Simultaneous Derivatization and Extraction of Volatile Amines with Fiber-Packed Needle and Subsequent Analysis in Gas Chromatography

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Abstract
A needle-type sample preparation device packed cyclohexanone-coated fibers as an extraction medium has been developed for the gas chromatographic (GC) analysis of volatile amines in air samples. For a simultaneous derivatization/extraction of monoethanolamine (MEA), a fiber-packed needle was employed, where a bundle of heat resistant filaments, Zylon, poly(p-phenylene-2,6-benzobisoxazole) was packed longitudinally into the specially-designed needle. To the needle-type device, cyclohexanone was loaded in the preconditioning process. Gaseous MEA was sampled by a vacuum air sampler connected to the needle, and a simultaneous derivatization/extraction was carried out therein. Desorption of MEA derivative was successfully made at a heated GC injection port without using any desorption solvent. Introducing the simultaneous derivatization with cyclohexanone, the sensitivity was significantly improved, allowing a more sensitive detection of volatile amines. Taking advantage of the specially-designed needle, the needle was able to be stored for several days at room temperature after the sampling, where the derivatives of the volatile amines were stably trapped on the surface of the Zylon filaments in the needle.

Keywords: Derivatization; Extraction; Monoethanolamine; Fiber; Needle extraction device; Gas chromatography

1. Introduction
Monoethanolamine (MEA), 2-aminoethanol, is widely used in the chemical industry such as a buffer, chemical intermediates, coatings, plasticizers, surface active agents, emulsifier in cosmetic formulations, wetting agent, alkalinizing agent and several other applications. The industrial hazards associated with the production and handling of MEA are skin and eye irritation [1,2]. The U.S. National Institute of Occupational Safety and Health (NIOSH) has adopted an exposure limit of 7.5 mg/m³ (7.5 ng/mL, 3 ppm) for MEA as time-weighted average values [3], and several analytical methods have been reported for the determination of MEA in air samples [4-10].

Derivatization of the target analyte is a method of choice to enhance the sensitivity, and a wide variety of derivatization reagents and the corresponding derivatization reactions have been developed [6-17]. Introducing a derivatization reaction before the analysis, the detectivity and sensitivity can be significantly improved. However, a type of sample preparation technique is often necessary for a selective and sensitive detection of target compounds, because the sample preparation step not only enhance the sensitivity of the analytes but also eliminate interferences from other compounds contained in the sample matrix.

Regarding the recent approach to the effective sample preparation, miniaturized sample preparation techniques have been developed, where a simultaneous processing of sample collection (sampling) and preconcentration is possible in small sample preparation device containing particulate extraction media [18-34]. On the basis of successful applications of the fiber-packed columns [35-40], a bundle of synthetic filaments as extraction medium was also introduced as the extraction medium, where several hundreds of the fine polymeric filaments were...
longitudinally packed into a specially-designed miniaturized extraction cartridges [41-47] or a needle-type device [11-17]. With the needle device, a trace amount of analytes in gaseous sample matrix could be extracted onto the surface of the fine filaments in the needle by simply passing the gas samples into the needle. The extracted analytes are desorbed by a heated injector in a gas chromatograph (GC) as similar to a conventional injection procedure in GC. In our previous studies, it has been demonstrated that a successful simultaneous processing of the derivatization and extraction [11-17]. Introducing the derivatization reactions in the needle extraction device, a simultaneous processing of sample collection, analyte derivatization and preconcentration is possible in a miniaturized sample preparation device.

As one of the extension of the previous investigations, in this work, a simultaneous derivatization/extraction of MEA was studied. The fundamental extraction performance of the fiber-packed needle extraction device was evaluated along with the optimization of several experimental parameters for the derivatization, extraction and desorption. Taking into account the on-site applications including the air environment analysis, the storage performance of the needle device for the extracted analytes under the room temperature was investigated. Applications to other volatile amines were also studied.

2. Experimental

2.1. Reagents

All solvents and reagents were of analytical grade, and used without further purification. MEA, cyclohexanone, acetonitrile (ACN), n-butylamine and ethylenediamine were purchased either from Wako Pure Chemical, Osaka, Japan or Kishida Chemical, Osaka, Japan.

2.2. Preparation of standard gas samples

Standard MEA gas samples having the corresponding required concentration were prepared as follows. First, a mixture of ACN and MEA (with molar ratio of 10:1, respectively) was prepared. Next, 5.2 μL of the solution was injected into a vacuum glass vessel having 1.0 L volume, where N₂ gas was used for dilution after the evaporation of the mixture in the vessel. Then, a few milliliters of above gas sample was injected into a gas sampling bag (1.0 L volume, Tedlar Bag; GL Sciences, Tokyo, Japan) and diluted with pure N₂, allowing the preparation of a set of standard gas samples of the corresponding desired concentration in the gas sampling bags. A similar process was repeatedly done for the standard gas samples having lower concentrations.

2.3. Preparation of the extraction needle

As heat-resistant fiber, Zylon, poly(p-phenylene-2,6-benzobisoxazole) was obtained from Toyobo, Otsu, Japan. For the preparation of the extraction needle, a bundle of the Zylon filaments, having ca. 11.5 μm o.d., was packed into the specially-designed needle (0.5 mm i.d., 0.7 mm o.d., 85 mm length). As described previously [13-17], a section about 30-mm length was packed with the filaments longitudinally, and one end of the packed section was positioned just before the side-hole near at the tip of the needle, where the total number of packed filaments were 664. In order to ensure the parallel alignment of all of the filaments in the needle, the packing process was carried out as follows [48,49].

An appropriate length of poly(vinylidene fluoride) (PVF) fishing line (64 μm o.d.) was inserted as a guide into the needle. The end of the PVF guide fiber has an extra length to form a loop outside of the needle, and then, second PVF fiber is inserted into the loop of the first guide fiber, and next, the first guide fiber is pulled from the other end of the needle. The bundle of filaments (a pre-cut length of 60 mm for a 30-mm packed section) to be packed is inserted into the loop of the second guide fiber, where the front-end of the bundle should be appropriately bent to make sure a smooth introduction. The second PVF guide fiber is pulled from the side-hole of the needle carefully to produce uniform introduction of the bundle. Finally, the second guide fiber is pulled out the needle with care, and then fiber-packed needle is attached to the syringe connector.

2.4. GC measurements

A GC-2014 gas chromatograph (Shimadzu, Kyoto, Japan) with a split injection port and a flame ionization detector (FID) was used for all the GC measurements. All the measurements were carried out by a split mode with a typical ratio of 100:1. Injector temperature was typically set at 270°C. N₂ was used as the carrier gas. For the GC separation, a fused-silica column coated with polydimethylsiloxane, HR-1 (0.25 mm i.d., 30 m length, 0.25 μm film thickness; Shinwa Chemical Industries, Kyoto, Japan) was employed with an appropriate preconditioning before use. Column temperature and detector temperature were set at 120°C and 270°C, respectively. The other separation conditions, such as carrier gas flowrate, column head pressure were systematically determined by the results of the preliminary experiments. Data was collected with ChromNAV Chromatography Data Handling Software (Jasco, Tokyo, Japan) running on a personal computer.

2.5. Derivatization/extraction and injection with the fiber-packed needle

On the basis of the preliminary experiments for the derivatization in the needle-type extraction device, as shown in Fig. 1, a derivatization reaction was carried out with cyclohexanone as the derivatization reagent. As
shown in Fig. 2, the sample preparation procedure was carried out as follows: (a)-(b) before the introduction of gas samples, cyclohexanone was pumped into the fiber-packed needle, and then (c) the remaining solution was vented by passing 20 mL of N₂ gas. Next, (d) the fiber-packed needle was attached to a commercially-available vacuum sampling device (Komyo Rikagaku Kogyo, Tokyo, Japan).

For the extraction process, the needle was inserted into the gas sampling bag containing gaseous MEA, and then the gas sample was vacuumed into the vacuum sampling device through the fiber-packed extraction needle containing cyclohexanone. Typical sampling volume was 50 mL. The completion of the gas sampling for each run was confirmed by the indicator equipped in the vacuum sampling device. After extraction and derivatization process, the needle was attached to as injection syringe containing pure N₂ gas, and inserted to the injection port of GC, as shown in Fig. 2e. Desorption and injection were simultaneously carried out by the flow of N₂ through the needle at the heated injection port.

The desorption temperature, volume of desorption gas and desorption time were optimized as 270ºC, 1.0 mL and 5.0 second, respectively, on the basis of preliminary experiments. The sampling flowrate was estimated as 10 mL/min on the basis of the sampling volume and time required for the sampling when the fiber-packed needle was attached directly to the sampling device. However, the derivatization/extraction was insufficient at a sampling flowrate of 10 mL/min. Therefore, the flowrate was optimized by connecting a stainless-steel capillary (0.13 mm i.d., 0.31 mm o.d.) as a restrictor between the needle and the aspirator, where the length of the capillary was hanged for the optimization. Since the recovery was almost constant at a flowrate slower than 1.43 mL/min, the flowrate obtained with a stainless-steel capillary of 40 cm length was used for the derivatization of volatile amines for further experiments.

3. Results and discussion

3.1. Determination of MEA

Under the optimized conditions, MEA gas was determined by the GC in the concentration range from 0.1 to 200 ppm, corresponds from 0.250 to 500 ng/mL. Since the amino group reacts with cyclohexanone, the peak shape was improved due to the decrease of amino groups. The peak area of MEA derivative was proportional to the MEA concentration of the sample gas, and the correlation coefficient (r) of the calibration curve was more than 0.99. All RSDs were less than 5% for the quantification of gaseous MEA sample using fiber-packed needle with cyclohexanone as the derivatization reagent. The RSD is only 4.3% even at the lowest concentration studied, 0.1 ppm (0.250 ng/mL), indicating a good reproducibility for the determination of MEA with the fiber-packed needle. The limit of detection (LOD) and the limit of quantitation (LOQ) for MEA using fiber-packed needle were 0.035 ng/mL (0.014 ppm) and 0.12 ng/mL (0.047 ppm), respectively. The LOQ was less than one tenth of the exposure limit recommended by NIOSH [3], showing that the developed method has a good quantification ability for practical applications.

In order to evaluate the desorption performance, the second and third injections were carried out without further sampling after the first injection. The results in Fig. 3 demonstrated that the peak area of MEA derivative at the second injection was less than LOQ, and also that no peak was detected in the third injection. Therefore, single and simple desorption with heating in a conventional GC injector is satisfactory to desorb more than 99.99% of the MEA derivative.

3.2. Evaluation of storage performance

The storage performance of the needle device was evaluated. After the gaseous MEA sample was extracted in the needle, it was sealed with a set of the plug and cap manufactured by a small piece of polytetrafluoroethylene (PTFE), as shown in Fig. 4, and stored at room temperature.
(about 24°C) for 72 hours. The storage performance of the fiber-packed needle was summarized in Table 1. The recovery was calculated based on the immediate quantification. As can be seen in the Table 1, the loss of the gaseous MEA sample in the fiber-packed needle was only 7.7% even after three days at room temperature. The reason for the slight loss of the sample after three days at room temperature was considered to be a leak from the gap between the needle and the plug or cap. However, as can be seen in Table 1, an immediate GC measurement after the sampling is not necessary with this needle device, suggesting an advantageous feature for the large number of on-site sampling at the same time.

### 3.3. Evaluation of extraction capacity

For the evaluation of extraction capacity, as illustrated in Fig. 5, two needles, a front needle and a back needle, were connected, and the end side of the back needle was attached to an aspirator. A gaseous MEA sample (50 mL) containing concentration of 125 ng/mL (50 ppm) was vacuumed through the needles from the front needle side. If MEA was overflowed from the front needle, the overflowed MEA was collected by the back needle. The operation was continuously repeated several times until the MEA derivative was detected from the back needle, allowing the determination of the maximum extraction capacity of the fiber-packed needle to MEA.

### Table 1. Storage performance of the needle extraction device for MEA at room temperature.

<table>
<thead>
<tr>
<th>storage time (h)</th>
<th>recovery (%)</th>
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<tbody>
<tr>
<td>0</td>
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<tr>
<td>1</td>
<td>100.7</td>
</tr>
<tr>
<td>6</td>
<td>98.4</td>
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<tr>
<td>24</td>
<td>95.0</td>
</tr>
<tr>
<td>72</td>
<td>92.3</td>
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</table>

The values are calculated as the recovery (%) based on the immediate analysis. Extraction conditions: flow-rate, 2.5 mL/min; sampling volume, 50 mL; desorption temperature, 270°C; analyte, MEA (200 ppm) in N₂. GC conditions: GC column, HR-1; column temperature, 120°C; column head pressure, 115.5 kPa; injection mode, split; split ratio, 1:100.
The relationship between the aspiration volume of the MEA gas sample and the peak area of the detected MEA derivative is shown in Fig. 6. In the front needle, the peak area was increased until the sampling volume up to 400 mL. In the case of the back needle, the MEA derivative was detected when the sampling volume was 400 mL or more. The peak area for the MEA derivative detected from the front needle increased proportionally to the sampling volume of less than 350 mL. The maximum extractable volume for the MEA sample was calculated as about 357 mL on the basis of the above data and calibration curve in Fig. 6. As 45 µg of MEA is contained in the above maximum extractable volume of the gaseous MEA sample, the adsorption capacity of the fiber-packed needle to the MEA was estimated as approximately 45 µg per needle.

3.4. Application to other amines

Upon successful determination of MEA with the developed method, the fiber-packed needle was applied to the determination of other amines, n-butylamine (NBA) and ethylenediamine (EDA), as shown in Fig. 7. For the simultaneous derivatization/extraction for NBA, a gaseous NBA of 600 ng/mL (200 ppm) was aspirated through the fiber-packed needle including cyclohexanone therein, where the extraction conditions are the same as that optimized for MEA.

\[ \text{(a) NBA} \]

\[ \text{(b) EDA} \]

Fig. 7. Reaction scheme of the derivatization reaction for (a) NBA and (b) EDA with cyclohexanone.

A significant improvement by the in-needle derivatization was confirmed using the fiber-packed needle, because unreacted NBA was not detected (Fig. 8a). In the case of EDA, two types of reaction products were expected. For the separation of the EDA derivatives, two peaks were observed as found in Fig. 8b. The first peak was considered as the reaction product of an EDA molecule and a cyclohexanone molecule, and the second peak was also considered as the reaction product of an EDA molecule and two cyclohexanone molecules. As the same as NBA, unreacted EDA was not observed, and the sensitivity was significantly improved using the needle with cyclohexanone therein as the derivatization reagent. The results also suggest that the fiber-packed needle device could be a powerful tool for simultaneous derivatization and extraction of not only MEA but also other volatile amines.

4. Conclusions

In this work, a fiber-packed sample preparation needle with cyclohexanone, as the derivatization reagent, for simultaneous derivatization/extraction of MEA in air samples, has been developed for the GC analysis. This method only requires very short processing time compared other conventional techniques [4-9]. A very simple operation is another advantageous feature of the needle extraction device, allowing a large number of on-site sampling at the same time, a significant decrease in the potential risk of sample loss during tedious multi-step processing. Furthermore, the desorption solvent is not necessary for the desorption of the derivatives using a heated GC injection port.

The extracted sample was determined even after the storage at room temperature for at least three days. The excellent storage power of the fiber-packed needle sample preparation device is quite remarkable. An improvement in the peak shape of amines in the subsequent GC analysis can be also expected after the derivatization reaction with cyclohexanone. Compared to other techniques reported earlier [4,5], the developed method showed a good sensitivity to gaseous MEA, suggesting a future possibility to real air samples analysis.
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References

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