration of polyimide-packed tube and experimental setup for the evaluation of the dynamic sampling/extraction.

Chapter 6

General Conclusions

6.1 General Conclusions

Novel packed-capillary columns have been developed in Chapter 2. These packed capillary columns developed herein clearly demonstrate good compatibility with rapid temperature-programmed elution. The advantages of packed capillary columns such as unique selectivity and good sample-loading capacity could make them attractive separation media for high-throughput analysis of various complex mixtures consisting of many components.

The proposed packed capillary columns can be installed in a conventional capillary GC system without any modifications or adapters; this enables easy introduction of packed capillary columns into most modern GC instruments that are now widely employed with commercially available open-tubular capillary columns.

In Chapter 3, a needle-type extraction device was introduced in the subsequent GC-MS analysis of volatile organic compounds (VOCs) in school facilities. Results showed that the needle extraction technique could be a suitable sample collection/extraction technique for indoor air analysis. The results also demonstrated that VOCs levels in most schoolrooms were low, although relatively higher VOC concentrations were found in some rooms specially designed for educational purposes. Moreover, some non-regulated VOCs were found in school facilities. Since samples could be stored for up to three days after sampling, multipoint sampling could be easily performed in

several rooms. The developed technique will be a powerful tool for more systematic assessments of indoor air analysis, especially in newly build public facilities and houses.

In Chapter 4, a novel cross-linked chitosan phase was prepared by introducing a cross-linking compound with aromatic and aliphatic functionalities. The resulting cross-linked chitosan material was evaluated for use as a stationary phase in micro-LC. The cross-linked chitosan stationary phase exhibited strong recognition power for molecular planarity relative to typical ODS stationary phases currently employed. The contribution to retention by aromatic functionality in the cross-linking reagent was clearly confirmed. The results suggest that selectivity for molecular shape can be tuned by changing the chemical structure of the cross-linking reagent and that further developments of chitosan-based stationary phases can be expected for various separation techniques such as an extraction media in sample preparation [1-5] and as a stationary phase in GC [6,7]. By using the biocompatibility and the characteristic adsorption behavior of stationary phases, further applications could be a more “human-friendly” wall paint or wallpaper materials that reduce concentrations of VOCs [4,5] in indoor air.

In Chapter 5, spherical polyimide particles have been introduced as an extraction medium of volatile organic compounds (VOCs) in air samples. As the stating materials of PMDA and ODA were used and resulting spherical

particles having an average diameter of about 5 μm were employed as the packing material in the extraction tube. The results clearly showed a good adsorption power of the PMDA-ODA particles to typical VOCs frequently found in indoor environments, suggesting a future possibility to develop more miniaturized sample preparation device specially-designed for on-site sampling of indoor air samples [8]. The molecular shape selectivity can be further tuned by optimizing the chemical structure of the polyimide, and the further development of polyimide-based stationary phases can be also expected in various separation techniques [9].

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Publications

Publications

1. Papers Related to this Dissertation

[1] **M. Inoue**, Y. Saito, I. Ueta, T. Miura, H. Ohkita, K. Fujimura and K. Jinno "Rapid Temperature-Programmed Separation and Retention Prediction on a Novel Packed-Capillary Column in Gas Chromatography" *Analytical Sciences*, **26**, 687-691 (2010).

[2] **M. Inoue**, A. Mizuguchi, I. Ueta, K. Takahashi and Y. Saito "Rapid On-Site Air Sampling with a Needle Extraction Device for Evaluating the Indoor Air Environment in School Facilities" *Analytical Sciences*, **29**, 519-525 (2013).

[3] **M. Inoue**, I. Ueta, Y. Shimizu and Y. Saito "Retention Behavior of Aromatic Hydrocarbons on a Novel Chitosan-Based Stationary Phase Synthesized with a Bifunctional Crosslinking Reagent Having Aliphatic and Aromatic Functionalities" *Chromatography*, **35**, 111-116 (2014).

[4] **M. Inoue**, H. Nakazaki , T. Tazawa, H. Takeuchi, A. Kobayashi, I . Ueta, Y. Shirai, K. Moriuchi, and Y. Saito

"Sample Preparation of Volatile Organic Compounds in Air Samples with a Novel Polyimide-Packed Cartridge Designed for the Subsequent Analysis in Capillary Gas Chromatography"

Chromatography, **36**, 33-37 (2015).

2. Other Publications

[1] K. Nakane, S. Shirai, Y. Saito, Y. Moriwake, I. Ueta, **M. Inoue**, and K. Jinno,
"High-Temperature Separation on a Polymer-Coated Fibrous Stationary Phase in Microcolumn Liquid Chromatography"
Analytical Sciences, **27**, 811-816 (2011).