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Development of a compact laser-based single photon ionization time-of-flight mass spectrometer

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ABSTRACT

We have developed a compact, laser-based, single photon ionization time-of-flight mass spectrometer (SPI-TOF-MS) for on-line monitoring of trace organic species. To obtain the mass spectrum, we use a nearly fragmentation-free SPI technique with 10.5 eV (118 nm) vacuum ultraviolet laser pulses generated by frequency tripling of the third harmonic of an Nd:YAG laser. The instrument can be operated in a linear TOF-MS mode or a reflectron TOF-MS mode in the coaxial design. We designed ion optics to optimize detection sensitivity and mass resolution. For data acquisition, the instrument is controlled using LabVIEW control software. The total power requirement for the vacuum unit, control electronics unit, ion optics, and detection system is approximately 100 W. We achieve a detection limit of parts per billion by volume (ppbv) for on-line trace analysis of several organic compounds. A mass resolution of 800 at about 100 amu is obtained for reflectron TOF-MS mode in a 0.35 m long instrument. The application of on-line monitoring of diesel engine exhaust was demonstrated.

1. Introduction

Mass spectrometry is one of the most powerful techniques for quantitative and qualitative analysis of trace gases such as volatile organic compounds (VOCs) in environmental air [1]. On-line pollutant gas measurement needs excellent selectivity to identify components from complex gas mixtures. For real-time trace-level detection of volatile organic compounds in industrial process analysis, environmental air monitoring and automobile exhaust gas monitoring, a detection sensitivity at ultra-low concentration of parts per billion by volume (ppbv) is required. A compact analytical instrument may potentially be used in numerous field applications where portability is required. The analytical system based on mass spectrometry presented in this paper has the potential to achieve these goals.

Several ionization methods have been developed for mass spectrometry of gaseous organic compounds. Single photon ionization (SPI) using vacuum ultraviolet (VUV) light is a threshold ionization method for analytical mass spectrometry. VUV-SPI is a soft ionization technique that can be adjusted to be nearly fragmentation free and the molecular ion peaks of most organic molecules can be observed. Recently, the VUV-SPI method has been widely used as an ionization source in mass spectrometers, as summarized in Ref. [2]. A coherent VUV laser at 10.5 eV (118 nm) generated by a frequency tripling of the third harmonic (355 nm) of an Nd:YAG laser is a good photoionizing light source due to its high intensity and tight collimation, and it can be easily generated using compact Nd:YAG lasers.

The main atmospheric components such as nitrogen, oxygen, carbon dioxide, and water are excluded at 10.5 eV photoionization due to higher ionization energies. However, the ionization energies of many VOCs existing in environmental air are at or below 10 eV [2], so that VUV light at 10.5 eV ionizes most VOCs and minimizes the possibility of producing fragment ions. For this reason, VUV light at 10.5 eV has been used as the photoionization source for molecules. The photoionization cross-sections of several organic compounds have recently been studied at a fixed energy of 10.5 eV [2,3], and the values differ very little from one another for molecules of roughly same size (several tens of Mb). Quantitative detection thus becomes possible with the relative intensities from the standard samples. Several groups have reported the VUV-SPI mass spectra of representative organic compounds around 10 eV using time-of-flight mass spectrometers (TOF-MS) or quadrupole mass spectrometers [2–7]. In gas monitoring for industrial process and environmental research compact and man-portable device is useful with high sensitivity of ppbv level. The TOF-MS instruments coupled with the VUV light source have high sensitivity to detect

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the VOCs existing in industrial process and vehicle exhaust gas [2,8–13].

Pulsed VUV lasers are well suited for high mass resolution for TOF-MS. A particular advantage of the TOF-MS is its compact size that is due to their inherently simple design. Compact TOF-MS based systems, coupled with the VUV-SPI method, have the potential for on-line monitoring of organic trace species in complex gas mixtures. Syagen Technology developed a man-portable SPI-TOF-MS coupled with a VUV lamp ionization source [8,9]. This instrument uses a quadrupole ion trap and a gas chromatograph interface that operates at low power (<100 W) with detection limits of 10–100 ppbv for a variety of air samples. Mühlberger et al. have developed a few compact TOF-MS instruments with VUV ionization sources. A laser-based compact (mountable in a 19-in. rack) TOF-MS offers three ionization methods: SPI, electron impact ionization, and resonance-enhanced multiphoton ionization [10]. They also developed a compact TOF-MS coupled with an electron-beam-pumped rare gas excimer lamp as a VUV light source for on-line, real-time process gas analysis [11,12].

We have developed a compact time-of-flight mass spectrometer coupled with a laser-based VUV-SPI. The ionization source is a 10.5 eV VUV laser generated by frequency tripling the third harmonic (355 nm) of an Nd:YAG laser in a rare gas cell. The detailed design of the laser-based compact SPI-TOF-MS is presented here. The instrument was conceived to be compact in overall size and man-portable. As a functional test of the device, we present here exhaust gas monitoring from a diesel engine car.

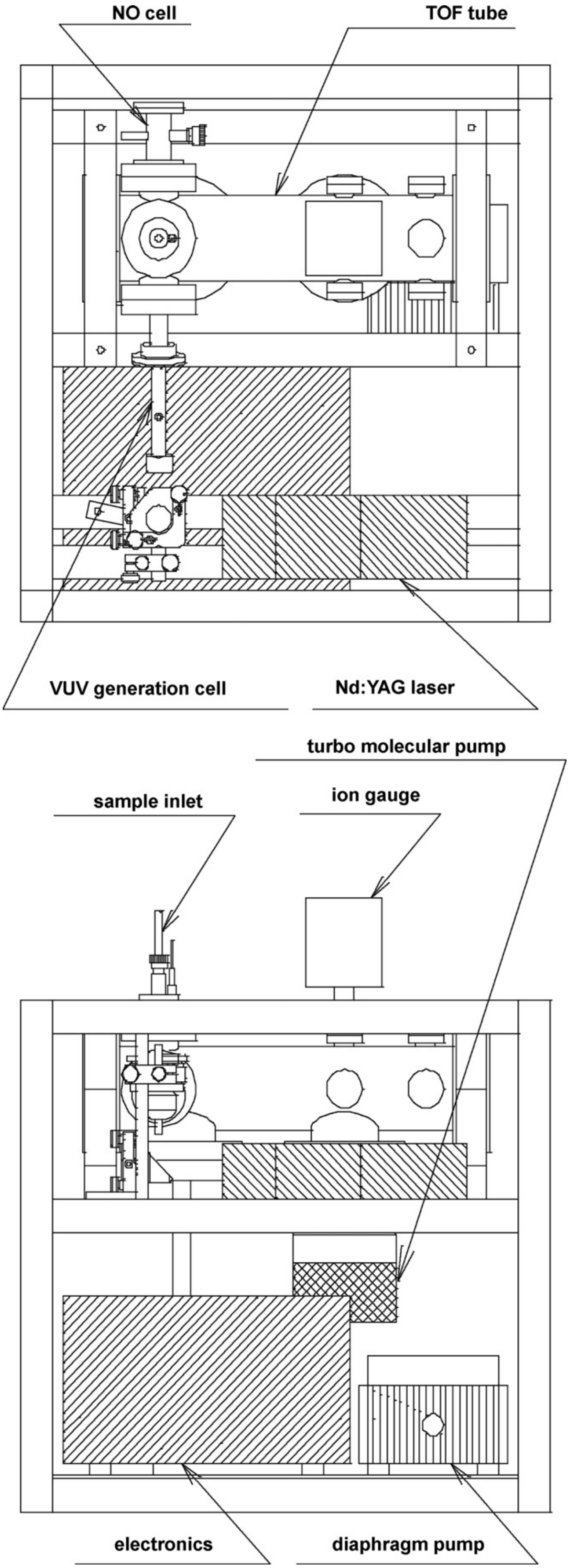

Fig. 1. Schematic drawing of the compact SPI-TOF-MS instrument.

2. Experimental and instrumental setup

The apparatus developed consists of a sample inlet system connected to a time-of-flight mass spectrometer (TOF-MS), as depicted in Fig. 1. A custom-built, compact mass spectrometer can be operated as a reflectron type TOF-MS [14] or a Wiley–McLaren-type [15] TOF-MS. The reflectron TOF-MS is based on a coaxial arrangement. The compact TOF-MS is mounted on a home-made rack made of 30 mm × 30 mm aluminum profiles as shown in Fig. 2. The size of the apparatus is 50 cm × 50 cm × 50 cm and the weight is ca. 30 kg, excluding the power supply for the Nd:YAG laser.

The ion source and the flight tube are pumped by a hybrid turbomolecular pump (pumping speed $30\,\mathrm{L\,s^{-1}}$, Alcatel ATH31+, Alcatel-Lucent Japan Ltd., Yokohama, Japan) powered by a 24 VDC bus miniaturized controller (Alcatel ATH201 H). The ion source is pumped by an intermediate port of the turbomolecular pump, while a detection chamber is pumped by a main port. A diaphragm pump (pumping speed $13\,\mathrm{L\,min^{-1}}$, N813.3 ANDC, KNF Neuberger GmbH, Friburg, Germany) is used as a backing pump. The pumping system achieves a base pressure of 1×10^{-5} Pa in the detection chamber, measured using an ion gauge (series 354 MICRO-ION$^{\mathrm{TM}}$ module, Helix Technology Corp. Yokohama, Japan). The vacuum chamber length with two ICF 114 Conflat flanges is 35 cm. Electric feed-through terminals for electrodes and reflectors are mounted on one of the ICF-114 flanges. The field free-drift region in the liner mode is approximately 23 cm and in the reflectron mode it is 34 cm. A typical high voltage value for the repeller electrode is 2 kV. The sample gases are introduced from a needle with a $100\,\mu\mathrm{m}$ diameter orifice into the middle position between the repeller and extractor electrode. An intermediate voltage between the repeller and extractor voltages is applied to the needle supported by a 1/8–1/4 in. Swagelok union made of polytetrafluoroethylene (PTFE). We control the height of the needle with respect to the ionization region to ensure a maximum ion signal.

An Einzel lens and deflectors are located just above the ion acceleration regions for controlling the ion trajectory. The ions pass into the field free-drift region through the center hole of

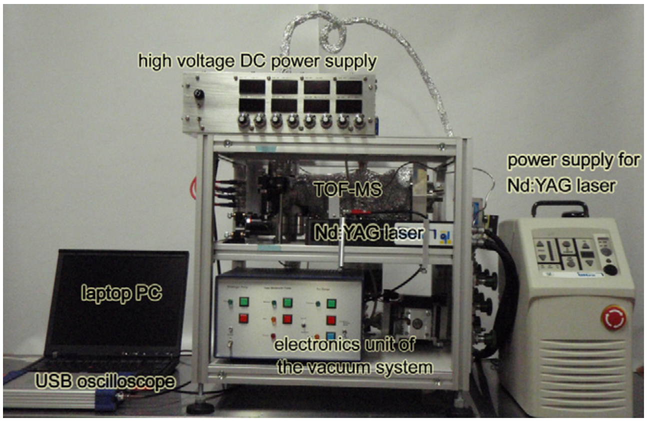

Fig. 2. Photograph of the compact SPI-TOF-MS instrument. The power supply for the ion optics is placed on the rack mount.

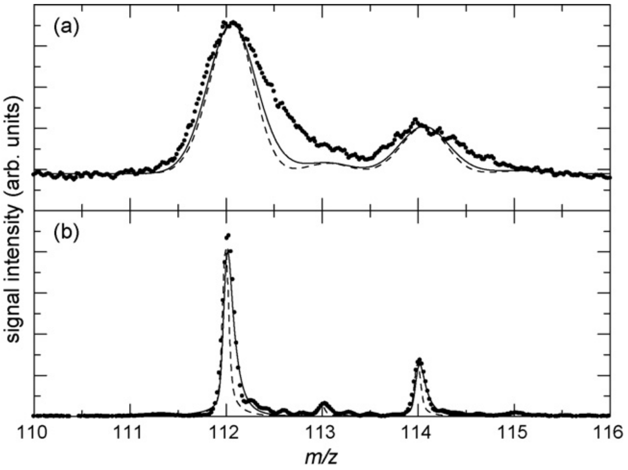

Fig. 3. Mass spectra of chlorobenzene measured at linear (a) and reflectron (b) TOF mode. Dots indicate experimental spectra. Solid and dashed lines indicate calculated spectra with and without taking account of the laser pulse decay constant, respectively. For ease in comparison, the calculated mass spectrum of linear TOF mode was added with constant value.

a custom-designed microchannel plate (MCP; $\phi = 27$ mm, center hole $\phi = 6$ mm, F2223-21SHX, gain $>1 \times 10^6$, Hamamatsu Photonics K. K. Hamamatsu, Japan), which is used for the reflectron TOF-MS mode. For the linear TOF-MS mode, we use a two-stage fast time response MCP (gain $>5 \times 10^7$, F4655-11, Hamamatsu Photonics K. K.) mounted behind the reflectors as an ion detector. For the electrodes and the detectors, we use high voltage DC power supplies with multiple DC-to-DC power supply modules (HVR series, Matsusada Precision Inc., Shiga, Japan), as shown in Fig. 2. The electrodes and their configuration were designed using the SIMION 8.0 software (Scientific Instrument Services, Inc. Ringoes, NJ). Gridless electrodes in the ion acceleration region and in the reflectors are employed to optimized ion transmissions. The electronics unit of the vacuum system is powered by 24 VDC and the high voltage power supply unit is powered by 12 VDC. The TOF-MS system, excluding the laser unit, consumes approximately 100 W during operation.

To generate coherent VUV light at 118 nm (10.5 eV), we use the 9th harmonic of a compact and rugged Nd:YAG laser (laser head weight 1 kg, Big Sky Laser series Ultra, Quantel, Bozeman, MT). The 9th harmonic is generated by focusing the 20 Hz third harmonic output (355 nm, 8 mJ pulse^{-1}) of the Nd:YAG laser using a 50 mm focal length quartz lens into an electrolytically polished stainless steel cell containing Xe gas. The VUV generation efficiency was maximized at the Xe pressure of 3 kPa. The quartz lens also constitutes the entrance window of the VUV generation cell and its position is adjustable by 3 mm. Frequency tripling in Xe gas [16] generates the VUV radiation, which is focused to spot a few hundred microns in diameter by a VUV-quality MgF_2 plano-convex lens ($\phi = 25$ mm, $f = 35$ mm at 118 nm) into the ionization region. The MgF_2 lens also serves as the window between the Xe cell and the vacuum chamber. The distance between the quartz lens and the MgF_2 lens was 100 mm. The 355 and 118 nm beams are directed 5 mm apart from the center of the MgF_2 lens which disperses the different wavelengths and allows the VUV passes through a 3 mm pinhole placed 70 mm below the MgF_2 lens so that only 118 nm light is introduced into the ionization region. The VUV light is monitored using a NO-containing photoionization cell in contact with the VUV generation cell. Since NO molecules have an ionization energy (IE) of 9.24 eV, an incident VUV photon at 10.5 eV can ionize NO molecules with a photoionization cross section of 3 Mb [17]. The resultant photocurrent generated ejected electrons or ionized NO molecules is monitored to measure the relative intensity of VUV light. The VUV pulses are approximately 6 ns in duration and the VUV intensity is roughly estimated to be $<10^{10}$ photons per pulse [16].

For typical trace species detection the MCPs are operated at ±2.5 kV. The MCP output signal is digitized by a 200 MHz, 2 GS/s digital oscilloscope (WaveSurfer 422, Iwatsu Electric Co., Ltd., Tokyo, Japan). A 250 MHz 1 GS/s USB oscilloscope (dimensions 170 mm × 255 mm × 40 mm, weight 0.9 kg, PicoScope 5203, Pico technology Ltd. Cambridge, UK) connected to a laptop PC (<2 kg, <15 W) is also used to provide the compact TOF mass spectrometer system. The TOF mass spectra can be recorded in real time or stored on the hard disk to be analyzed by home-written LabVIEW software programs (LabVIEW 7.1, National Instrument, Austin, TX).

Premixed gas of 10 ppmv benzene/10 ppmv toluene/10 ppmv chlorobenzene in N_2 calibrated by gas-chromatography MS was obtained from Takachiho Co. Ltd. (Tokyo, Japan). The diluted sample gases (less than 1 ppmv mixtures in the N_2 buffer gas) prepared from the premixed gas are stored in 6 L canisters (Entech Instruments, Inc., Simi Valley, CA) coated with Silonite, and then used to measure the limits of detection. The gas inlet system is heated to 100 °C to prevent wall adsorption effects in the lines.

For car exhaust gas monitoring, the sample inlet system of SPI-TOF-MS was connected with a car exhaust port using a 1/4″ Cu tube with a length of 3 m. Exhaust gas was introduced into the sample inlet system at a gas flow rate of 30 sccm regulated with a mass-flow controller KOFLOC 3660. To prevent clogging and considerable interference from air dust and aerosols, the sampled air was filtered using a welded in-line filter made of SUS 316 with the pore size of 0.5 μm before introduction into the mass spectrometer. Premixed gas of 1 ppmv 50 VOCs (T.E.R.R.A. series, Takachiho Co. Ltd. Tokyo, Japan) was used as a calibration gas.

In the mass spectrum, the molecular ion signals from sample gases used in this study monotonically increased with increasing VUV laser fluence. The ion signal intensity is linear in VUV laser intensity, indicating that the ionization process is a single photon process, and ionization by a VUV multiphoton process could be ruled out.

3. Results and discussion

3.1. Mass resolution and limits of detection

The mass resolution R of the time-of-flight mass spectrum is defined as the ratio of the mass number M to the detectable mass difference ΔM, $R = M/\Delta M = t/2\Delta t$, where t is the total flight time. ΔM and Δt are commonly measured as the full width at half maximum (FWHM). In principle, the R is proportional to the flight time. In this study, we use $R_{50\%}$; i.e., the 50% valley definition of resolution.

We used a standard sample of 10 ppmv chlorobenzene diluted in nitrogen to estimate the $R_{50\%}$ in the linear and reflectron TOF mode. Fig. 3 shows the mass spectra of chlorobenzene measured in the linear and reflectron TOF mode. The background signal observed in the linear mode spectrum is 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 [10,18]. Since the N_2 LEI signal in the reflectron mode is sharper than in the linear mode, the background signal in the reflectron mode of Fig. 3(b) is negligible. The simulated mass spectra in Fig. 3 were calculated on the basis of the principles of Wiley–McLaren and reflectron TOF-MS as described in Refs. [15,19], assuming that the ionization region was characterized by a Gaussian function with a standard deviation of 1 mm and that the initial kinetic energy obeyed the Boltzmann distribution for 298 K. The calculated time profiles were convoluted by $\exp(-t/\tau)$, where τ is the decay time constant of 118 nm VUV laser pulse and assumed to be 3 ns, and were converted to mass spectra. The isotope peaks of $^{13}C^{12}C_5H_5{}^{35}Cl$, $^{12}C_6H_5{}^{37}Cl$, and $^{13}C_{12}C_5H_5{}^{37}Cl$ at m/z = 113, 114, and 115 are clearly seen in the experimental mass spectra of chlorobenzene measured in the reflectron TOF mode. On the other hand, only the isotope peak for $^{12}C_6H_5{}^{37}Cl$ at m/z = 114 is observed in the linear TOF mode. From the experimental mass spectra, the mass resolution $R_{50\%}$ at m/z = 112 is estimated to be 150 and 800 for the linear and reflectron TOF modes, respectively. Taking account of the laser pulse width, theoretical $R_{50\%}$ values at m/z = 112 are depleted from 210 to 190 and from 1240 to 900 for the linear and reflectron TOF modes, respectively. The experimentally determined $R_{50\%}$ value was well reproduced with the laser pulse decay constant of 3 ns. For both simulation and experiment, the mass resolution in the reflectron TOF mode is roughly 5 times improved compared with the linear TOF mode. We conclude from these results that the broadening of the mass spectra is caused by the laser pulse width.

The limits of detection (LOD) for the mass spectrometer in the reflectron TOF modes is estimated by measuring with the premixed gases of 0.01, 0.1, 1 and 10 ppmv of benzene, toluene, and chlorobenzene in N_2. Fig. 4 shows mass spectra of 0.1 ppmv benzene, toluene, and chlorobenzene. In Fig. 4, signal intensities are normalized by the standard deviation of the noise that was calculated using intensities between m/z = 75 and 77 for benzene, between m/z = 89 and 91 for toluene, and between m/z = 109 and 111 for chlorobenzene. Molecular ion peaks at m/z = 78, 92, and 112 are above the noise level and are identified as ion signals from 0.1 ppmv benzene, toluene, and chlorobenzene, respectively. The LODs for benzene, toluene, and chlorobenzene at a signal-to-noise (S/N) ratio of 2 were estimated using LOD = $2\sigma c/h$ [10], where c is the concentration of the samples, σ is the standard deviation of the noise, and h is the ion signal intensity. Signal intensities of each sample were averaged for 100 measurements (analysis time 5 s). The LODs for benzene, toluene, and chlorobenzene at the reflectron TOF mode were estimated to be 8, 11, and 18 ppbv, respectively. Butcher et al. measured the mass spectra of photoionized benzene and toluene at 10.5 eV and determined the LODs for 5 s measurements to be 40 and 70 ppbv, respectively [20]. Mühlbereger et al. also measured the TOF mass spectra for benzene, toluene, and chlorobenzene and determined their LODs for 10 s measurements to be 1.5, 2, and 7 ppbv, respectively [21]. In our previous study, we achieved LODs of 2.2, 2.7, and 0.9 ppbv for benzene, toluene, and chlorobenzene, respectively [2]. The LODs of the compact laser-based SPI-TOF-MS apparatus developed in this study are comparable to what was found in these previous studies. The other VOCs in environmental air would be also detected with same detection sensitivity, since the photoionization cross-sections of VOCs at 10.5 eV are same orders of magnitude with aromatic compounds [2]. Note that the gain of the MCP used in the present study (>1 × 10^6) is lower compared with that of the MCP used for the pervious study in Ref. [2] (>5 × 10^7). We believe LODs can be further improved by one order of magnitude using a Z-stack MCP with higher gain (>10^7).

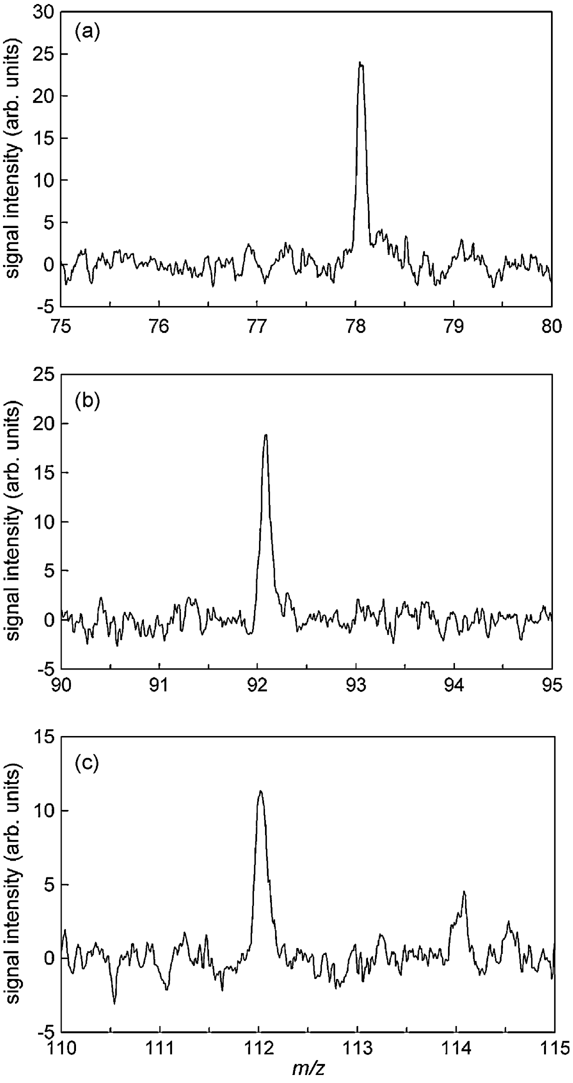

Fig. 4. Mass spectra of 0.1 ppmv benzene (a), toluene (b) and chlorobenzene (c) measured at reflectron TOF mode.

3.2. Exhaust gas monitoring

On-line monitoring of diesel engine exhaust was demonstrated using a SPI-TOF-MS at National Traffic Safety and Environmental Laboratory. Because automotive exhaust constantly changes in synchronization with engine operation, a fast sampling frequency is required to analyze the species in exhaust gas. The tested diesel vehicle which was a light duty truck equipped with a diesel oxidation catalyst for the after treatment system was driven on a chassis dynamometer in the JE05 mode (Japanese type approval test cycle for heavy duty vehicles). The exhaust gas was sampled in an exhaust pipe. The TOF mass spectra of the sampled gas were averaged and recorded every 3 s (60 single-shot spectra). Fig. 5 shows the mass spectra of on-line measurements of the diesel exhaust gas. The ion signals with lower m/z than about 30 could not be measured

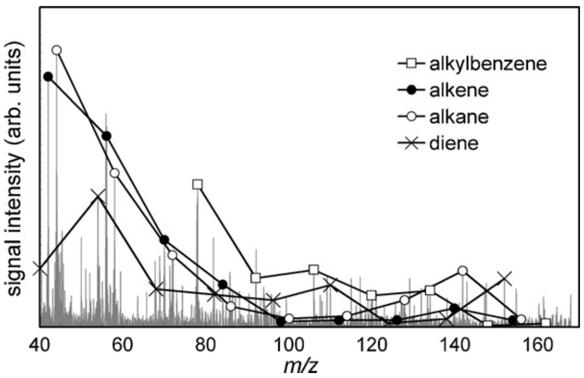

Fig. 5. On-line measured 10.5 eV SPI-TOF mass spectrum of diesel exhaust gas.

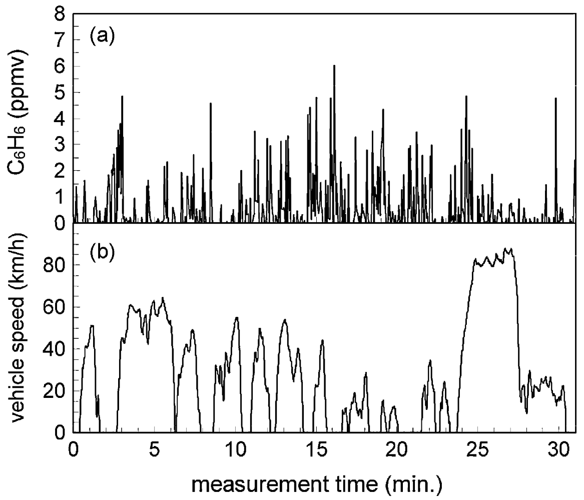

Fig. 6. Temporal profile of (a) the 10.5 eV SPI-TOF signal at $m/z = 78$ and (b) vehicle speed.

due to interference of large signals from N_2 ionized by LEI and nitrogen monoxide. Major signals were detected at $m/z = 42$, 44, 54, 56, 58, 70, 72, 78, 92, 106, 120, 134 and 142. Based on the result of gasoline engine vehicle exhaust measurement [10], the observed peaks for the SPI-TOF mass spectrum of the diesel exhaust gas may be assigned to butadiene for the peak at $m/z = 54$, butene for $m/z = 56$, acetone for $m/z = 58$, pentene for $m/z = 70$, butanale, butanone and pentane for $m/z = 72$, benzene for $m/z = 78$, toluene for $m/z = 92$, xylene and ethylbenzene for $m/z = 106$, trimethylbenzene for $m/z = 120$, tetramethylbenzene for $m/z = 134$, and methylnaphtalene for $m/z = 142$. Other hydrocarbons such as alkylbenzens, alkenes, alkanes, and dienes were also measured. The ion signals assigned to hydrocarbons with low carbon number were observed with relatively high intensities except C_3H_4 (m/z 40). The signal intensity of hydrocarbon in the exhaust gas decreases with the mass number, as shown in Fig. 5.

Fig. 6 shows the temporal profile of the ion signal at $m/z = 78$ as a function of experimental time. The origin on x-axis is time when the engine started. In Fig.6(a), the ion signal at $m/z = 78$ is moved 30 s earlier on x-axis because an appearance of the signal delayed compared with the change of the vehicle speed. The delay would be caused by a long Cu tube (about 3 m) connecting the SPI-TOF-MS with a vehicle exhaust port. The ion signal at $m/z = 78$ was assigned to be benzene mentioned above. The concentration of benzene was relatively high at low vehicle speed and idling. On the other hand, the low concentration of benzene was measured at high vehicle speed. Temporal profiles of other hydrocarbons showed the same tendency as that of benzene. It is noted that the high concentrations of hydrocarbons are emitted at low vehicle speed and idling in the car used.

4. Conclusion

In this study, we have developed and tested a compact, laser-based SPI-TOF-MS to monitor VOCs in environmental air. We characterized the apparatus performance, the limits of detection, the mass resolution, etc. The instrument demonstrated a laboratory-measured detection limit for aromatic compounds at ppbv level for 5 s measurements. The detection limit is comparable with previously reported VUV-SPI instruments, but the developed instrument is better suited for on-site measurements of complex gas mixtures such as exhaust gases due to its potential for ease of portability. Applications for compact VUV-SPI-TOF-MS systems include gas monitoring for industrial process and environmental research.

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