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Membrane introduction system for trace analysis of volatile organic compounds using a single photon ionization time-of-flight mass spectrometer

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ABSTRACT

A silicone membrane sample introduction system combined with a vacuum ultraviolet single photon ionization time-of-flight mass spectrometer (VUV-SPI-TOFMS) has been developed to detect trace volatile organic compounds in environmental air. The maximum enrichment factors of benzene, toluene, and chlorobenzene using the membrane introduction system relative to a direct introduction system were found to be 15.3, 11.0, and 12.1, respectively. The gas permeability of toluene through the silicone membrane was consistent with that of the manufacturer's reported value. The gas permeabilities of the silicone membrane used in the present study were estimated for benzene and chlorobenzene by theoretical calculations using the enrichment factors. The enrichment factors of benzene, toluene, and chlorobenzene were independent of their mixing ratios at <34 ppmv. The detection limits of benzene and chlorobenzene with the membrane introduction system were improved by one order of magnitude relative to direct introduction. Detection of almost sub-ppbv level of benzene and chlorobenzene was achieved in the membrane introduction VUV-SPI-TOFMS.

1. Introduction

Volatile organic compounds (VOCs) play an important role in the production of ozone and the organic aerosols in the troposphere. To understand the composition and concentration of VOCs in the environment, it is important to understand tropospheric chemistry. Thus, it is necessary to develop new techniques that can perform *in situ* and real-time measurement of VOCs to allow for the identification of the sources and the distributions of VOCs. Mass spectrometry (MS) is one of the most powerful techniques for quantitative and qualitative analysis of trace gases such as VOCs in the environment [1]. The main advantages of MS for air analysis are excellent sensitivity and real-time response. Several ionization methods have been developed for the analysis of gaseous organic compounds with MS. The major ionization technique for MS has been electron impact (EI) ionization [2–6]. EI ionization causes ionization by impact with thermal electron at an energy of 70 eV. EI ionization causes massive fragmentation of VOCs due to the high energy relative to ionization energies of most VOCs [7,8]. Another commonly used ionization technique for VOCs is single photon ionization (SPI) using vacuum ultraviolet (VUV) light. SPI using VUV is a threshold ionization method for analytical mass spectrometry. VUV-SPI is a soft ionization technique, which means only the precursor molecular ion peaks of most organic molecules are observed. Thus, the VUV-SPI method has been widely applied as an ionization source in mass spectrometers [7–11].

Gas chromatography–mass spectrometry (GC/MS) is a conventional technique for the analysis of VOCs in air. In this method, air samples containing VOCs are collected with containers such as denuder tubes or canisters before analysis. Another widely used method is membrane introduction mass spectrometry (MIMS). This is a selective introduction method without any extraction or pretreatment steps. The membrane selectively introduces the VOCs into the ionization source of a mass spectrometer, since the membrane has higher gas permeability for VOCs than for the main components of the atmosphere such as nitrogen and oxygen, as shown in Table 1. MIMS is widely used for the trace level detection of VOCs in environmental gaseous samples [3,5,6,12–16]. MIMS has also been used for the analysis of liquid samples [17–20]. Silicone membranes in sheet type [3,6,13–16] or hollow fiber type [12,18–21] are typically used for the MIMS. Recently, membrane introduction systems coupled with an electron impact ion source time-of-flight mass spectrometer (TOFMS) have been developed to detect VOCs in air with detection limits less than ten parts per billion by volume (ppbv) [3,5]. White et al. developed a man-transportable MIMS-TOF with an annular type of electron impact ion source [3]. Their apparatus reached ppbv detection limits for benzene, toluene, and xylene. Oh et al. achieved a detection limit

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Table 1
Gas permeabilities of the silicone membrane used in the present work for nitrogen, oxygen and aromatic hydrocarbons.

Compound	Chemical formula	Gas permeability 10^{-6} cm^3 STP cm/(s cm^2 cm Hg)	
		Reported value[a]	Present work
Nitrogen	N_2	0.028	–
Oxygen	O_2	0.060	–
Benzene	C_6H_6	–	1.33 ± 0.31[b]
Toluene	$C_6H_5CH_3$	0.913	0.66 ± 0.40[b]
Chlorobenzene	C_6H_5Cl	–	0.89 ± 0.47[b]

[a] Data from the supplier.
[b] Errors are 2σ.

of tens of ppbv for toluene using a compact TOFMS with a conventional electron impact ion source [5]. Hou et al. developed a membrane inlet interface coupled to a SPI-TOFMS with a krypton discharge lamp as an ionization source [16]. This achieved a detection limit as low as 25 ppbv for benzene. Most recently, the detection limits of VOCs by MIMS have been at sub-pptv levels. Thompson et al. have achieved a detection limit of toluene at several tens of pptv with an electron-impact-ionization quadrupole ion trap mass spectrometer equipped with a MIMS interface [22]. As well as MIMS, direct sample introduction with proton transfer reaction (PTR) MS with the detection limit of several tens of pptv for both benzene and toluene without membrane has been used for a field measurement of VOCs [23].

In the present study, a sheet-membrane introduction system was combined with a compact VUV-SPI-TOFMS developed in our laboratory to detect VOCs in environmental air at sub-ppbv level. Enrichment factors of benzene, toluene, and chlorobenzene from the membrane introduction system relative to a direct introduction method without the membrane were experimentally obtained as a function of the mixing ratios of aromatic hydrocarbons (AHs) and pressure difference across the membrane. For toluene, experimentally obtained gas permeability was compared with the manufacturer's reported value. The gas permeabilities of benzene and chlorobenzene were determined from the enrichment factors measured in the present work by theoretical calculations. The improvement in the detection limit by using MIMS relative to direct introduction methods has been estimated for these AHs with the compact VUV-SPI-TOFMS system using the membrane introduction system.

2. Experimental procedures

A cross-sectional view of membrane assembly is shown in Fig. 1. A silicone sheet membrane containing ca. 50% dimethylsiloxane (TSE221-5U, GE Momentive Performance Materials Japan, Tokyo) 50 μm thick was used to concentrate the VOCs. The membrane was placed on a stainless steel support mesh (diameter = 11.6 cm, hole diameter = 1 mm, aperture ratio = 40.3%) and set into modified ICF 152 conflat flanges seal with a Viton o-ring. The effective area of the membrane was 43 cm^2. The analyte flew into the membrane assembly through a 1/4″ stainless steel tube. The portion of the analyte that was transmitted through the membrane was introduced to a compact VUV-SPI-TOFMS. The membrane was maintained at room temperature (295 ± 3 K). The gas tubing after the membrane was heated at 70 °C to prevent adsorption of the sample VOCs on the inner surface of the tubing. Pressures of sample gases before and after the membrane were measured with capacitance manometers set at each point. The pressure before-the membrane (P_{bm}) was constant at 770 Torr (1 Torr = 133 Pa). The pressure after the membrane (P_{am}) was set to about 30, 60, 90, 120 and 150 Torr by adjusting the sample flow rate using a needle valve. The sample gases in the after membrane areas were additionally controlled with another needle valve in order to maintain the pressure inside the TOFMS before the sample gases were introduced. The enrichment factors of benzene, toluene, and chlorobenzene were determined from the signal intensities of the VUV-SPI-TOFMS obtained by both direct- and membrane introduction methods.

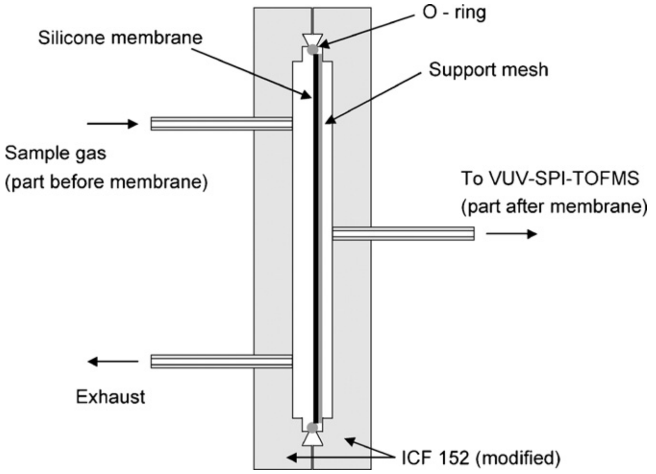

Fig. 1. Cross-sectional view of a membrane introduction assembly. A 50-μm thick silicone membrane was placed on the stainless steel support mesh. A portion of the analyte that transited the membrane was introduced to the ion source of VUV-SPI-TOFMS.

The membrane introduction system was connected to a custom-made compact VUV-SPI-TOFMS. The detailed configuration of the VUV-SPI-TOFMS has been described elsewhere [24]. The size of the VUV-SPI-TOFMS was 50 cm × 50 cm × 50 cm including the mechanical pumps. The TOFMS could be operated at a reflectron-type TOFMS (REF-TOFMS) [25] or a Wiley–McLaren (linear) type TOFMS (L-TOFMS) [26]. Ionization was accomplished by photoionization at 10.5 eV (λ = 118 nm) generated from the third harmonic of a Nd:YAG laser at 355 nm (Big Sky Laser Technologies Ultra). The 355-nm laser was focused using a 50-mm focal length quartz lens in a cell containing Xe gas. The 355-nm and 118-nm beams were directed 5 mm apart from the center of the MgF_2 lens (ϕ = 25 mm, f = 35 mm at 118 nm) placed in the cell, which disperses the different wavelengths and allows the VUV to pass through a 3-mm pinhole placed 70 mm below the MgF_2 lens so that only 118-nm light was introduced into the ionization region. The laser was operated at 20-Hz repetition. The field free-drift region in the L-TOFMS was approximately 23 cm and in the REFTOFMS it was 34 cm. A typical high voltage value for the repeller electrode was 2 kV. The sample gases from the membrane introduction system were introduced into the TOFMS with a 100-μm diameter orifice into the middle position between the repeller and extractor electrode. An intermediate voltage between the repeller and extractor voltages was applied to the needle supported by a 1/8–1/4″ Swagelok union made of polytetrafluoroethylene (PTFE). The height of the needle was adjusted with respect to the ionization region to ensure a maximum ion signal. The pressure inside the TOFMS chamber was maintained at less than 5×10^{-3} Pa while sample gases were introduced. The ion signal was detected using a two-stage microchannel plate (MCP; Hamamatsu Photonics K. K. F4655-10 in the L-TOFMS and F2223-21SHX in the REF-TOFMS). The signal intensities of the molecular ion of benzene, toluene, and chlorobenzene were measured at m/z = 78, 92 and 112, respectively. For these compounds, fragmentation free mass spectra in the photoionization at 10.5 eV can be archived [7]. The output signal from the MCP was fed into a digital oscilloscope (200 MHz, 2 GS/s, Iwatsu WaveSurfer 422). The TOF spectra was recorded in real time and stored on the hard disk to be analyzed by home-written LabVIEW software programs (LabVIEW 7.1, National Instrument, Austin, TX).

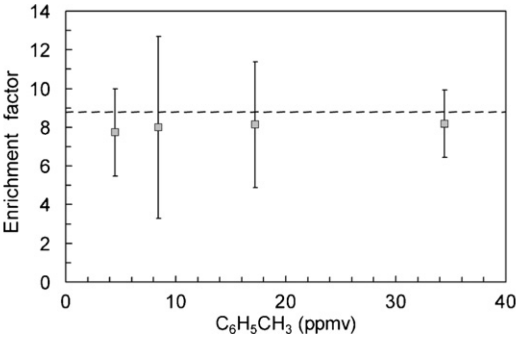

Fig. 2. Enrichment factors of toluene with $\Delta P/P_{bm} = 0.92$ as a function of the concentration. The closed boxes indicate experimental results. Error bars of experimental results are 2σ. The broken line denotes the calculated enrichment factor of 8.8 from the manufacturer reported value of gas permeability and pressures.

Sample gases were prepared by volatilization of liquid benzene (Wako 99.7%) at 30 °C, toluene (Wako 99.8%), and chlorobenzene (Aldrich 99.8%) at 40 °C and were diluted with air in a permeator (GASTEC PD-1B-2) using a diffusion tube so as to bring the sample gases to the desired concentrations. Dilution air, dried by an activated charcoal filter, was fed into the permeator using a compressor. The concentration ranges of benzene, toluene, and chlorobenzene used in this work were from 2.5 to 10 ppmv, from 4.3 to 34 ppmv, and from 3.2 to 23 ppmv, respectively. A premixed gas of 1 ppmv benzene/1 ppmv chlorobenzene in N_2 calibrated by GC/MS was purchased from Takachiho Co. Ltd. The diluted sample gases (less than 1-ppmv mixtures in the nitrogen buffer gas) prepared from the premixed gases were stored in 6-L canisters (Entech instruments, inc.) coated with Silonite, and then used to measure the limit of detection (LOD) with membrane introduction.

3. Results and discussion

3.1. Experimental determination of the enrichment factors

The concentration dependence of the enrichment factors for benzene, toluene, and chlorobenzene were experimentally measured for $\Delta P/P_{bm} = 0.92$, where ΔP is the difference in pressure across the membrane, ($\Delta P = P_{bm} - P_{am} = 770 - 60 = 710$). All measurements were carried out in the REF-TOFMS. Typical enrichment factors as a function of the mixing ratio for toluene are shown in Fig. 2. Experimentally obtained enrichment factors of toluene for the initial concentration of 4.5–34 ppmv were between 7.7 and 8.2. These values are effectively independent of the concentration.

The enrichment factors of benzene, toluene and chlorobenzene were also measured at $\Delta P/P_{bm}$ ratios of 0.81–0.96. Fig. 3 shows the experimental enrichment factors of benzene, toluene and chlorobenzene using the membrane introduction system. The enrichment factors for benzene, toluene, and chlorobenzene at each $\Delta P/P_{bm}$ are an average of four measurements carried out at different concentrations of the AHs: 2.5, 3.3, 5.0, and 10 ppmv for benzene, 4.3, 8.4, 17, and 34 ppmv for toluene, and 3.2, 6.0, 12, and 24 ppmv for chlorobenzene. High $\Delta P/P_{bm}$ leads to higher concentration of the AHs using the membrane introduction than at low $\Delta P/P_{bm}$. Benzene, toluene, and chlorobenzene were concentrated by 15.3, 11.0, and 12.1 times, respectively, with the maximum enrichment effect occurring at $\Delta P/P_{bm} = 0.96$, where P_{bm} was 770 Torr and P_{am} was 30 Torr. As shown in Fig. 3, the enrichment factors decreased to 4.7 for benzene, 3.9 for toluene, and 4.1 for chlorobenzene at $\Delta P/P_{bm} = 0.81$, where the pressure of P_{bm} and P_{am} were 770 and 150 Torr, respectively.

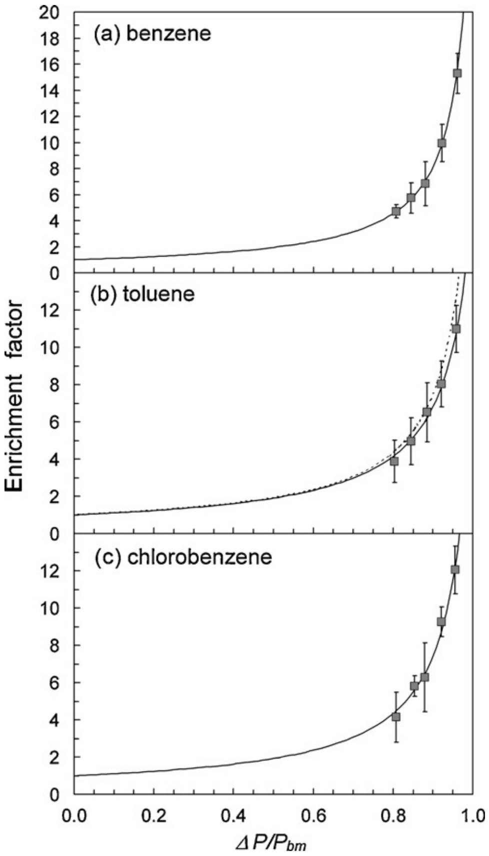

Fig. 3. Enrichment factors of (a) benzene, (b) toluene, and (c) chlorobenzene as a function of $\Delta P/P_{bm}$. The closed boxes denote experimental results with 2σ errors. The solid lines indicate the calculated enrichment factors from the experimental results. The broken line in (b) is the enrichment factors calculated from the manufacturer reported gas permeability of 0.91×10^{-6} cm^3 STP cm/(s cm^2 cm Hg).

3.2. Theoretical determination of gas permeabilities

In the MIMS method, the permeation process of an analyte through the membrane occurs in three steps [27]: (a) selective partitioning of an analyte into the membrane polymer matrix, (b) selective diffusion of an analyte through the membrane, and (c) desorption of an analyte from the membrane into the vacuum of the mass spectrometer. In the permeation process, the flux of membrane-permeating gas, J, is obtained by the following equation as a function of gas permeability, C, the difference in pressure across the membrane, ΔP, and the thickness of membrane, d:

$$J = \frac{C\Delta P}{d}. \tag{1}$$

Using Eq. (1), the flux of membrane-permeating gas of component i in a mixed gas is expressed as:

$$J_i = Jx_{i,am} = C_i\frac{P_{bm}x_{i,bm} - P_{am}x_{i,am}}{d} \tag{2}$$

where x is the mole fraction. The following equation should hold because the sum of all the mole fractions must be unity.

$$\sum x_{i,am} = \sum \frac{C_i P_{bm} x_{i,bm}}{Jd + C_i P_{am}} = 1 \tag{3}$$

From Eq. (3), one can obtain the mole fraction of component i in the membrane-permeated gas. In this calculation, the sample gas was assumed to be a mixture of nitrogen, oxygen, and AH with mole fractions of $N_2/O_2/AH = 0.78/0.22/1 \times 10^{-5}$. The gas permeabilities of nitrogen and oxygen were obtained from the supplier of the membrane as given in Table 1. The gas permeabilities for the silicone membrane were calculated by Eqs. (2) and (3). Each gas permeability value gave one enrichment factor at a particular $\Delta P/P_{bm}$ ratio, and the average of five permeabilities at different $\Delta P/P_{bm}$ ratios for each AH was calculated. The gas permeabilities of the membrane used in the present study were estimated to be (1.33 ± 0.31), (0.66 ± 0.40), and (0.89 ± 0.47) × 10^{-6} cm^3 STP cm/(s cm^2 cm Hg) for benzene, toluene, and chlorobenzene, respectively. The gas permeability of toluene obtained in the present study has a large uncertainty but the manufacturer's reported value of 0.91 × 10^{-6} cm^3 STP cm/(s cm^2 cm Hg) is within 2σ of our value. The gas permeabilities of benzene and chlorobenzene calculated in the present study are also acceptable within 2σ because the theoretical and experimental methods obtained the gas permeabilities of benzene and chlorobenzene are the similar to those obtained for toluene. The permeation process of the sample gas through the membrane is an interaction between the gas species and the membrane material such as dissolution and diffusion. The gas permeability of the membrane thus depends on the polarity and the hydrophobicity of sample materials [28]. Benzene, toluene, and chlorobenzene are all non- or low-polarity compounds. The hydrophobicity of toluene and chlorobenzene are comparable, while benzene is less hydrophobic. Hydrophobicity may contribute significantly to the gas permeability. Benzene is less hydrophobic and has higher gas permeability than toluene and chlorobenzene as shown in Table 1. The relationship between hydrophobicity and permeability in the present work is different from that of Boscaini et al. [28], which showed highly hydrophobic materials are more gas permeable than less hydrophobic materials. On the other hand, the (poly)dimethylsiloxane membrane (SSP-M100C, SSP Inc.) used in Liu et al. has a higher gas permeability for benzene than that for toluene [29].

The calculations of the enrichment factors for benzene, toluene, and chlorobenzene are shown in Fig. 3 with experimental results as a function of the pressure ratio, $\Delta P/P_{bm}$. The enrichment factors for benzene, toluene, and chlorobenzene using the membrane introduction system increased almost exponentially with $\Delta P/P_{bm}$. All four enrichment factors as a function of the toluene-mixing ratio in Fig. 2 are within 2σ of the calculated value of 8.8.

3.3. Improvement of limit of detection by the membrane introduction system

Based on the results described above, the LODs of VOCs by the VUV-SPI-TOFMS with the membrane introduction system are expected to improve by one order of magnitude relative to direct sample introduction. The LODs of benzene and chlorobenzene with membrane introduction system were examined at 1.4 ppbv diluted by nitrogen at P_{bm} and P_{am} of 660 and 40 Torr, respectively, giving a $\Delta P/P_{bm} = 0.94$. In these conditions, the enrichment factors predicted from the gas permeabilities of benzene and chlorobenzene were 11.7 and 10.3, respectively. The signal intensities of the $m/z = 78$ for benzene and $m/z = 112$ for chlorobenzene were measured with a data acquisition time of 5 s for 100 measurement runs. Fig. 4 shows the mass spectrum of 1.4-ppbv chlorobenzene measured in the L-TOFMS accompanied by the result of the simulation performed with SIMION 8.0 software (Scientific Instrument Services, Inc., Ringoes, NJ). In this figure, the signal intensity was normalized to the standard deviation of background intensities between $m/z = 109$ and 111. The LODs of benzene and chlorobenzene at a signal-to-noise ratio of 3 were estimated with the formula $\text{LOD} = 3\sigma c/h$, which is a modification of the formula in [30], where c is the concentration of the samples, σ is the standard deviation of the noise, and h is the signal intensity of sample. The standard deviation of background noise intensity of benzene was calculated using the intensity between $m/z = 75$ and 77. The signal intensity at $m/z = 112$, gave an h/σ of 6.6. The LODs for benzene and chlorobenzene were estimated to be 1.35 and 0.63 ppbv, respectively. The LODs of benzene and chlorobenzene using the direct introduction system in the L-TOFMS were 8.4 and 6.5 ppbv, respectively. Thus, the improvement factors for the detection limits using the membrane introduction relative to the direct introduction were 6.2 ± 2.8 and 10.2 ± 2.9 for benzene and chlorobenzene, respectively. The predicted improvement factors of benzene and chlorobenzene relative to the direct introduction calculated at $\Delta P/P_{bm} = 0.94$ and the gas permeabilities estimated above were 11.7 and 10.3, respectively. The improvement factor for chlorobenzene relative to the direct introduction was consistent with the value of 10.3 but that of benzene was lower than predicted. The lower improvement factor of benzene than predicted might be due to the large contribution of the background signal caused by the tail of the broad N_2 ion signal. Although N_2 is not ionized by 10.5 eV SPI, it can be ionized by light-induced electron impact ionization (LEI); i.e., collisions with electrons emitted by the photoelectric effect and accelerated by the ion optics [30,31]. The N_2-ion signal obtained by LEI gave a broader peak than by SPI because light-induced electrons had a broader range of energies and ionization point of N_2 covered a wide range. The N_2-ion signal also had an intensity several orders of magnitude larger than the low-concentration benzene at 1.4 ppbv. Thus, the N_2 ion gave a broad range of time-of-flight and this peak became broad enough to obscure the $m/z = 78$ of benzene.

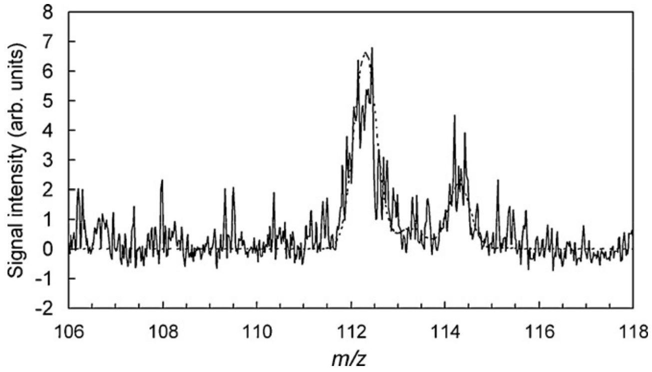

Fig. 4. Mass spectrum of 1.4 ppbv chlorobenzene measured at linear mode of TOFMS. The solid line indicates experimental results. The dashed line denotes simulated spectrum made by SIMION 8.0.

The LODs for other VOCs are expected to be also sub-ppbv level using this system, since the photoionization cross-sections of VOCs at 10.5 eV are at the same order of magnitude for most aromatic compounds [7] and the gas permeabilities of most VOCs are higher than those of the main components of the atmosphere such as nitrogen and oxygen [28,32,33].

The LODs of several VOCs using MIMS from other works are listed in Ref. [21]. Ketola et al. reported LODs of 1 $\mu\text{g m}^{-3}$ (0.3 ppbv) for benzene and 0.5 $\mu\text{g m}^{-3}$ (0.1 ppbv) for chlorobenzene [13]. They developed an electron impact ion source quadrupole-MS (QMS) coupled with a membrane sample introduction system using a polydimethylsiloxane sheet-membrane 25 μm thick and 28 mm^2 in area. The LODs of benzene and chlorobenzene with the membrane introduction system combined with a VUV-SPI-TOFMS developed in the present study are comparable to those by Ketola et al. [21]. Most recently, detection limits of sub-ppbv levels for VOCs have been achieved by mass spectrometry with and without a membrane inlet system [22,23]. Oser et al. have developed a resonance enhanced multiphoton ionization (REMPI) MS, which has detection limits of tens of ppqv to pptv for benzene, xylene, and chlorobenzene in water samples [20]. The custom-made VUV-SPI-TOFMS connected to the membrane introduction system developed in our work is compact: 50 cm × 50 cm × 50 cm including the mechanical pumps. VUV-SPI does not cause fragmentation unlike electron impact ionization. The VUV-SPI-TOFMS system described here also achieves high mass resolution of over 800 at about 100 amu with REF-TOFMS [24].

4. Conclusions

A silicone sheet-membrane introduction system combined with VUV-SPI-TOFMS has been shown to improve the detection sensitivity of volatile organic compounds relative to the direct introduction. The enrichment factors of benzene, toluene, and chlorobenzene were found to increase exponentially with $\Delta P/P_{bm}$ by both experimental and theoretical techniques. The signal intensities of benzene, toluene, and chlorobenzene using the membrane introduction system have been increased by a factor of 15.3, 11.0, and 12.1, respectively, at $\Delta P/P_{bm} = 0.96$. We also confirmed the independence of the enrichment factors with sample concentration between 2.5 and 34 ppmv. The gas permeabilities of benzene and chlorobenzene through the silicone membrane used in this work were estimated theoretically. Almost sub-ppbv levels of benzene and chlorobenzene have been detected using the VUV-SPI-TOFMS coupled with the membrane introduction system. The advantages of the VUV-SPI-TOFMS coupled with the membrane introduction system developed in the present work are its high sensitivity, high mass resolution for VOCs in air analysis, and transportability.

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