Focusing Review

Sample Preparation of Volatile Organic Compounds with Needle–Type Extraction Device

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Abstract

Needle–type extraction devices have been developed for the simple and sensitive determination of gaseous volatile organic compounds (VOCs) in gas chromatography (GC). The needle–type extraction device allows direct insertion of the extraction medium into the GC injection port, therefore, simple and rapid desorption of the extracted analytes could be achieved. For simultaneous derivatization and preconcentration of VOCs, fiber–packed needle was developed. The fiber–packed needle was prepared with a bundle of fine filaments typically coated with methyl–polysiloxane. During the extraction, target analytes, such as volatile aldehydes or ethylene oxide, were simultaneously derivatized and concentrated in the extraction needle.

Particle–packed needle has been developed for the extraction of VOCs commonly found in environmental gaseous samples. Several particulate materials, such as porous polymer particles or activated carbon, were employed as the extraction media for the respective target analytes. The particle–packed extraction needle was successfully applied for various analytical situations, such as in–door air analysis, fire investigation and human breath analysis.

Keywords : Sample preparation, VOCs, Extraction, Needle, Gas chromatography

1. Introduction

Quantification of volatile organic compounds (VOCs) in environmental air has been recently focused because of their adverse effects on human health, including the so–called multiple chemical sensitivity and sick building syndrome [1,2]. To investigate the effect of VOCs on human health and prevent the above illnesses, a sensitive and reliable method for determining the VOCs in air samples is desired. For the determination of gaseous VOCs, the analysis in gas chromatography (GC) is one of the most promising methods, because of its selectivity and sensitivity, as well as wide availability [3,4]. However, a sample preconcentration process should still be needed for an accurate and precise determination of these VOCs.

Typically, two types of sample preparation methods have been employed for the concentration of VOCs in air samples, i.e., solvent desorption and thermal desorption (TD) methods. The solvent desorption method showed relatively low sensitivity, and the solvent peak can often interferes some analytes in the chromatogram. The TD is a solvent–free technique and has a high sensitivity, however, it requires a relatively expensive, specially–designed desorption instrument.

Solid–phase microextraction (SPME) is one of the most advanced sampling techniques for typical VOCs analysis in GC, and it has several attractive features over other traditional sample preparation techniques [5]. However, most of the SPME techniques are based on static sampling, therefore, a relatively long extraction time is needed to obtain a satisfactory sensitivity. As an alternative to the active extraction of VOCs, the use of needle–type extraction

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devices has been recognized to be an effective sample preparation technique [6,7]. Compared to the conventional SPME, the needle–type sampling device has been regarded to have a good mechanical strength and also a high extraction capacity.

In our previous investigations, the authors developed miniaturized needle–type extraction devices for rapid and sensitive determination of gaseous VOCs in GC [8–10]. The needle–type extraction devices were prepared with an extraction sorbent in a specially–designed stainless steel needle. The target analytes are extracted on the sorbent when a gaseous sample is passed through the packed sorbent section in the needle. The extracted analytes can then be thermally desorbed in the heated GC injection port [11–17]. This technique does not require any additional desorption instrument and/or cryogenic focusing process. Therefore, the extraction employing a needle–type device can be regarded as a simple, rapid, and useful extraction/sample preparation method, and actually, several applications have already been reported for the determination of trace level of VOCs in gaseous samples.

In this review, simultaneous derivatization/preconcentration of VOCs using a fiber–packed extraction needle is described [18,19]. The determination of typical VOCs with a particle–packed extraction needle [20] and its applications for several analytical situations are also reviewed [21–25].

2. Fiber–packed needle for simultaneous derivatization/preconcentration of VOCs

The fiber–packed extraction needle was designed for the derivatization and concentration of VOCs, such as volatile aldehydes, ketones and ethylene oxide (EO). Illustration of the fiber–packed needle was shown in Fig. 1A. In the fiber–packed needle, a bundle of Zylon filaments was packed, because of their excellent thermal stability and also their high–resistance to typical organic solvents

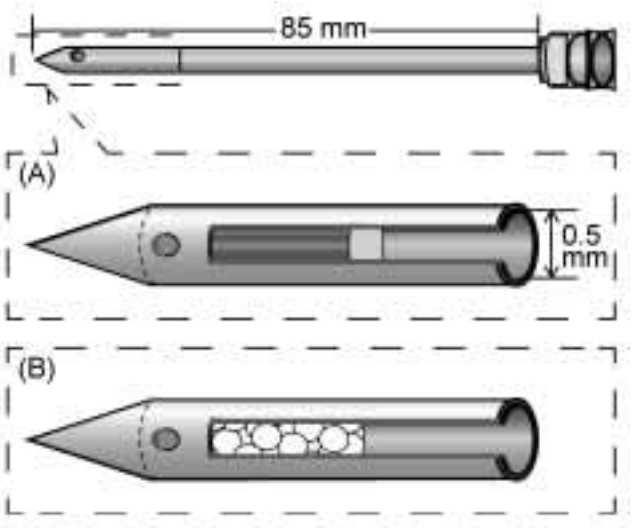

Fig. 1 Schematic illustration of needle–type extraction devices. (A) Fiber–packed needle and (B) particle–packed needle.

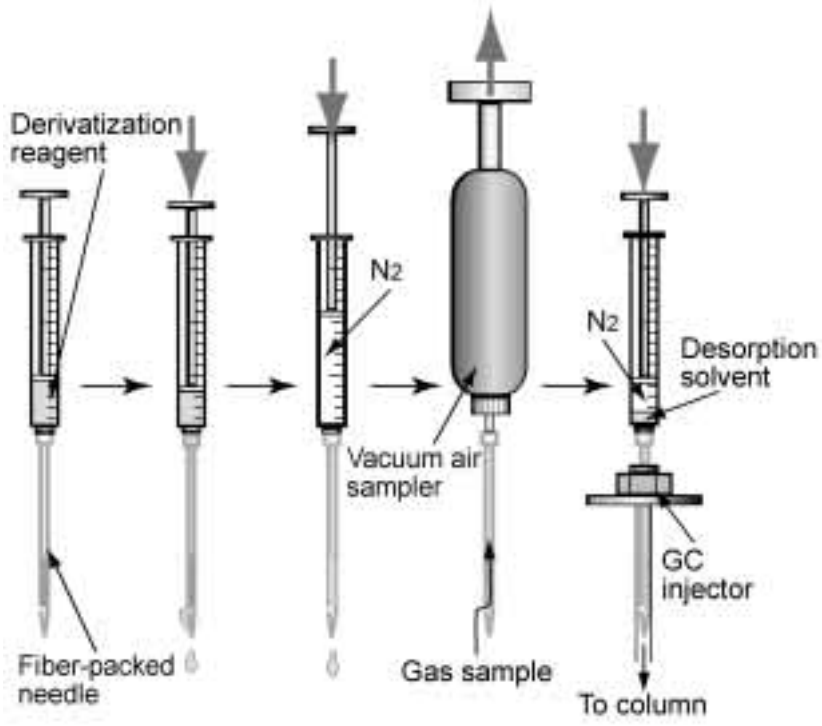

Fig. 2 Schematic diagram of the extraction/derivatization and desorption of analytes using fiber–packed needle. Modified from Fig. 4 in reference 18 with permission.

[26,27]. The surface of the filament was coated with an HR−1 material (100%−methyl−polysiloxane; Shinwa Chemical Industries, Kyoto, Japan). To prepare the fiber−packed needle, a 4 cm of the polymer−coated filaments (415 filaments) was folded in half, and then packed into the needle (85 mm × 0.5 mm I.D., 0.7 mm O.D.). The resulting a section of about 20 mm in length (830 filaments) was packed with the filaments, and one end of the packed section was positioned just before the side hole of the needle. Approximately 8 min of the extraction time was required for the extraction of 50 mL of gaseous sample with the needle. The derivatized analytes were determined by gas chromatography−mass spectrometry (GC−MS). The scheme for the extraction of the air sample and the desorption of the analytes using the fiber−packed needle is illustrated in Fig. 2.

2.1. Determination of volatile aldehydes and ketones

For the determination of volatile aldehydes and ketones in air samples, 2,4−dinitrophenylhydrazine (DNPH) was employed as the derivatization reagent [28]. Prior to the introduction of the sample gas into the fiber−packed needle, as illustrated in Fig. 2, the DNPH solution of approximately 50 μL (0.1 mg/mL in acetonitrile) was pumped through the needle, and then the remaining solution was vented by pumping 1 mL of N_2 through the needle. Next, the needle was attached to a commercially−available vacuum gas sampling device. Reacted with DNPH in the needle, aldehydes and ketones in the air samples were derivatized to be the corresponding hydrazones, and simultaneously extracted in the extraction needle. After the derivatization/extraction process, the needle was attached to an injection syringe containing acetonitrile and N_2 gas, and inserted into the GC injector. Desorption and injection were performed simultaneously by injecting acetonitrile and N_2 through the needle at the heated injector, as shown in Fig. 2. Injection was performed immediately after the insertion of the needle into the injector, because it was found in the preliminary experiments that no preheating time was necessary for an effective desorption under the optimized desorption conditions.

The extraction performance was evaluated based on the optimized volume of the desorption solvent and the desorption temperature, where a practically complete desorption (more than 99.99%) at the first desorption. Typical chromatogram for the separation of aldehydes sample with time−programmed SIM monitoring is shown in Fig. 3A. In Fig. 3B, separation of acetone and methyl ethyl ketone (MEK) is also presented. The limit of detection (LOD) and limit of quantification (LOQ) of the proposed method was summarized in Table 1. Taking into account the sampled gas volume of 50 mL and the concentration range found in typical in−house air measurements, the data in Table 1 clearly demonstrate a practical quantification level for these compounds.

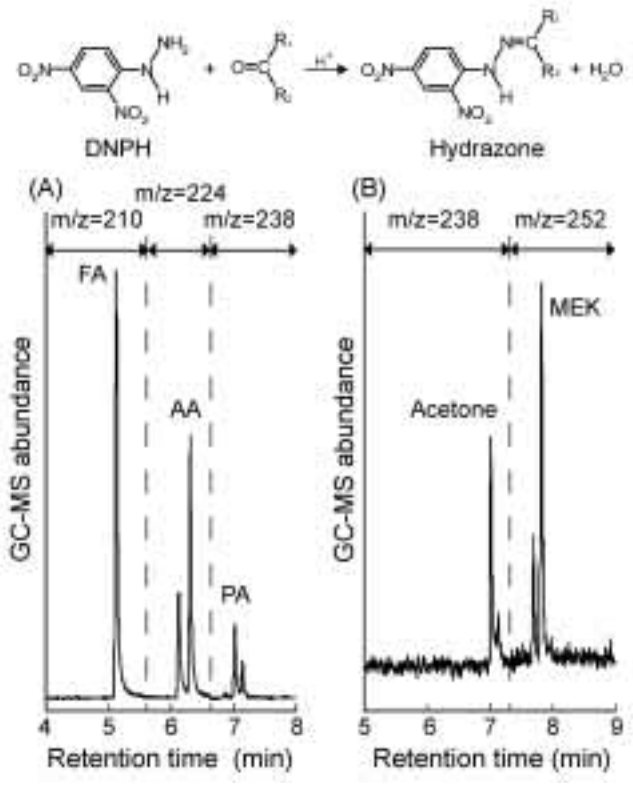

Fig. 3 Chromatograms for the separation of DNPH derivatives of (A) aldehydes and (B) ketones in programmed SIM mode. Sample concentration: Formaldehyde (FA), 25 ng/L; acetaldehyde (AA), 300 ng/L; propionaldehyde (PA), 400 ng/L; acetone, 500 ng/L and MEK, 600 ng/L. GC conditions: column, DB−1 fused−silica capillary (15 m × 0.25 mm I.D., film thickness 0.25 μm); temperature program, A 150°C (1.0 min) to 230°C at 10°C/min and B 150°C (1.0 min) to 230°C at 10°C/min; column head pressure, He 80 kPa. Modified from Fig. 8 in reference 18 with permission.

Table 1. LODs and LOQ for aldehydes, ketones and EO using fiber−packed needle.

Analyte	LOD(ng/L)	LOQ(ng/L)
Formaldehyde	1.2	3.6
Acetaldehyde	3.6	10.8
Propionaldehyde	4.7	14.1
Acetone	11.7	35.1
EO	1.8	5.4

In order to evaluate the storage performance of the fiber−packed needle, the sampled needles were stored at room temperature, at about 24 °C, for up to 3 days after the sampling. During this storage period, all of the needles were sealed with a set of cap and plug individually manufactured from a small piece of polytetrafluoroethylene (PTFE). The results demonstrated an excellent storage performance of the fiber−packed needle. The extracted samples could be almost quantitatively determined after the storage period, which

is an additional advantageous feature, especially for a large number of samples were extracted on–site at the same time [20].

An alternative derivatization reaction of carbonyl compounds with *O*–(2,3,4,5,6–pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was also successfully introduced. On the basis of the preliminary derivatization experiments in the polymer–coated fiber –packed needle device, an aqueous solution of PFBHA (10 mg/mL) was used as the derivatization reaction. For the desorption of PFBHA derivatives, pure water (30 μL) and N_2 gas were used. Formaldehyde and acetaldehyde in a smoker's breath sample were measured with both DNPH and PFBHA derivatization methods using the same fiber–packed needle, and these quantitative results could have a good agreement [21].

2.2. Sample preparation of EO

As an extension to the above studies, the fiber–packed needle was further applied to a rapid and sensitive determination of gaseous EO. An aqueous solution of HBr was used for the derivatization of EO. In the needle, EO was successfully reacting with HBr to form 2–bromoethanol at room temperature. The derivatized analyte was desorbed by passing a small amount of methanol in the needle. The LOD and LOQ of EO in this method were summarized in Table 1. Satisfactory storage performance for 3 days at room temperature was also confirmed. Taking advantage of the rapid reaction with HBr in the fiber–packed needle extraction device, tobacco smoke and automobile exhaust were analyzed. The results clearly indicated a successful determination of EO from these complex sample mixtures [19].

3. Particle–packed needle for typical VOCs in environmental samples

The particle–packed needle was developed as a miniaturized sample preparation device for the analysis of typical VOCs in environmental air samples. For the sample preparation of the VOCs in air samples, porous polymer beads or activated carbon (AC) particles (150 to 180 μm diameter) were packed into the stainless steel needle as shown in Fig. 1B. The extraction needles packed with these particulate media allow a selection of suitable extraction medium for respective analytes. The target analytes are extracted on the sorbent when a gaseous sample is passed through the packed sorbent section in the needle. The extraction time for 50 mL gaseous sample using the particle–packed needle was approximately 5 min. The extracted analytes can then be thermally desorbed in the heated GC injector. The basic extraction/desorption and storage performances of the particle–packed extraction needle for typical VOCs were confirmed with an extraction sorbent consisted of a copolymer of methacrylic acid (MA) and ethylene glycol dimethacrylate (EGDMA) [20].

3.1. Determination of tobacco–related VOCs

Three smoking–related samples, i.e., side stream, main stream and smoker's breath, were collected in gas sampling bags, and a 50 mL portion of each sample was extracted by MA/EGDMA particle –packed needle followed by the analysis in gas chromatography–flame ionization detection (GC–FID). Compared to the side stream, nicotine in the main stream seemed to be eliminated mainly by the tobacco filter, however, as expected, it still contained various types of organic compounds. In addition, a significantly lower level of organic compounds in smoker's breath was confirmed. One can conclude from above comparison that most of the VOCs generated during the smoking might remain trapped in their respiratory system [21].

In recent years, a new smoking hazard has been reported, so–called "third–hand smokin" [29]. This is residual tobacco smoke pollution, which occurs after smoking. The MA/EGDMA particle–packed extraction needle was applied to the evaluation of a potential risk of third–hand smoking. Five different types of fabrics were exposed to side–stream smoke, and VOCs desorbed from the each fabric samples were determined (Fig. 4). Significantly higher concentrations for ammonia and 2–furaldehyde (data not shown) were observed for the cotton and linen fabric, however, higher concentrations for other smoking–related aromatic VOCs were obtained with the acetate fabric. Although a more extensive study, including a consideration for the chemical structure of each fiber, should be needed to reach the final conclusion, these results indicate that the adsorption behavior of VOCs was associated with the chemical structure of the fabric, and that the proposed method could be applied to the development of a new evaluation method for preventing third–hand smoking pollution.

Smoker's breath sample which collected at just after the final puff was analyzed by GC–MS. The peaks of acetone, benzene and toluene were also detected in non–smoker's breath samples; however, these concentrations were clearly higher in the smoker's breath. In addition, many VOCs were only detected in the smokers' breath; especially 2,5–dimethyfurane has been recognized as a tobacco smoke biomarker in the smoker's breath, and actually detected only in the smokers' breath in this work. The time variations of the tobacco–related VOCs level in smoker's breath are also measured, and it was confirmed that these VOCs were continuously expired from the smoker's breath for about 10 min, although the concentrations of these VOCs were significantly higher over the first 5 min. [23].

3.2. Determination of fire accelerants–related VOCs for fire investigation

Among the approximately 60,000 fires that occur in Japan every year, arson represents the worst cause [24]. In the case of arson,

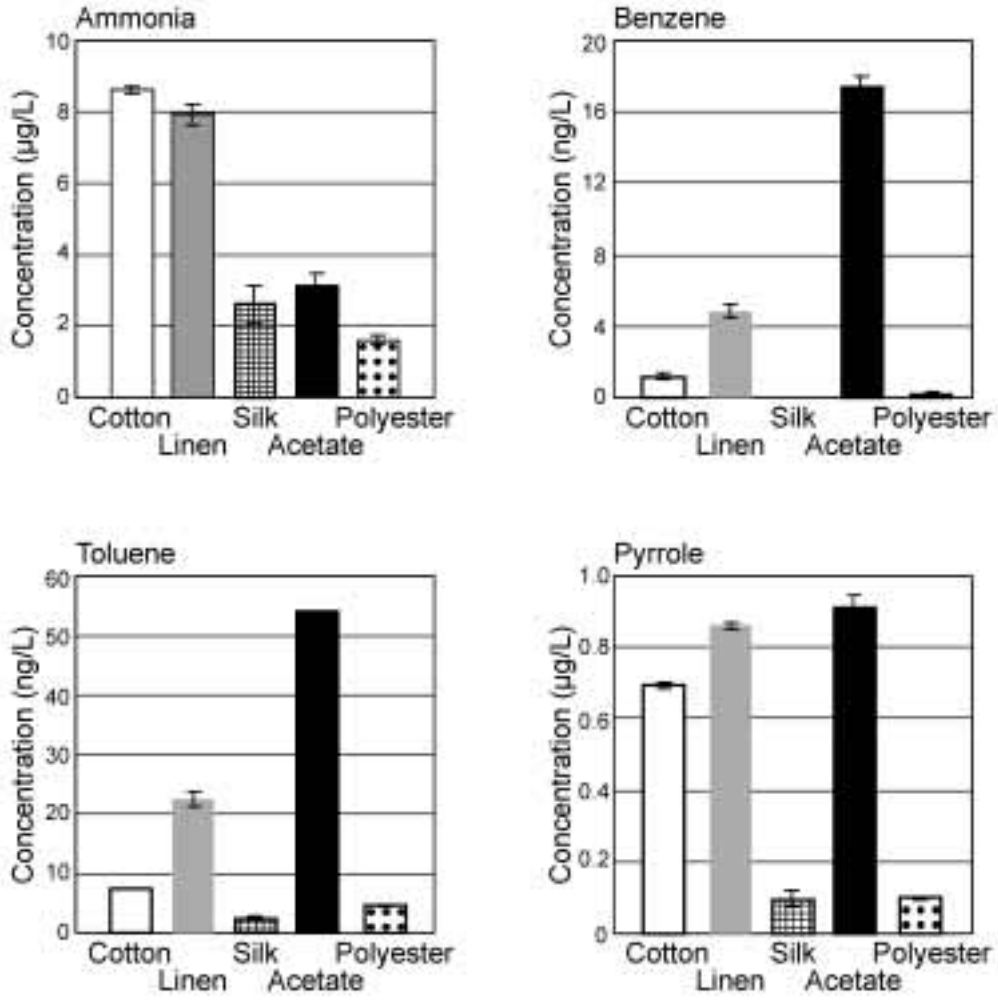

Fig. 4 Comparison of smoking–related VOCs adsorbed on 5 types of fabrics.
The concentration of ammonia was determined by a commercially available detection tube. Other compounds were determined by GC–MS in the SIM mode. Modified from Fig. 3 in reference 23 with permission.

fire accelerants, such as gasoline and kerosene, are often used to start fires. Because these fire accelerants consist of mixtures of VOCs, accurate and sensitive determinations of the VOCs found at the scenes of fires can be quite important in forensic investigations, especially if arson is suspected from fire debris. In this work, a new method for fire investigations has been developed using a divinylbenzene (DVB)–packed extraction needle and subsequent GC analysis.

The time–variation profiles of VOCs evaporated from fuel–spiked uncombusted samples of cotton fabric, carpet and wood, were measured for up to 48 h. The results indicated successful detection of these fuel–related compounds, as well as fingerprint patterns. Fire accelerants–related VOCs, emitted from combusted carpets and woods samples, were then measured. Although the surfaces of the carpet samples and the accelerants thereon were mostly combusted, the accelerants that had penetrated into the carpet samples were successfully detected. For combusted woods samples, the representative fire accelerant VOCs were detected in Japanese cypress up to weight losses of approximately 30%, and approximately 50% in both pine and plywood samples.

The proposed method was applied to the determination of fire accelerants in simulated fires using two prefabricated rooms. The rooms used in these simulations were prefabricated rooms with volumes of 15.1 m^3, 2.7 m (width) × 2.0 m (height) × 2.8 m (depth), and were made to represent the typical interior of a small Japanese room in winter. The first case was assumed to be a fire that resulted from misfueling of gasoline into a kerosene heater. The second case was assumed to be an arson fire in which approximately 4 L of kerosene was poured onto the floor before ignition. After the power of each fire had somewhat decreased from the maximum, each fire was extinguished by water. Room air sample which suspected to be a headspace of the origin of the fire was extracted using extraction needles 30 min after the extinction, and the extracted VOCs were analyzed in GC. Fig. 5 shows typical chro-

matograms for separations of the air samples taken from the two types of simulated fire scenes. The chromatogram shown in Fig. 5A was monitored with an FID, and the chromatogram showed a good agreement with that of headspace of pure gasoline. In Fig. 5B, a set of characteristic aliphatic hydrocarbons clearly indicated the presence of kerosene at the fire scene. The above results also suggest that the needle extraction method could be applied to not only the investigation of the arson–related fire, but also the investigation of unintentional fire, such as misfueling [24].

3.3. Human breath analysis

Acetone is normally included in human breath at ppb level, and has been regarded as a promising biomarker of diabetes. In this study, the MA/EGDMA particle–packed extraction needle was applied to the GC–MS analysis of breath acetone taken from 21 of controlled type–2 diabetes patients. All the patients have received either oral medication (O.M.) or insulin injection (I.I.) from the doctor. The breath samples were collected in 1 L gas sampling bag of Tedlar Bag, and its 50 mL was extracted by the particle–packed needle. The breath acetone level in controlled diabetic patients was in the range from 0.19 to 0.66 ppm, suggesting that no significant difference was observed between healthy persons and controlled type–2 diabetic patients. The results have a good agreement with that obtained by the urine test strip, where only negative results were obtained for all these patients' urine samples.

On the other hand, glycosylated hemoglobin level (HbA 1 c%) of the controlled diabetic patients was significantly higher than healthy persons. Correlation between the HbA 1 c% level and the breath acetone level of the diabetic patients was shown in Fig. 6. Interestingly, a clear correlation was found between the HbA 1 c% and the concentration of the breath acetone.

The breath acetone concentration of a medically untreated type–2 diabetic patient was also determined. The HbA 1 c% in the last several years was stable at the value of about 6.0%. The average breath acetone concentration was range from 0.92 ppm to 1.20 ppm, indicating a significant difference from a group of healthy persons.

It is well–known that breath acetone level increases during fasting condition as the same physiology as insulin dependent diabetes. Therefore, 4 healthy persons were fasted for 24 h, and breath acetone and urine acetone were monitored during this period. Typical

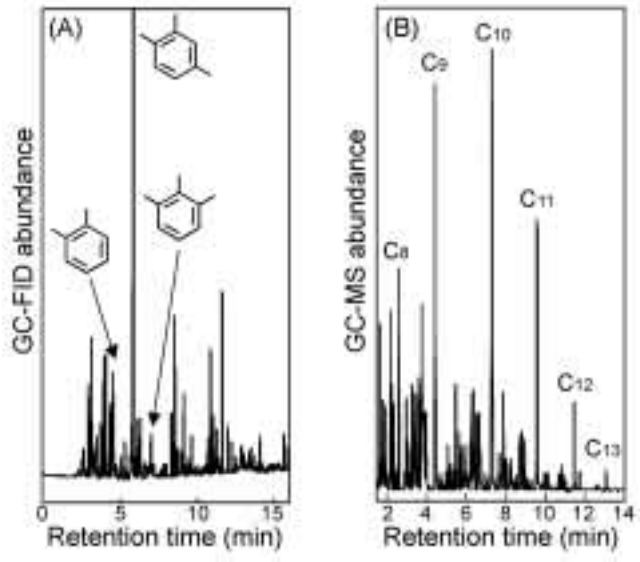

Fig. 5 Typical chromatograms for the separation of the air samples containing fire accelerants–related VOCs obtained after simulated fires.
(A) Simulation of misfueling of gasoline into kerosene heater and (B) simulation of an arson fire using kerosene. Conditions: gas sampling volume, 100 mL ; column, HR–1 fused–silica capillary column (30 m × 0.25 mm I.D. film thickness 0.25 μm); oven temperature, 50°C (5 min) to 250°C (5 min) at 10°C /min ; monitoring mode, (A) FID 250°C and (B) TIM (m/z : 50–250). (B) is modified from Fig. 5 in reference 24 with permission.

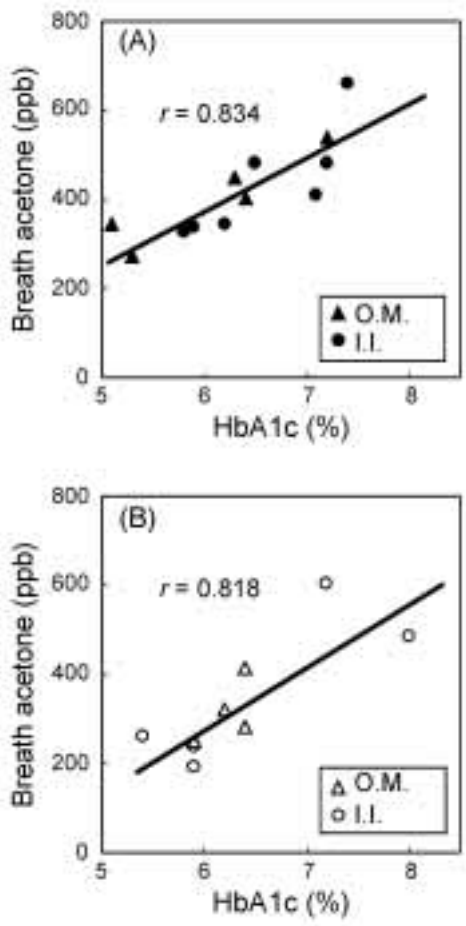

Fig. 6 Relationships between the HbA 1 c% and breath acetone concentration of controlled diabetic patients.
(A) Male patients and (B) female patients. Modified from Fig. 3 in reference 22 with permission.

profiles for the time variations of the breath and urine acetone under the fasting condition are illustrated in Fig. 7, where the X–axis indicates the duration since last meal. Urine ketone level was measured by commercially available test strips. It can be seen that the acetone concentrations in the breath and urine were gradually increased after the fasting period of about 20 h, and then, rapidly decreased after the meal. A good correlation was found between the acetone concentration of urine headspace and the results obtained with urine ketone test strips. The correlation coefficient between the acetone concentration in the breath and urine samples in Fig. 7 was 0.933, and similar higher correlations were also obtained from other three healthy subjects, $r = 0.981$, 0.980 and 0.918. Above results clearly demonstrated a good precision and versatility of proposed method, and also suggested a future possibility as an initial screening method for diabetes in medical scene [22].

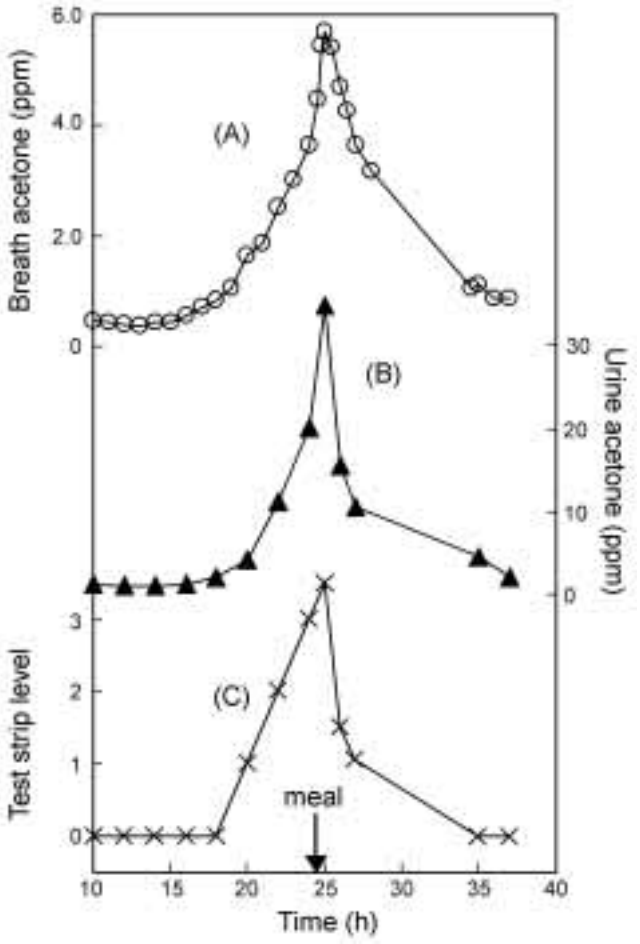

Fig. 7 Time variation profiles of breath and urine acetone in healthy male under the fasting condition. Breath acetone (A) and urine acetone (B) were measured using the particle–packed extraction needle. Urine ketone level (C) was determined by commercially available test strips (Ketostix). Modified from Fig. 4 in reference 22 with permission.

3.4. In–door room air analysis

In recent years, much attention has been paid for the multiple chemical sensitivity and/or sick building syndrome by VOCs in indoor air. In Japan, the Ministry of Health, Labour and Welfare (MHLW) adopted reference values and a measurement method for 13 VOCs in indoor air [30]. Among them, two sample preparation methods are proposed for typical VOCs: solvent desorption and thermal desorption (TD) followed by GC analysis [31]. However, these methods have some disadvantages as described above. In addition, in the guideline established by the MHLW, the officially–stated sampling time of the gaseous sample is approximately 30 min.

In this study, a novel needle–type sample preparation device was specially developed for the effective preconcentration of VOCs in indoor air samples. Four types of sorbent particles, including MA/EGDMA, Tenax TA, DVB and AC–based particle of Shincarbon ST, and their multi–bed combinations were investigated on the basis of the evaluation of their extraction and desorption performance for standard samples. Successful extraction and desorption of VOCs sample were accomplished using a double–bed sorbent packed with DVB and AC particles in series. The optimum packing length of the packed sections of DVB and AC were determined to be 25 and 5 mm, respectively. This extraction needle was designed for the extraction of low–volatility organic compounds (LVOCs) on the DVB sorbent and high–volatility organic compounds (HVOCs) on the AC sorbent. To confirm this extraction behavior, several VOCs were extracted by DVB–packed needle and DVB/AC–packed needle as demonstrated in Fig. 8. For the DVB/AC–packed extraction needle, the peak areas of all the investigated VOCs increased linearly up to a sampling volume of approximately 800 mL (40 min), whereas for the DVB–packed needle, clear symptoms of breakthrough were observed, especially for HVOCs. After the optimization of several desorption conditions, such as desorption temperature, desorption gas volume and desorption time, more than 99.9% of extracted analytes were desorbed in a single desorption without any observable carryover. Extraction recovery of the needle was also more than 99.9% for typical VOCs, and the recovery was not susceptible to humidity when extracting VOCs.

The LOQs of typical VOCs in the proposed method are less than 0.01 ng/L, showing the sufficient sensitivity of typical VOCs. The relative standard deviations (RSDs) of the peak areas for each compound for 50 ng/L standard samples using one extraction needle ($n = 5$) were less than 5.0%, and the RSDs of needle–to–needle comparisons using five different extraction needles were less than 7.0%. The storage performance of the extracted VOCs in the extraction needle was also evaluated, and the results demonstrate an excellent storage performance of the developed needle for up to 3

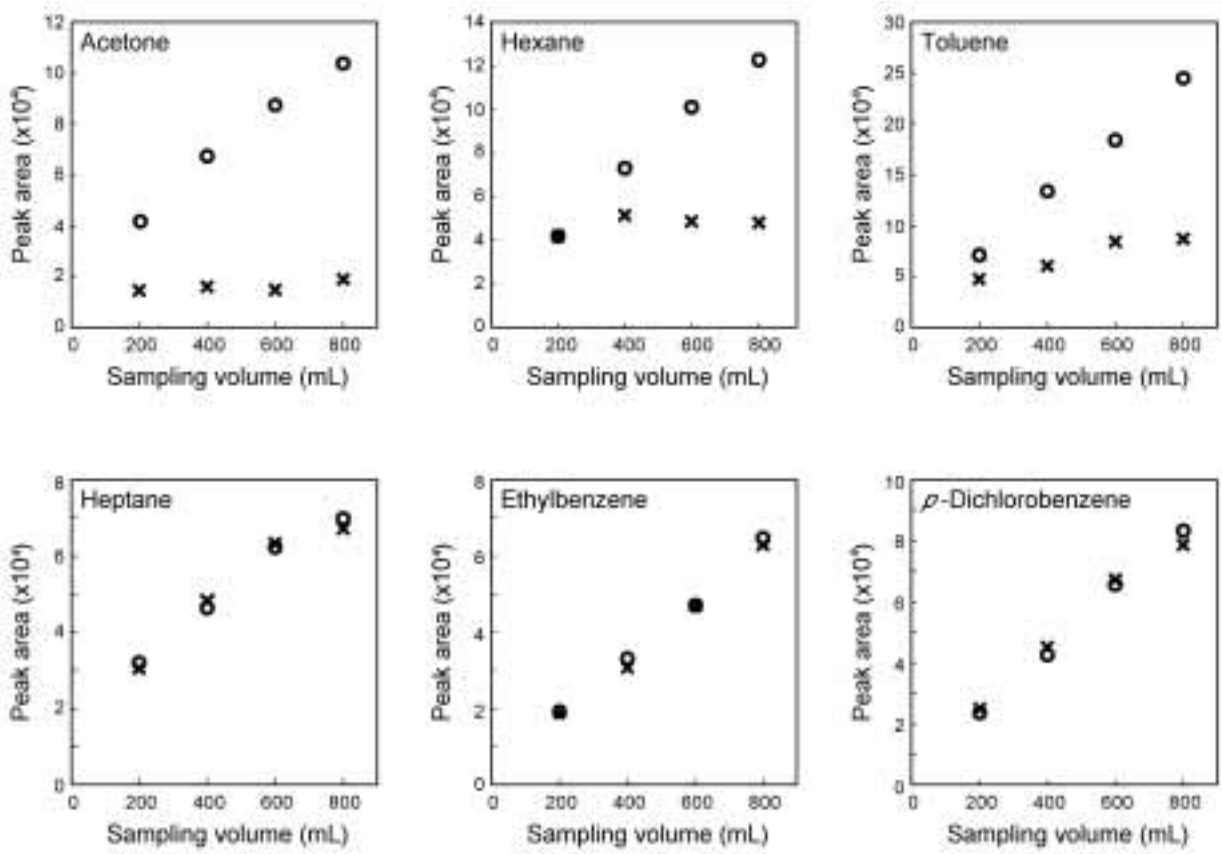

Fig. 8 Sampling volume profiles of the DVB/AC–packed needle (circles) and DVB–packed needle (crosses). Conditions: standard gas sample concentration, 50 ng/L; sampling rate, 20 mL/min. Modified from Fig. 5 in reference 25 with permission.

days at room temperature.

The developed method was applied to the real indoor air analysis, and the results were compared to that obtained in the conventional solvent extraction method. Four compounds, including toluene, ethylbenzene, xylene and styrene, were quantified by both analytical methods in 11 rooms. A significantly large data difference could be found especially at a high toluene concentration. One of the reasons for this difference could be the loss of volatile compounds during solvent evaporation in the solvent extraction method [31]. At low concentrations, a good agreement was observed between the data for these two extraction methods for all the analytes. Although further study is needed for a more precise comparison of the developed extraction method and the conventional one, the benefits of the needle extraction device, such as a simple and rapid desorption process, for the analysis of indoor air VOCs were clearly demonstrated in the real sample analysis, and most of the obtained results showed a good agreement with those of a conventional solvent extraction method [25].

4. Conclusions

The needle–type extraction devices were successfully developed for the analysis of VOCs in several environmental air samples. The analytical method using the needle–type devices allows rapid, simple and precise extraction/desorption for sensitive determination of VOCs in GC, and also overcoming several drawbacks which are frequently found in traditional sample preparation methods. Further applications of the needle extraction method could be expected for other analysis, such as initial screening of several diseases based on the proposed breath analysis method and determination of VOCs in water and soil samples. In order to be a more popular analytical method, this technique should be further investigated, including development of automatic extraction and desorption instruments with the needle–type extraction device.

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