Development of a Portable Instrument for the Continuous Analysis of Volatile Organic Compounds (VOCs) and Its Application to Environmental Monitoring

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A small, time efficient and sensitive instrument for the continuous analysis of very volatile organic compounds (VOCs) with a boiling point lower than 100°C in addition to the analysis of VOCs with a boiling point in the range of 100–150°C was developed and applied to the measurement of VOCs in the course of university research and environmental monitoring. VOCs, such as n-hexane, acetone, ethyl acetate, alcohols, benzene, toluene and xylene, were continuously measured once every 30 min. The detection limits of hexane, ethyl acetate, benzene and toluene at a preconcentration time of 10 min were 0.41 µg/m³ (0.12 ppb), 0.67 µg/m³ (0.19 ppb), 0.22 µg/m³ (0.07 ppb) and 0.22 µg/m³ (0.06 ppb), respectively. The relative standard deviations of VOCs were less than 5%. The sensitivities of the present method VOCs were higher than those of the conventional method. The temporal changes in VOC concentrations in several laboratories and at a plant for the disposal of organic liquid wastes were measured, and the behavior of VOCs was analyzed. All the VOC concentrations, except that of ethyl acetate, determined using the portable instrument were slightly lower than those determined using a passive sampler. The portable instrument developed in the course of this study can be used for the risk assessment and management of chemicals.

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1. Introduction

Volatile organic compounds (VOCs) are substantial contributors to the formation of ozone and other photochemical oxidants. Some VOCs have been identified as toxic or mutagenic pollutants at concentrations sometimes present in urban environments.\(^{(1)}\) In particular, benzene is an aromatic VOC characterized by the U.S. Environmental Protection Agency as a human carcinogen.\(^{(2)}\) In Japan, the assessment of the human health risk due to exposure to ambient VOCs is limited due to the paucity of available data on VOC levels, which are not routinely monitored in many locations throughout Japan.\(^{(3,4)}\) In a previous study, a simple analysis of VOCs at low levels in the atmosphere was conducted using passive samplers, and the behaviors and origins of VOCs in Kyoto City were analyzed.\(^{(5)}\)

Furthermore, it is important to elucidate the human health risk and environmental load due to the occurrence of VOCs in the course of research. The Labor, Safety, and Health Law started to apply to Japanese universities in 2004. A portable instrument is necessary for the continuous analysis of chemicals with a boiling point (bp) lower than 100°C in addition to the analysis of chemicals with a bp in the range of 100–150°C, because these chemicals are often used in research. VOCs are classified into very volatile organic compounds (VVOCs) with a bp lower than 100°C and VOCs with a bp in the range of 100–260°C by WHO.\(^{(6)}\) For the continuous analysis of VOCs, the uses of a nonmethane hydrocarbon analyzer, a GC system with a photoionization detector, and a GC-MS system after collecting VOCs with an adsorbent have been reported; however, these instruments are not portable.\(^{(6–8)}\) Although some portable VOC monitors are commercially available, they were developed for the analysis of VOCs with a bp higher than 100°C, and the constituents of VOCs cannot be detected.\(^{(9)}\) We therefore developed a small, time efficient and sensitive instrument for the continuous analysis of VOCs with a lower bp than 100°C such as hexane, ethyl acetate and benzene in addition to toluene and xylene.\(^{(10)}\) However, as the separation of VOCs with a bp lower than 100°C is not very good in a packed column and these VOCs are often used in the course of research, the use of a capillary column was investigated in this study. The use of a capillary column improved the separation of VOCs with a boiling point lower than 100°C. This improved instrument was applied to the measurement of VOC constituents in the course of university research and environmental monitoring. The VOCs investigated in this study and their bps are listed in Table 1.

Table 1
Classification of volatile organic compounds (VOCs) according to boiling point.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Boiling point</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>VVOCs *</td>
<td>50–100°C</td>
<td>acetone (56.3), methanol (64.7), n-hexane (68.7), ethyl acetate (76.8) ethanol (78.3), benzene (80.1)</td>
</tr>
<tr>
<td>VOCs</td>
<td>100–260°C</td>
<td>toluene (110.6), ethyl benzene (136.2), p-xylene (138.4), m-xylene (139.1) o-xylene (144.4), styrene (145.2)</td>
</tr>
</tbody>
</table>

* VVOCs: very volatile organic compounds
The values in parentheses are the boiling points (°C) of the solvents.
2. Materials and Methods

2.1 Reagents and apparatus

A mixture of reference VOCs (hexane, acetone, ethyl acetate, benzene, ethyl benzene, toluene, o-xylene, m-xylene and p-xylene, 1 mg/ml each) in carbon disulfide (CS₂) was prepared by diluting chemicals obtained from Wako Pure Chemicals (Osaka). Standard solutions of these compounds were prepared by diluting the above-described solution with CS₂. All other chemicals were of analytical reagent grade.

A GC-14B gas chromatograph equipped with a flame ionization detector (FID) (Shimadzu, Kyoto) and a GC-MS QP5050A (Shimadzu, Kyoto) were used.

2.2 Determination of atmospheric VOCs with passive and active samplers

Gas-tube samplers (Shibata, Tokyo) packed with activated carbon (20–40 mesh, 200 mg) were used as passive samplers for the determination of VOCs. After the VOCs adsorbed on the samplers were extracted and then placed into 1 ml of CS₂ in a septum vial, and 1 l of an extracted sample was injected and measured by FID-GC or GC-MS. The GC column was a capillary column, J&W Scientific DB-VRX (0.45 mm × 75 m, 2.55 μm film thickness), and helium was used as the carrier gas. The injection temperature and detection temperature were maintained at 200°C and 250°C, respectively. The column temperature was maintained at 35°C for 5 min, increased from 35°C to 200°C at a rate of 5°C/min, and held at 200°C for 10 min.

The daily mean VOC concentration, C (μg/m³), during the exposure time, t (min), was calculated using the following equation:

\[ C = \frac{10^6 M}{Kt} \]  \hspace{1cm} (1)

where M is the amount of VOC in μg and K is the sampling rate (ml/min). The values of the sampling rate for benzene, toluene, p-xylene and o-xylene are 54.8 ml/min, 47 ml/min, 42.2 ml/min, and 42.2 ml/min, respectively.

Activated carbon tubes for the organic gas sampler (20–40 mesh, 50 and 100 mg, Shibata, Tokyo) were used as an active sampler for the determination of VOCs using a pump at a flow rate of 0.1 L/min. The VOCs adsorbed on the active samplers were determined according to a procedure similar to that for the VOCs adsorbed on the passive samplers.

2.3 Instrument developed for continuous analysis of VOCs

A flow chart of the small instrument (440(W) × 340(H) × 270(D) mm) used for the continuous analysis of VOCs is shown in Fig. 1. The analytical procedure for VOCs is based on gas chromatography.

This instrument was operated as follows. After the sample gas is injected into this instrument from the input (A) by the pump (P2) at a flow rate of 0.1 L/min, gaseous VOCs are preconcentrated on the adsorbent (I, Tenax TA, 40 mg) at room temperature (15 s – 10 min) and desorbed by heating at 150°C. Then, by changing the position of the switching valve, the VOCs desorbed are introduced into a metal capillary column (II, Ultra alloy UAC-W, polyethylene glycol, 0.53 mm × 30 m, 1.0 μm film thickness) and separated at 50°C.
Separated VOCs are detected by two semiconductor gas sensors, D1 (Figaro 2600) and D2 (Figaro 2602). VOCs are detected through a decrease in the resistances of the tin oxides of these gas sensors. Compressed air, after eliminating water and VOCs with silica gel and activated carbon, is used as a carrier gas, at a flow rate of 6.6 ml/min. After the desorption of VOCs, the adsorbent is purged with this compressed air at 150°C and cooled down for the next measurement.

A standard gas (0.31 ppm each of toluene, p-xylene, ethyl-benzene and styrene, N₂ balance; Sumitomo Seika Chemicals Co., Ltd.) and the dilution method were used for the calibration of this instrument. Hexane, acetone, methanol, ethanol, ethyl acetate, benzene, ethyl benzene, toluene, o-xylene, m-xylene and p-xylene obtained from Wako Pure Chemicals (Osaka) were used for the dilution method.

3. Results and Discussion

3.1 Improvement of VOC separation

A packed column [SP-1200 + Bentone 34 (5+1.75)% Uniport HP 80/100 mesh, 2 φ x 2 m] was used at 60°C. However, the separation of VOCs with a bp lower than that of benzene was not very successful. Therefore, the use of a metal capillary column (UA-CW, 0.53 mm x 30 m) was investigated. Gas chromatograms of standard VOCs at 50°C are shown in Fig. 2. The separation of n-hexane, ethyl acetate and benzene with the capillary column was better than that with the packed column. Accordingly, the metal capillary column was used instead of the packed column in this portable instrument. An unidentified peak (RT =

Fig. 1. Flow chart of small instrument used for continuous analysis of VOCs.
7.3 min) was detected by the D1 gas sensor. This may have been due to water. VOCs, such as n-hexane, ethyl acetate, alcohols, benzene, toluene and xylene, can be continuously measured once every 30 min with this instrument.

The calibration curves of benzene, ethyl acetate and toluene determined by two semiconductor gas sensors, D1 and D2, are shown in Fig. 3. Good linear calibration curves were obtained. The sensitivities for all the VOCs with a bp lower than 100°C, except acetone, were almost the same as that of benzene determined by the D1 sensor. On the other hand, the relative sensitivities for VOCs with a bp higher than 100°C compared with that for benzene were lower than 0.5 using the D1 sensor and about 4.0 using the D2 sensor. D1 is a sensitive gas sensor for VOCs with a bp lower than 100°C, whereas D2 is a sensitive gas sensor for VOCs with a bp higher than 100°C. From these results, the concentrations of VOCs with a bp lower than 100°C were calculated from the data from the D1 sensor, and those of VOCs with a bp higher than 100°C were calculated from the data from the D2 sensor. However, chlorinated organic compounds such as chloroform cannot be detected with these semiconductor gas sensors because these sensors are not sensitive to chlorinated organic compounds. The detection limits of hexane, ethyl acetate, benzene and toluene at the preconcentration time of 10 min were 0.41 µg/m³ (0.12 ppb), 0.67 µg/m³ (0.19 ppb), 0.22 µg/m³ (0.07 ppb) and 0.22 µg/m³ (0.06 ppb), respectively. The relative standard deviation of benzene at a concentration of 200 µg/m³ was less than 5% (n = 5). However, the detection limits of benzene and toluene by GC-MS after the adsorption of benzene and toluene using active carbon for 30 min were 13.7 µg/m³ and 16.4 µg/m³, respectively. From these results, the sensitivities of the present method for VOCs were higher than those of conventional methods (FID-GC or GC-MS after adsorption of VOCs using activated carbon).
3.2 A comparison of VOC data obtained with use of portable instrument and passive sampler

The concentrations of VOCs were also measured using a passive sampler and compared with those obtained with the portable instrument. The relationships between the results for hexane and ethyl acetate using continuous analysis (y) and the passive sampler (x) are shown in Fig. 4. The regression equations for hexane and ethyl acetate were \( y = 0.293x + 6.48 \) (\( R^2 = 0.413 \)) and \( y = 1.26x - 0.335 \) (\( R^2 = 0.371 \)), respectively. The regression equations for benzene and toluene were \( y = 0.433x + 0.19 \) (\( R^2 = 0.801 \)) and \( y = 0.265x + 0.007 \) (\( R^2 = 0.87 \)), respectively. All the VOC concentrations, except that of ethyl acetate, obtained with the portable instrument were slightly lower than those obtained with the passive sampler.

3.3 Temporal changes in concentrations of VOCs in several laboratories and at disposal plant using a portable instrument

The concentrations of VOCs were continuously measured using this portable instrument in three laboratories (L1–L3) and at a plant for the disposal of organic liquid wastes. The pre-concentration time was 15 s. The temporal changes in the concentrations of hexane, ethyl acetate and benzene obtained in an organic chemistry laboratory (L2) from March 3 to 13, 2005, are shown in Fig. 5. VOCs with a bp lower than 100°C were detected by the D1 sensor, whereas VOCs with a bp higher than 100°C were detected with the D2 sensor. The area of the L2 room was 50 square meters and two drafts were installed on the south side of the room. Two 10-liter polyethylene containers for waste solvents were placed at the side of the draft. There were a ventilation fan and an air conditioner at the top of the windows and the ventilation fan, air conditioner and drafts were confirmed to work in the experiment.

The concentrations of hexane and ethyl acetate were especially high at 12:00–13:00 on
Clear peaks of hexane and ethyl acetate were attributed to the column chromatography procedure using a mixture of hexane and ethyl acetate in the experimental room. The concentrations of VOCs and their variations in the daytime were higher than those obtained at night. Furthermore, the results showed that

Fig. 4. Relationships between results for hexane (A) and ethyl acetate (B) using continuous analysis (y) and passive sampler (x).

Fig. 5. Temporal changes in concentrations of VOCs in organic chemistry laboratory (March, 2005). hexane, ethyl acetate, benzene.

3/5, at 12:00–19:00 on 3/7 and at 10:00–20:00 on 3/12. Clear peaks of hexane and ethyl acetate were attributed to the column chromatography procedure using a mixture of hexane and ethyl acetate in the experimental room. The concentrations of VOCs and their variations in the daytime were higher than those obtained at night. Furthermore, the results showed that
the concentrations of VOCs also increased after closing the room at night and remained nearly constant before opening the room the following morning on 3/6, 3/7, 3/8, 3/9 and 3/12. These results suggest that gaseous VOCs may be present while experiments are being performed and in the evenings and on holidays, when chemicals are not used.

Temporal changes in the concentrations of benzene, toluene and T-LVOCs indoors at the plant for the disposal of organic liquid wastes are shown in Fig. 6. T-LVOCs are shown as the total concentration of VOCs with bp lower than that of benzene. The disposal of organic liquid wastes was performed from 9:00 to 16:00. The room was opened at 8:00 and closed at 18:00 during the disposal period. For example, on 10/28, the concentrations of benzene, toluene, and T-LVOCs increased at 10:00, 12:00 and 15:00. These results indicate that the concentrations of VOCs in the disposal plant increased during the transport process when liquid organic wastes were pumped from a polyethylene container into the tank. Moreover, the VOC concentrations also increased after closing the plant at 18:00 and remained nearly constant before opening the room at 8:00 the next morning; the results were similar to those obtained in the experimental room. The increase in the concentrations of VOCs may be due to the vaporization of VOCs in polyethylene containers and the tank of organic liquid wastes.

Furthermore, the VOC concentrations obtained outdoors at the plant for the disposal of organic liquid wastes were continuously measured at a preconcentration time of 10 min. The measurements were taken for one week (A) during normal operations and for one week (B) when the plant was closed. Temporal changes in the concentrations of hexane, ethyl acetate and benzene measured outdoors at the plant for the disposal of organic waste under conditions (A) and (B) are shown in Fig. 7. The outdoor VOC concentrations were
considerably lower than those obtained indoors. Moreover, the outdoor VOC concentrations under condition (A) were higher than those under condition (B) because the plant for the disposal of organic liquid wastes was in operation. In particular, the hexane concentration was higher than 100 µg/m³ from 14:00 to 20:00 during normal operation. The concentrations of ethyl acetate under conditions (A) and (B) were 1.2–38.5 µg/m³ and 1.1–44.9 µg/m³, respectively. The concentrations of benzene and toluene were low.

3.4 Behavior of VOCs in course of university research

The analytical results of VOC concentrations in the course of research at Kyoto Institute of Technology from 2004 to 2005 are listed in Table 2. Hexane, ethyl acetate and benzene were detected at fairly high levels. The toluene concentration was low, and no xylene was detected. The ranges of the VOC concentrations were considerably lower than the legal criteria. The legal criteria for hexane, ethyl acetate, benzene and toluene are 40 ppm, 200 ppm, 1 ppm and 50 ppm, respectively. The hexane concentration in the organic chemistry laboratory (L2) showed a high level in the range of 990–22,300 µg/m³ (0.28–6.3 ppm) in July, but maintained a lower level of about 200–5000 µg/m³ in March and December. The seasonal changes in the concentrations of ethyl acetate, benzene and toluene were small. Moreover, the VOC concentrations in the organic chemistry laboratory during the operating time (8:00–22:00) were compared with those at night (22:00–8:00) (Table 3). The VOC concentrations during the operating time were higher than those obtained at night in March.
Table 2
Analytical results of VOC concentrations measured indoors and outdoors in organic chemistry laboratories and at plant for disposal of organic liquid wastes in Kyoto Institute of Technology.

<table>
<thead>
<tr>
<th>Sampling station</th>
<th>VOC concentration (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hexane</td>
</tr>
<tr>
<td>Organic chemistry laboratory</td>
<td></td>
</tr>
<tr>
<td>L1 Indoors I</td>
<td>335–5870 (95–1670)</td>
</tr>
<tr>
<td>Plant for the disposal of organic liquid wastes</td>
<td></td>
</tr>
<tr>
<td>Indoors II</td>
<td>4.5–103.9 (1–30)</td>
</tr>
<tr>
<td>Outdoors V</td>
<td>4.5–103.9 (1–30)</td>
</tr>
</tbody>
</table>

The values in parentheses are the VOC concentrations (ppb).

Table 3
Comparison of VOC concentrations in the organic chemistry laboratory during the operating time (8:00–22:00) with those during night (22:00–8:00).

<table>
<thead>
<tr>
<th>VOC</th>
<th>March</th>
<th>July</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8:00–22:00</td>
<td>22:00–8:00</td>
</tr>
<tr>
<td>Hexane</td>
<td>280–2430</td>
<td>237–949</td>
</tr>
<tr>
<td>Benzene</td>
<td>189–910</td>
<td>174–758</td>
</tr>
<tr>
<td>Toluene</td>
<td>177–594</td>
<td>174–283</td>
</tr>
</tbody>
</table>

However, the VOC concentrations obtained at night were quite similar to those obtained during the operating time in July. The average temperatures in March and July were 7.5°C and 28.3°C, respectively. However, because an air conditioner was working during the operating time (8:00–22:00) in March and July, the average room temperatures were about 20°C and 25°C, respectively. These results indicate that the increase in the gaseous VOC concentrations in laboratories may depend on an increase in temperature of the room.

These results indicate that this portable instrument is very effective for the continuous analysis of VOCs at comparatively low levels in the course of university research and environmental monitoring, and that it can be used for the risk assessment and management of chemicals.

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