

A real-time gas monitoring system based on ion mobility spectrometry for workplace environmental measurements

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Abstract: A volatile organic compounds (VOC) gas monitor was developed using an ion mobility spectrometer (IMS). It was designed for real-time monitoring in work environments, where gas chromatography/mass spectrometry (GC/MS) does not perform well. To evaluate the identification capability, response time, and quantitative accuracy of this device, experiments were conducted using methyl ethyl ketone. This is widely used in many factories, and its short-term exposure limit (STEL) has been set by the American Conference of Governmental Industrial Hygienists. Because the ionizable amount of methyl ethyl ketone has already been exceeded in STEL value of 300 ppm which belongs to the measurement range of interest in this study, this study estimated the peak shift amount rather than the peak intensity. Calibration curves with high accuracy were obtained in a range including 300 ppm which is the STEL of methyl ethyl ketone. The results of the experiment suggest that the device can be used for monitoring chemical substances in a work environment.

Key words: Ion mobility spectrometer, Real-time gas monitoring, Work environments, Industrial hygiene, Organic solvents

Introduction

Various toxic chemical substances have widely been used in the workplace. The time-weighted average has been adopted as a typical exposure risk index because the health effects of most chemicals can be evaluated once a worker's total exposure is known. However, the health effects of some chemical substances depend on the peak concentration of exposure, and hygienists have to know this peak

value and/or the short-term concentration of those chemicals to assess workers' health risks¹⁻³.

An official method for determining the concentration of chemical substances in the workplace has been established using gas chromatography/mass spectroscopy (GC/MS). However, measurement by this method is very time-consuming which makes short-term and real-time information about the concentration of chemical substances difficult to obtain.

A photo-ionization detector (PID) has been a popular alternative to check the concentration of a chemical substance in real-time⁴. PID estimates the concentration from the current value by irradiating and ionizing a chemical substance with ultraviolet light. Since PID irradiates all of

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the chemical substances in the air introduced to the instrument, those with an ionization energy lower than the energy of the ultraviolet light are ionized. In a work environment where many chemical substances are used, substances with relatively low toxicity (high permissible concentration) may coexist at high concentrations. Individual quantification is extremely difficult resulting in a difficult quantitative analysis. Another problem with PID is that only chemical substances in the database provided by the manufacturer can be qualitatively and quantitatively determined.

The aims of this study are first to realize real-time measurement of the concentrations of chemical substances known to have a health impact on workers, and second, to examine in detail the short-term exposure to chemical substances that is difficult to achieve with conventional GC/MS analysis. In a previous study, we have developed a volatile organic compounds gas monitor by using an ion mobility spectrometer (IMS)⁵. This instrument does not require pretreatment as do conventional GC/MS methods, and hence is suitable for real-time monitoring of chemical substances in a work environment. As the IMS device can perform qualitative and quantitative analysis of chemical substances at atmospheric pressure⁶, the device does not require a vacuum apparatus as opposed to GC/MS. Therefore, the IMS device is portable and can be carried by workers. Additionally, the time required for analysis is extremely short requiring only about several tens of seconds. Moreover, unlike mass spectrometers, this analyzer can identify different chemical substances with the same mass number, because they are detected, not by mass number, but by molecular geometric structure (collision cross-section)⁷.

Methyl ethyl ketone, widely used in factories to dissolve paints, inks, and adhesives, and to perform various types of cleaning of acrylic, urethane, and epoxy resins was selected as a sample vapor. This chemical substance has a short-term exposure limit (STEL)⁸ defined as the allowable amount for short-term exposure to chemical substances. In this study, the identification capability, response time, and quantitative accuracy of the IMS device⁵ were assessed for practical use in actual work sites. Quantitative accuracy was estimated based on the amount of peak shift from reactant ion peak (RIP).

Materials and Methods

Measurement principle

Measurements by the IMS device used in this study were

performed at atmospheric pressure and without a vacuum device allowing the analyzer to be portable. Moreover, its short analysis time makes it possible to measure the concentration of chemical substances in a work environment in real-time. In IMS, the sample ions ionized by corona discharge is moved inside a drift tube filled with a buffer gas (air in this study) having the role of target particle under a uniform electric field, E . The substance is identified based on ion velocity^{9–11}. As shown in Fig. 1, when a weak uniform electric field is applied to a gas, a steady flow of ions develops as deceleration (by collisions with the buffer gas molecules) and acceleration (by the electric field) become balanced. The drift velocity v_d of the ions is proportional to the intensity of the electric field E ,

$$v_d = KE \quad (1)$$

where K is defined as mobility. Since mobility is inversely proportional to the number density N of gas molecules, mobility converted to gas density under standard conditions (273.15 K and 101325 Pa) is called the reduced mobility K_0 ^{12,13} as noted in the following equation:

$$K_0 = \frac{v_d}{N} \frac{N}{E} = \frac{273.15}{T} K \quad (2)$$

where T is the gas temperature, N_0 is the number density of an ideal gas under standard conditions, the Loschmidt number ($N_0 = 2.687 \times 10^{19} \text{ cm}^{-3}$). In the IMS device, if the shape of the ion is complicated or the size is large, the drift velocity decreases due to the increased collision cross-section with the buffer gas. This results in a decrease in the gas mobility. Therefore, information such as the shape and size of a substance can be obtained from the mobility which eventually enables the identification of the chemical substance.

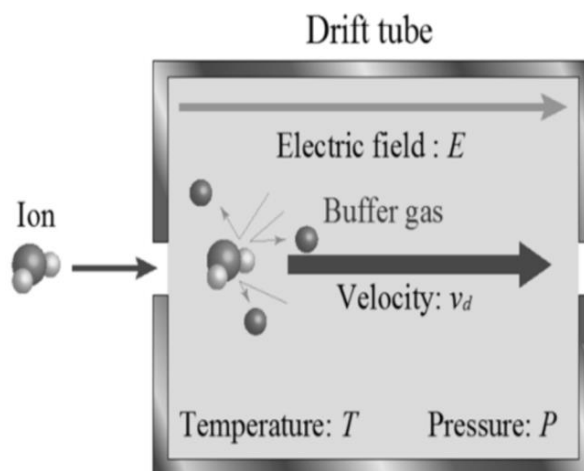
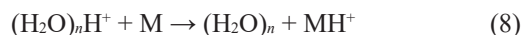
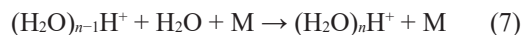
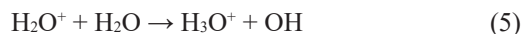


Fig. 1. Conceptual diagram of the ion drift tube method.

Experimental apparatus

Fig. 2 shows the IMS device used in this study. The device consists of 11 guard ring electrodes D1–D11. D1 and D2 form an ionization chamber, D3 is a gate electrode, and D4–D11 form a drift tube with a total length of 11 cm. A high voltage divided by resistance is applied to each guard ring to obtain an electric field gradient as shown in the upper left of Fig. 2. The space between guard rings is insulated with a 2 mm-thick Teflon plate. In this study, the sample vapor with a concentration adjusted by a calibration gas generation system PD-1B (GASTEC Corporation, Ayase, Kanagawa, Japan) is continuously injected into the IMS. The sample vapor is ionized by corona discharge by applying a high voltage (4.7 kV, 2.6 kV, and 1 μ A) to the two discharge needles installed in the ionization chamber D2.

The ionization mechanism is described by the following process⁵⁾:



First, nitrogen molecules in the air are ionized by corona discharge (3). Then, through subsequent electron transfer reaction (4), proton transfer reaction (5), three-body reaction (6) (7), and proton transfer reaction (8), the sample ion, MH^+ , with the addition of a proton is generated. In particu-

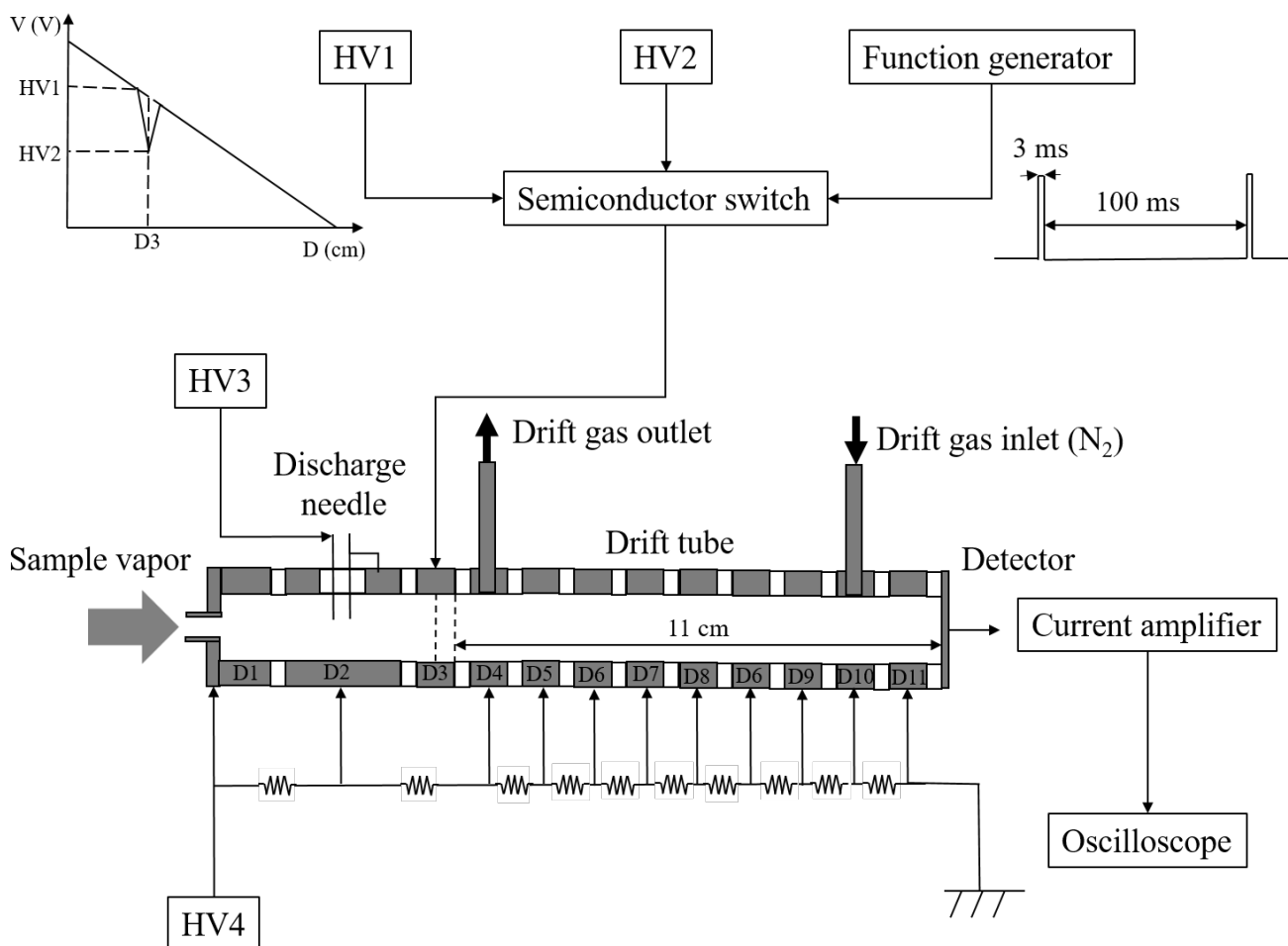


Fig. 2. Schematic of the experimental apparatus—the sample vapor is ionized by corona discharge by applying a high voltage (HV) (HV1=4.7 kV, HV2=2.6 kV).

lar, the water cluster ion $(\text{H}_2\text{O})_n\text{H}^+$ in (8) is called the reactant ion and has a very important role in ionization in the IMS device.

The continuous incident sample ion MH^+ , ionized in the ionization chamber, was pulsed by a blocking voltage applied to two meshes installed in D3 typically with a duration of 3 ms and a frequency of 10 Hz. The ions cannot overcome the potential barrier in the gate. A DG1022U device manufactured by RIGOL was used as the function generator. The flight time was measured by using this electrical gate pulse as a start signal and the electric signal from the detector as a stop signal. The ion signal detected by the detector is amplified by a current amplifier DLPCS-200 (FEMTO Messtechnik GmbH, Berlin, Germany) and then measured by the oscilloscope. Finally, in the drift tube, a drift gas (N_2 50 ml/min) is constantly flowing from the back of the tube to keep the interior clean.

Experimental method

In this study, the performance of the device was evaluated based on three factors: identification capability, response time, and quantitative accuracy. For identification capability, methyl ethyl ketone, acetone, and ethanol, each of which has been widely used in many factories, were selected as sample vapors, and the reduced mobility K_0 was obtained from the arrival time of each substance.

Response time was evaluated by measuring the spectral shift after introducing methyl ethyl ketone into the drift tube. The time taken to detect the spectral shift after sample introduction was evaluated. Additionally, the spectral shift after methyl ethyl ketone was eliminated was also measured, and the time taken to detect the spectral shift after elimination of methyl ethyl ketone was determined. In assessing quantitative accuracy, the size of water clusters is dependent upon the ambient temperature and humidity which can affect the relationship between the arrival time and the concentration of a target substance. Thus, two different ambient conditions were considered. Condition 1 had an ambient temperature of 20°C and relative humidity (RH) of 20%, and condition 2 had a temperature of 17°C and 33% RH. Arrival time spectra were obtained by continuously supplying methyl ethyl ketone to the device using the permeator at concentrations of 108, 203, 371, and 489 ppm in condition 1 and 140, 264, and 483 ppm in condition 2.

Since methyl ethyl ketone has a higher proton affinity compared with many other chemical substances present in the work environment¹⁴, it is hardly affected by the presence of these other chemical substances. The measurement range of interest in this study includes 100 to 500 ppm

which encompasses the STEL value of 300 ppm defined by the American Conference of Governmental Industrial Hygienists (ACGIH). However, the concentration level cannot be estimated from the peak intensity because the amount of methyl ethyl ketone ionizable at a STEL value of 300 ppm has already reached the maximum ionizable amount. Therefore, this study estimated the concentration based on the degree of peak shift from the RIP. Since the peak of methyl ethyl ketone overlaps with the peak of the water clusters (RIP), the peak observed in this study is one nominal peak. It is assumed that if the concentration of methyl ethyl ketone increases, the concentration of water cluster ions will decrease, and the nominal peak shifts from the peak position of RIP.

Results and Discussion

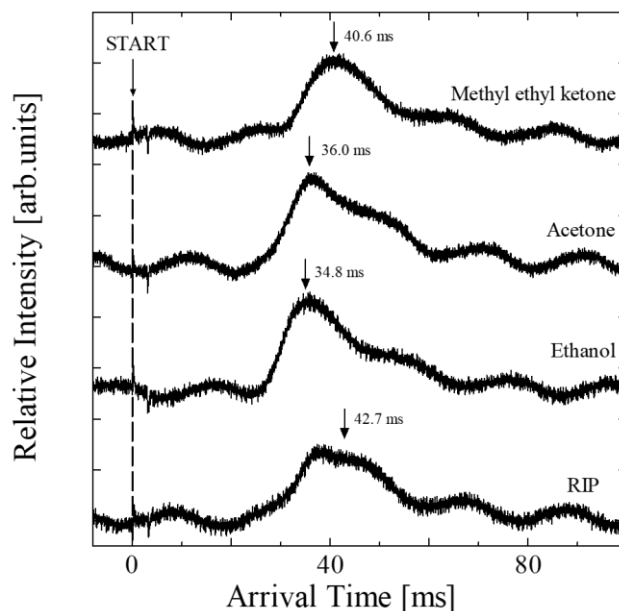


Fig. 3. Arrival time spectra of methyl ethyl ketone, acetone, ethanol, RIP—these spectra are measured at the electric field E of 186 V/cm. The reactant ion peak (RIP) is the background spectrum obtained from water cluster ions.

Fig. 3 shows the arrival time spectra of methyl ethyl ketone, acetone, and ethanol measured under identical conditions of ambient temperature, humidity, and device setup. The vertical line shows the relative intensity. As shown in Fig. 3, the peak position varies depending on the chemical substance. Since the maximum measurement error of this device is very small (approximately 1%), it was possible to distinguish the three chemical substances from one another. The current values of these chemicals are in pA order.

RIP is the background spectrum obtained from water

cluster ions present in the air. The reduced mobilities, K_0 , obtained from the arrival times of methyl ethyl ketone, acetone, and ethanol are 1.46, 1.64, and 1.70 cm^2/Vs , respectively. The experimental results obtained in this study were lower than those obtained by the theoretical mobility calculation software MOBCAL^{15–17}. This device does not have enough resolution to separate the peak of a target substance from that of water clusters, which results in overlapping of these two peaks into one nominal peak. As the arrival time of water clusters is generally later than that of the target substance, the observed nominal peak is shifted later than the peak of the target substance resulting in a large arrival time. Since the reduced mobility K_0 is inversely proportional to the arrival time, the K_0 experimentally obtained from the nominal peak is lower than the theoretically calculated K_0 .

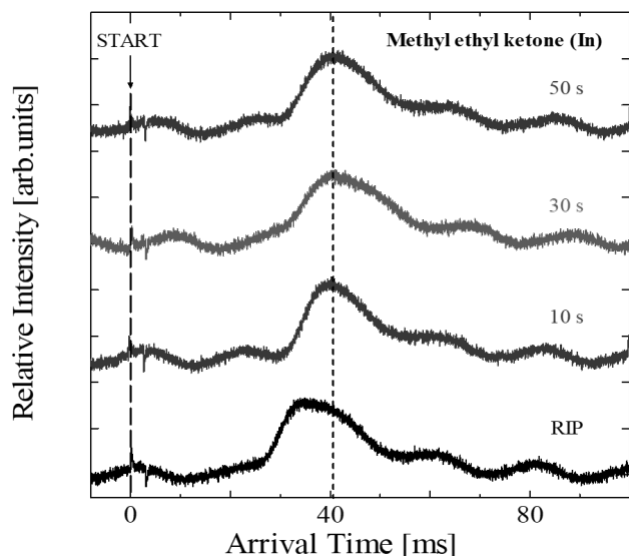


Fig. 4. Arrival time spectra obtained using methyl ethyl ketone at the electric field E of 186 V/cm —the period elapsing between methyl ethyl ketone introduction and the spectra obtained are from bottom to up: RIP, 10, 30, and 50 s. The reactant ion peak (RIP) is the background spectrum obtained from water cluster ions.

Fig. 4 shows the time shift of the arrival time spectrum following the introduction of methyl ethyl ketone. The vertical line indicates the relative intensity and the horizontal axis the arrival time. It can be seen that the peak has completely shifted 10 s after the introduction of methyl ethyl ketone. Fig. 5 shows the time shift after methyl ethyl ketone has been removed from the system. The vertical line and the horizontal axis are the same as in Fig. 4. By only 10 s after elimination, the peak position has completely returned to the background RIP position. This means that

methyl ethyl ketone can be analyzed in about 10 s using this device. Therefore, real-time monitoring difficulties with GC/MS in a work environment can be overcome by using this device.

The RIP peak positions shown in Figs. 3, 4, and 5 are different because the ambient temperature and humidity were significantly different on the different days of measurement (Fig. 3, 22°C, 82% RH; Figs. 4 and 5, 14°C, 50% RH), as were the amount and size of water clusters.

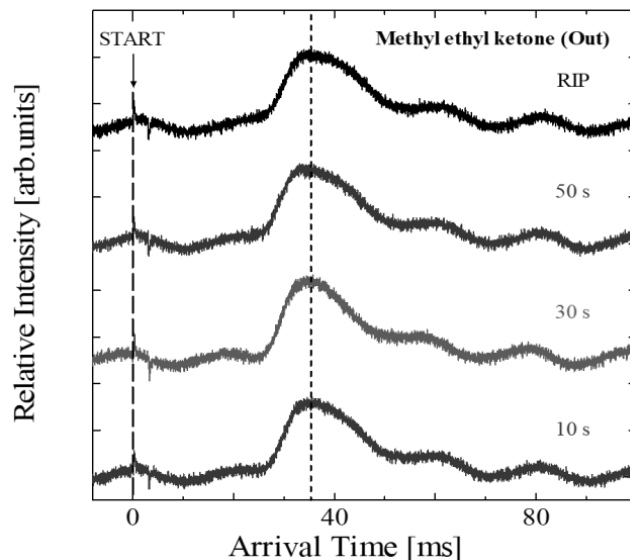


Fig. 5. Arrival time spectra obtained using methyl ethyl ketone at the electric field E of 186 V/cm —the period elapsing between methyl ethyl ketone exhaust and the spectra obtained are from bottom to up: 10, 30, 50 s, and RIP. The reactant ion peak (RIP) is the background spectrum obtained from water cluster ions.

Fig. 6 shows calibration curves for methyl ethyl ketone in the range of 100 to 500 ppm. The vertical axis shows the concentration and the horizontal axis the arrival time. The flow rate measurement error at the permeator in this study was estimated to be about 3%. Although change in the ambient conditions resulted in an arrival time shift, the same correlation between the arrival time and the concentration of methyl ethyl ketone was obtained from the two different ambient conditions. Calibration curves under the two different conditions could be obtained with high accuracy (R^2 , 0.997 and 0.998, respectively). Since the STEL of methyl ethyl ketone defined by the ACGIH is 300 $\text{ppm}^{(8)}$, this IMS device can adequately monitor short-term exposure to methyl ethyl ketone in the work environment.

Future studies will evaluate the identification capability, response time, and quantitative accuracy of the IMS device not only for methyl ethyl ketone but also for other chemical substances used in various work environments. If a chemi-

cal substance with not as high a proton affinity as methyl ethyl ketone for coexisting substances is to be qualitatively and quantitatively analyzed, it is necessary to separate the spectrum of the target substance completely from those of the coexisting ones. For that purpose, it will be necessary to improve the resolution of the device. This includes lengthening the drift tube as well as shortening the pulse width to obtain better time resolution.

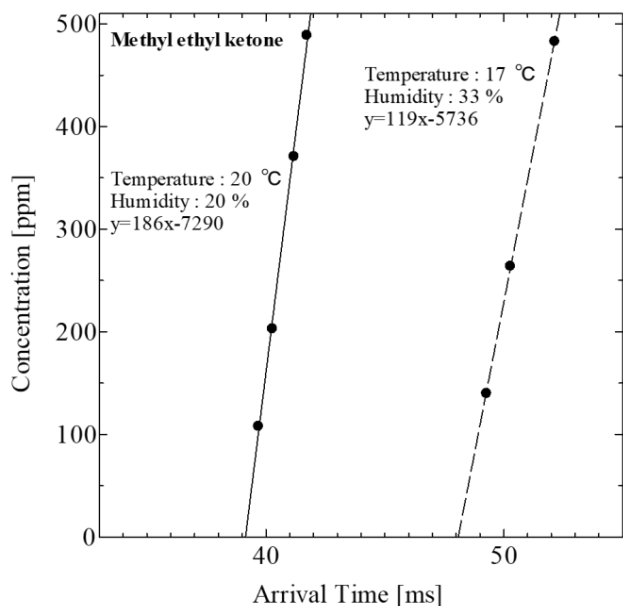


Fig. 6. Relationship between arrival time and concentration at methyl ethyl ketone. Solid line is the calibration at Temperature: 20°C, Humidity: 20%RH. Dotted lines are the calibration at Temperature: 17°C, Humidity: 33%RH. The measurement error of the flow rate at the permeator used in this study was estimated to be about 3%.

The size of the IMS device is 52 cm in width × 30 cm in depth × 36 cm in height and it weighs 23.5 kg. At present, it is possible to carry the device to the work site for measurements. Eventually, it would be optimal to make the device wearable by miniaturization and weight reduction which would enable real-time measurement of individual workers' exposure.

In the future, we envisage real-time monitoring focusing not only on STEL but also on a ceiling value. In particular, toluene has a ceiling value of 300 ppm regulated by Occupational Safety and Health Administration¹⁸⁾, which is substantially the same concentration level as the STEL value of methyl ethyl ketone. Toluene, widely used for cleaning in many factories, is one of the organic solvents that cause poisoning accidents. It is thus very useful to realize real-time monitoring using this device. As the proton affinity

of toluene, 784 kJ/mol¹⁹⁾ is as high as that of methyl ethyl ketone, 827 kJ/mol¹⁴⁾, short-term measurement of the concentration of toluene may be feasible with this device. However, the proton affinity of toluene is not as high as that of methyl ethyl ketone. This might cause interference by other coexisting substances with a proton affinity similar to toluene resulting in decreased accuracy of the toluene concentration. For this reason, the device requires some improvements to accurately measure the STEL and ceiling values of toluene. These improvements will enable the device to measure the concentration of multiple chemical substances in the work environment in a shorter time and more accurately than is possible with the traditional method.

Conclusion

In this study, we developed an IMS device for real-time measurement of chemical substances in the work environment. Experiments were conducted to examine the performance of the device from three aspects: identification capability, response time, and quantitative accuracy using methyl ethyl ketone which is widely used in factories as a test sample. Qualitative measurements of three chemical substances commonly used in many factories were obtained. The response time of this device was 10 s or less, suggesting that real-time monitoring can be performed in the work environment. As far as quantitative accuracy, calibration curves of methyl ethyl ketone were obtained. Methyl ethyl ketone has a large proton affinity and is not easily affected by other chemical substances existing in the work environment. However, since saturation has already occurred near the STEL concentration of the target substance, the concentration cannot be estimated based on the ion intensity of the spectrum. Therefore, the concentration was estimated from the peak shift amount, and calibration curves with high accuracy near 300 ppm, the STEL of methyl ethyl ketone, were obtained. This means that the error of quite is small in the range from 100 to 500 ppm and accurate measurements can be performed. It was confirmed that methyl ethyl ketone could be adequately monitored in real-time in a work environment by using this device.

References

- 1) Vehviläinen T, Lindholm H, Rintamäki H, Pääkkönen R, Hirvonen A, Niemi O, Vinha J (2016) High indoor CO₂ concentrations in an office environment increases the transcutaneous CO₂ level and sleepiness during cognitive

- work. *J Occup Environ Hyg* **13**, 19–29.
- 2) Johannessen LN, Grimstad HJ, Skjetne JE, Myklebust IN, Svendsen KVH (2020) Embedded systems and the Internet of Things: can low-cost gas sensors be used in risk assessment of occupational exposure? *J Occup Environ Hyg* **17**, 495–503.
 - 3) Wilson MP, Hammond SK, Nicas M, Hubbard AE (2007) Worker exposure to volatile organic compounds in the vehicle repair industry. *J Occup Environ Hyg* **4**, 301–10.
 - 4) Brown KK, Norton AE, Neu DT, Shaw PB (2019) Robotic direct reading device with spatial, temporal, and PID sensors for laboratory VOC exposure assessment. *J Occup Environ Hyg* **16**, 717–26.
 - 5) Eiceman GA, Karpas K (2005) *Ion mobility spectrometry*, 2nd ed., CRC Press, Florida.
 - 6) Takaya K, Nakaoka H, Suzuki N, Nakayama Y, Shimoda M, Todaka E, Mori C (2017) [Prospects for development of portable real-time VOC analyzer.] *Jpn J Clin Ecol* **26**, 92–7 (in Japanese).
 - 7) Sugai T (2010) [Fundamentals of mass spectrometry – Ion mobility spectrometry–.] *J Mass Spectrum Soc Jpn* **58**, 47–73 (in Japanese).
 - 8) American Conference of Governmental Industrial Hygienists (2018) 2018 TLVs and BEIs based on the documentation of the threshold limit values for chemical substances and physical agents & biological exposure indices, ACGIH Signature Publications, Ohio.
 - 9) Takaya K, Hasegawa Y, Koizumi T, Tanuma H (2016) Mobilities of polyatomic molecular ions in He gas. *Int J Ion Mobil Spec* **19**, 183–7.
 - 10) Takaya K, Hasegawa Y, Koizumi T (2017) Mobilities of CH_3O^+ , $\text{C}_2\text{H}_5\text{O}^+$ and $\text{C}_3\text{H}_7\text{O}^+$ ions in He gas. *Chem Phys Lett* **679**, 21–4.
 - 11) Takaya K, Hasegawa Y, Koizumi T (2020) Comparison of isomeric $\text{C}_3\text{H}_7\text{O}^+$ ion mobilities using fragment ions from 2-butanol and tert-butanol in He and Ne. *Chem Phys Lett* **739**, 137045.
 - 12) McDaniel EW, Mason EA (1973) *The mobility and diffusion of ions in gases*, John Wiley & Sons, New Jersey.
 - 13) Mason EA, McDaniel EW (1988) *Transport properties of ions in gases*, John Wiley & Sons, New Jersey.
 - 14) Edward PLH, Sharon GL (1998) Evaluated gas phase basicities and proton affinities of molecules: an update. *J Phys Chem* **27**, 413–656.
 - 15) Takaya K, Kaneko T, Tanuma H, Nishide T, Sugiyama H, Nakano N, Nagashima H, Seto Y (2016) Model calculation for ion mobility in air using the MOBCAL program. *Int J Ion Mobil Spec* **19**, 227–32.
 - 16) Meslch MF, Hunter JM, Shvartsburg AA, Schatz GC, Jarrold MF (1996) Structural information from ion mobility measurements: effects of the long-range potential. *J Phys Chem* **100**, 16082–6.
 - 17) Shvartsburg AA, Jarrold MF (1996) An exact hard-spheres scattering model for the mobilities of polyatomic ions. *Chem Phys Lett* **261**, 86–91.
 - 18) Department of Health and Human Services Centers for Disease Control and Prevention National Institute for Occupational Safety and Health (2007) *Niosh Pocket Guide to Chemical Hazards*, Superintendent of Documents U.S. Government Printing Office, Pennsylvania.
 - 19) Aue DH, Guidoni M, Betowski LD (2000) Ab initio calculated gas-phase basicities of polynuclear aromatic hydrocarbons. *Int Mass Spectrum* **201**, 283–95.