Atmospheric
Measurement
Techniques

Real-time monitoring of trace-level VOCs by an ultrasensitive lamp-based VUV photoionization mass spectrometer

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Abstract. In this study, we report on the development of a lamp-based vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS) in our laboratory; it is composed of a radio-frequency-powered VUV lamp, a VUV photoionizer, an ion-migration lens assembly, and a reflection time-of-flight mass spectrometer. By utilizing the novel photoionizer consisting of a photoionization cavity and a VUV light baffle, the baselines of the mass spectra decreased from 263.6 ± 15.7 counts to 4.1 ± 1.8 counts. A detection limit (2σ) of 3 pptv was achieved for benzene after an acquisition time of 10 s. To examine its potential for real-time monitoring applications of samples, the developed VUV-PIMS was employed for the continuous measurement of urban air for 6 days in Beijing, China. Strong signals of trace-level volatile organic compounds, such as benzene and its alkylated derivatives, were observed in the mass spectra. These initial experimental results reveal that the instrument can be used for the online monitoring of trace-level species in the atmosphere.

1 Introduction

Volatile organic compounds (VOCs) are an important group of air pollutants: they are active in the formation of photochemical smog and ground-level ozone production; several VOCs present in urban air, such as benzene and its alkylated derivatives, are considered carcinogenic (Gee and Sollars, 1998; Lee et al., 2005). The average volume fractions of VOCs in the atmosphere are generally less than 1×10^{-9} (ppbv) (Elsom, 1996; Schubert et al., 1999). Because of this low VOC concentration, sample enrichment is often necessary prior to VOC analysis. During sampling or analysis,

some active species might be oxidized by ozone (Jaouen et al., 1995) or other oxidizing agents, thereby decreasing the representativity of sampling. Meanwhile, conventional detection approaches such as gas chromatography–mass spectrometry and high-performance liquid chromatography–mass spectrometry involve a time-consuming chromatographic separation step (Muhlberger et al., 2002). For these reasons, it is imperative to develop real-time online monitoring instruments with high sensitivity for the detection of VOCs.

The use of the highly sensitive proton-transfer-reaction mass spectrometer (PTR-MS) has been demonstrated for the real-time measurement of trace gases in the atmosphere with limits of detection (LODs) at the pptv level (de Gouw and Warneke, 2007). On the other hand, laser-based photoionization techniques including resonance-enhanced multiphoton ionization MS (Heger et al., 1999; Muhlberger et al., 2004) and single-photon ionization (SPI) MS (Muhlberger et al., 2004; Tonokura et al., 2010) have also been applied for the online detection of VOCs at trace levels (ppbv pptv^{-1}). However, they suffer from limitations such as the use of expensive, bulky, and sophisticated laser systems to achieve nonlinear optical processes (Muhlberger et al., 2002). Meanwhile, the lamp-based vacuum ultraviolet photoionization MS (VUV-PIMS) is another type of instrument that has been attracting significant attention (Muhlberger et al., 2005a). Mühlberger et al. (2007, 2005a, b; 2002) have developed a series of VUV-PIMSs with an electron-beam-pumped rare gas excimer VUV lamp. There is an improvement in the LOD for benzene, toluene, and xylene from ppmv to tens of ppbv. Meanwhile, Hua et al. (2011) have designed a VUV-MS based on a commercial krypton lamp, exhibiting both SPI
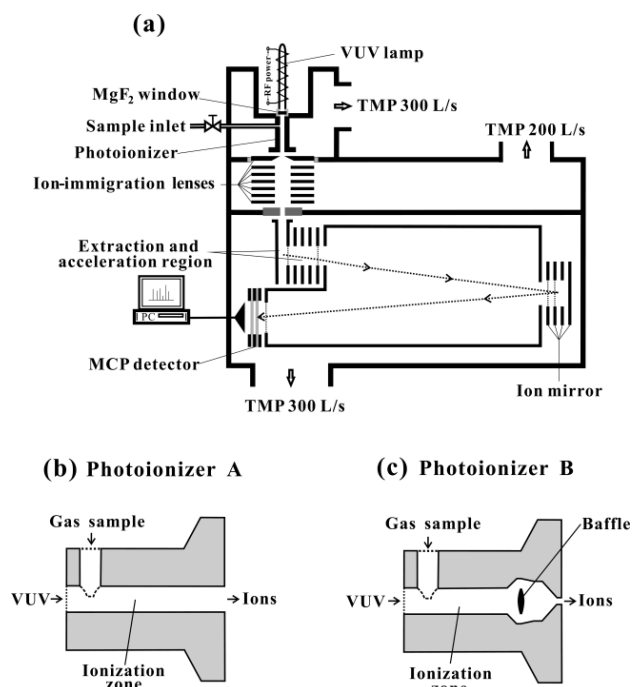
(a)

(b) Photoionizer A   **(c) Photoionizer B**

Figure 1. Schematic of the VUV-PIMS **(a)**, photoionizer A **(b)**, and photoionizer B **(c)**. TMP: turbo molecular pump.

and chemical ionization capabilities. The LODs observed for benzene, toluene, and xylene are as low as 3, 4, and 6 ppbv, respectively, in the SPI mode. Meanwhile, Kuribayashi et al. (2005) have developed a VUV-PI-ion-trap MS with a microwave-excited VUV lamp and observed an LOD of 10 pptv for trichlorobenzene after an acquisition time of 18 s.

In this paper, we report the design of a sensitive VUV-PIMS, which was employed to measure trace-level VOCs such as benzene. The instrument design, calibration results, and urban air measurements will be discussed in the following sections.

2 Experimental section

2.1 Instrumentation

Figure 1a shows the laboratory-built VUV-PIMS. Its main components include a radio-frequency-powered (RF) VUV lamp, a VUV photoionizer, an ion-migration lens assembly, and a reflection time-of-flight MS (TOF-MS).

The VUV lamp, which is constructed in our laboratory, is a krypton lamp. Its structure has been reported in detail in the study by Shu et al. (2013). A plano-convex MgF$_2$ lens ($f = 50$ mm) is used as a window for focusing VUV light into the photoionizer. The output of the lamp is $\sim 5 \times 10^{14}$ photon s^{-1} at 123.9 nm. Table 1 lists the compar-

ison of several sources of VUV light typically used for the detection of VOCs by mass spectrometry.

Figure 1b and c show photoionizers A and B, respectively, used in the test, which are made of stainless steel. They are interchangeable in the corresponding position of the VUV-PIMS. Photoionizer A is a straight channel with a length of 30 mm and an internal diameter of 6 mm. On the other hand, photoionizer B is designed with an optical baffle for preventing VUV light from entering the ion-migration lens assembly. The diameter of the VUV light baffle is ~ 2 mm, and the diameter of the exit orifice of photoionizer B is 1.5 mm. First, the sample is introduced into the photoionizer via a stainless-steel tube (1/8-inch outer diameter; OD) using a needle valve. Moreover, the signal intensity is optimized by controlling the sample flow by adjusting the needle valve. The pressure in the photoionizer is not measured directly but is measured indirectly by the pressure of the foreline measured using a convectron gauge. The estimated pressures inside the photoionizers A and B are ~ 100–300 and ~ 500–1000 Pa, respectively.

Meanwhile, the ion-migration lens assembly contains seven ion-migration lenses. The ions ejected from the photoionizer are focused by the electrostatic fields generated from the ion lenses into a narrow beam and then enter into the reflection MS. To obtain a stronger ion beam, the excitation tube of the VUV lamp, the photoionizer, and the ion-migration lens assembly are concentric.

A V-shaped laboratory-built reflection MS was employed, which consisted of a 230 mm TOF cavity, an extraction grid, an ion mirror, and a chevron multichannel plate detector. The relatively short TOF cavity is selected to make the instrument compact; hence, a high repetition rate of 35 000 s^{-1} is obtained for better LODs. The path of the ion flight is orthogonal to the axis of the ion-migration lens assembly. The generated ions are extracted with a pulsed electric field of 600 V, 35 000 Hz. The voltage of the acceleration field is 1800 V. The chevron microchannel plates used to detect ions are biased at 2100 V. The signal is amplified using a 100× amplifier (Ortec VT120C) and recorded with a TOF multiscaler (FAST Comtec, P7888). Each mass spectrum is obtained by accumulating ion extractions up to 350 000 times, equal to an acquisition time of 10 s (averaging time).

The three-stage differential pumping system is composed of three chambers: a source chamber, differential chamber, and detection chamber. These chambers are pumped by 300, 200, and 300 L s^{-1} turbo molecular pumps (TMPs), respectively. The first two TMPs are backed by a rotary pump (8.3 L s^{-1}), while the outlet of the third TMP joins the source chamber. Furthermore, during sampling, the working pressures of the reflection MS for photoionizers A and B are $\sim 2 \times 10^{-3}$ and $\sim 3 \times 10^{-3}$ Pa, respectively.

Table 1. Performance of instruments using different light sources.

Type of VUV	Photon flux (photon s^{-1})	LOD	Type of MS	Year	Ref.
Radio-frequency-powered VUV lamp	$\sim 5 \times 10^{14}$, Kr, 123.9 nm	3 pptv for benzene	TOF	2015	this study
Laser	$\sim 1.6 \times 10^{18}$, 118 nm	10 ppbv for benzene	TOF	2010	(Tonokura et al., 2010)
Electron-beam-pumped rare gas excimer VUV lamp (EBEL)	3×10^{17}, kr$_2$*, 147 nm	2 ppmv for benzene	TOF	2002	(Muhlberger et al., 2002)
EBEL	1.9×10^{19}, Ar*, 126 nm	50 ppbv for benzene	TOF	2005	(Muhlberger et al., 2005a)
EBEL	$\sim 1.5 \times 10^{13}$, Ar*, 126 nm	50 ppbv for benzene	Quadrupole	2005	(Muhlberger et al., 2005b)
Lyman-α atomic-radiation-based microwave discharge lamp	$\sim 10^{14}$, H$_2$/He, 121.6 nm	10 pptv for trichlorobenzene	Ion trap + TOF	2005	(Kuribayashi et al., 2005)
Commercial Kr VUV lamp	10^{11}, Kr, 116.5 nm	35 ppbv for toluene	TOF	2011	(Hua et al., 2011)

2.2 Sample preparation

Samples of 10 and 400 ppbv benzene were used in the experiment, which were prepared by triple dilution. First, pure benzene was diluted 4.1-fold with dichloromethane; then 0.1 mL of this diluted solution was injected into a 6.35 L narrow-mouthed bottle filled with synthetic air (80 % N$_2$ + 20 % O$_2$), which was prepared by two mass-flow meters using high-purity nitrogen and oxygen. Thus, the concentration of benzene obtained in the bottle was 1000 ppmv. The 10 ppbv sample was prepared by adding 1.2 mL of 1000 ppmv benzene into a 120 L smog chamber with a syringe. The chamber was composed of a thin-walled open-head stainless-steel drum and a thin Tedlar polyvinyl fluoride film bag. Adequate mixing was ensured by using a magnetic stirring fan set at the bottom of the chamber. This sample was initially used for optimizing the parameters of the VUV-PIMS such as the RF power and the ion source pressures of photoionizers A and B. The 400 ppbv sample was prepared by injecting 0.1 mL of 1000 ppmv benzene into a 0.24 L cylinder. The cylinder was made of stainless steel with two 1/4-inch tubes serving as the gas inlet and outlet, respectively. Synthetic air at a flow rate of 0.2 L min^{-1} was continuously injected into the cylinder to dilute the 400 ppbv sample. The dynamical concentrations of the continuously diluted sample were calculated by an exponential equation reported in literature (Gamez et al., 2008; Lovelock, 1961). This exponential dilution method was used to obtain the VUV-PI mass spectra using photoionizers A and B as well as the LODs of the instrument. A 1000 μL MicroPette™ pipettor (Eppendorf Co. Limited), a 100 μL MicroPette™ pipettor (Eppendorf Co. Limited), and

an ordinary injection syringe were used in the preparation. The uncertainty for dilution was estimated to be ±5 %.

For the measurement of urban air, outdoor air was introduced into the VUV-PIMS through a stainless tube (240 cm length, 1/8 inch OD). The tube was heated at ~ 60 °C, and a glass microfiber filter (aperture size: 0.7 μm) was placed at the inlet of the tube to filter the particles present in the outdoor air. The end of the tube was set at ~ 2 m from the outer wall of the laboratory building and at a height of ~ 20 m from the ground.

Benzene (Beijing Beihua Fine Chemicals Co. Ltd., > 99.5 %) and dichloromethane (J. T. Baker Co., chromatographic grade) were used in the experiment. High-purity nitrogen (> 99.999 %) and high-purity oxygen (> 99.999 %) were purchased from Beijing Haikeyuanchang Practical Gas Co. Ltd. and Beijing Huayuan Gas Chemical Industry Co. Ltd, respectively.

3 Results and discussion

3.1 Mass spectra obtained with photoionizers A and B

Figure 2a and b show the mass spectra of 0 and 8.6 ppbv benzene in synthetic air, respectively, which were obtained using photoionizer A. In each spectrum, strong mass peaks are observed at an m/z of 28 ($\sim 2 \times 10^5$ counts) and 32 ($\sim 3 \times 10^5$ counts), which correspond to the background ions of N$_2^+$ and O$_2^+$, respectively. N$_2$ (ionization potential = 15.6 eV) and O$_2$ (ionization potential = 12.1 eV) are not ionized by the 10.0 eV VUV photons emitted from the krypton lamp (Shu et al., 2013), but they are ionized by the bom-

bardment of accelerated light-induced electrons (photoelectron ionization, PEI) (Gamez et al., 2008; Muhlberger et al., 2001) [Wiley, 1955]. For photoionizer A, VUV light directly illuminates the ion lenses biased at dozens of volts, thereby generating numerous photoelectrons with kinetic energies of dozens of electron volts (photoelectric effect). These energetic photoelectrons induce several secondary N_2^+ and O_2^+ species. The noise levels of the mass spectra shown in Fig. 2a and b are as high as 263.6 ± 15.7 counts, predominantly caused by stray VUV photons in the TOF chamber and secondary ions formed outside the focusing region of the ion lenses. Furthermore, in the inset of Fig. 2b, a mass peak is observed at an m/z of 78, corresponding to the molecular ion of benzene. The mass resolution at an m/z of 78 is ~ 200. Meanwhile, small mass peaks are observed at m/z values of 16, 18, 19, and 44, corresponding to O^+, H_2O^+, H_3O^+, and CO_2^+, respectively; these peaks are also generated by PEI. Moreover, other small mass peaks are observed at m/z values of 29 and 34, possibly attributed to the impurities present in synthetic air.

Figure 2c and d show the mass spectra of 0 and 8.6 ppbv benzene in synthetic air, respectively, recorded using photoionizer B. Compared with the mass spectra in Fig. 2a and b, those in Fig. 2c and d exhibit a decrease in the intensities of N_2^+ and O_2^+ mass peaks by 3 orders of magnitude. This decrease is attributed to the fact that the optical baffle of photoionizer B prevents VUV light from entering the ion-migration lens assembly; as a result, the formation of N_2^+ and O_2^+ is significantly suppressed. Meanwhile, the baseline level decreases from 263.6 ± 15.7 counts (Fig. 2a) to 4.1 ± 1.8 counts (Fig. 2c). On the other hand, the mass signal intensity for benzene observed in Fig. 2d is slightly higher than that observed in Fig. 2b. Such an enhancement in the photoionization efficiency possibly originates from the reflectance of VUV light by the optical baffle in photoionizer B (Zhu et al., 2014). In addition, Fig. 2d shows relatively strong mass peaks at m/z values of 19, 37, and 55, which correspond to H_3O^+ (protonated water), $(H_2O)_2H^+$, and $(H_2O)_3H^+$ (protonated water clusters), respectively. Protonated water and water clusters are formed by multiple molecular reactions (Hansel et al., 1995).

The above experimental results indicate that photoionizer B significantly reduces the background noise. Hence, the VUV-PIMS with photoionizer B is further calibrated and used for outdoor measurements.

3.2 Limits of detection

To demonstrate its linearity of response as well as detection sensitivity, VUV-PIMS was calibrated using benzene. The benzene concentrations employed in the calibration were in the low ppbv range considering that benzene is present at the level of several micrograms per meter in the atmosphere (Cheng et al., 2010). Figure 3 shows the linear calibration curve and the corresponding linear regression
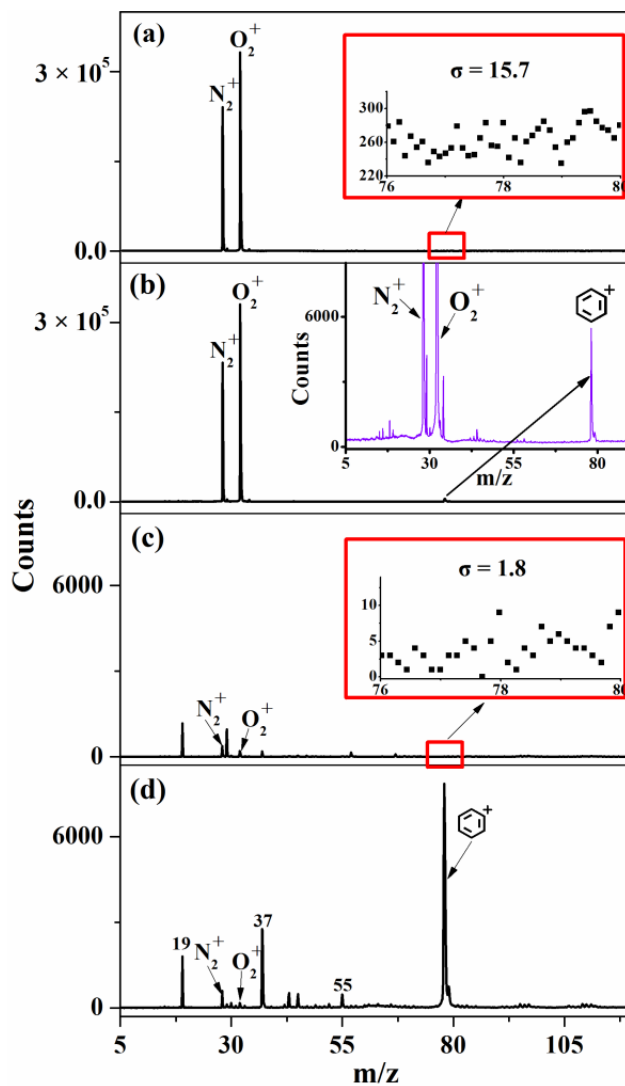

Figure 2. Mass spectra of synthetic air **(a)** and 8.6 ppbv benzene **(b)** obtained with photoionizer A. Mass spectra of synthetic air **(c)** and 8.6 ppbv benzene **(d)** obtained with photoionizer B. The acquisition time for each mass spectrum is 10 s. The insets in Fig. 2a and c show the magnified baselines of the mass spectra at an m/z of 78. The inset in Fig. 2b shows the magnification of the benzene mass peak.

equation ($y = 1.5 + 1254\times$). A satisfactory linear response ($R^2 = 0.997$) is obtained over 3 orders of magnitude. The slope of the fitted line indicates that the detection sensitivity of the VUV-PIMS is $\sim 1.25 \pm 0.02$ counts pptv^{-1} (an uncertainty of 0.02 is obtained from five measurements).

The LOD for benzene at a signal-to-noise ratio of 2 is estimated by $\text{LOD} = 2\sigma c / h$ (Muhlberger et al., 2001), where c is the sample concentration, σ is the standard deviation of the noise, and h is the ion signal intensity. Detection sensitivity is given by h/c. Based on the mass spectra shown in
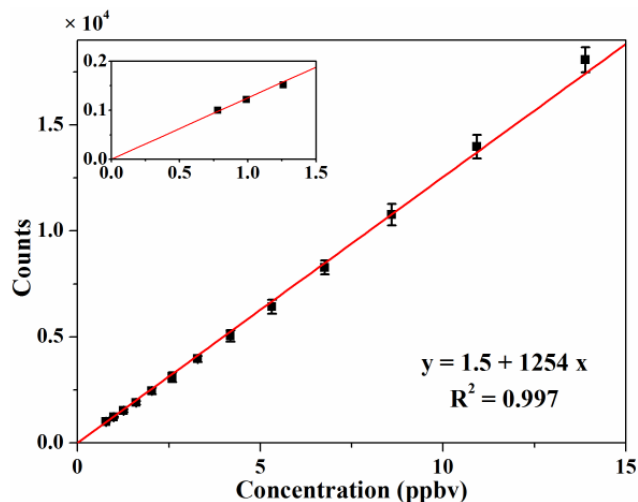
Figure 3. Signal intensities versus concentrations of benzene measured by the VUV-PIMS equipped with photoionizer B. Black squares represent the data points, and the line represents the result from linear fitting.
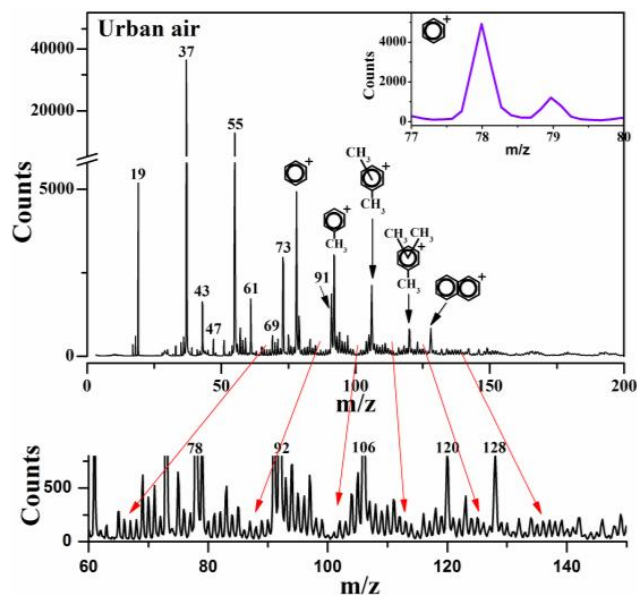

Figure 4. Mass spectrum of outdoor air obtained using the VUV-PIMS at 00:14 on 7 March 2015. The magnified plots are discussed in the text.

Fig. 2c, σ is determined to be 1.8. The LOD is calculated to be ~ 3 pptv.

Table 1 shows the sensitivities of similar instruments reported in literature. Compared with the series of lamp-based VUV-PIMS developed by Mühlberger et al. (2007, 2005a, b, 2002) and that by Hua et al. (2011), the VUV-PIMS developed herein exhibits an improvement in sensitivity by 3 orders of magnitude. The sensitivity of this instrument even exceeded that of the lamp-based VUV-PI-ion-trap-MS developed by Kuribayashi et al. (2005). Considering that both Kuribayashi et al. and our group utilized similar VUV photon fluxes, we believe that the ion-migration lens assembly designed herein is very effective. The sensitivity of this instrument is close to that of the mobile resonance-enhanced multiphoton ionization MS designed by Heger et al. (1999) and the widely used PTR-MS (de Gouw and Warneke, 2007).

3.3 Atmospheric measurements

To demonstrate the utility of the developed VUV-PIMS for field measurements further, real-time measurements of urban air were conducted for 6 days between 7 March 2015 and 12 March 2015. Air from outside our laboratory building (Beijing, China) was continuously sampled into the VUV-PIMS. The operating parameters were the same as those employed in the benzene calibration study. Spectra were recorded every 3 min.

Figure 4 shows the VUV-PIMS spectrum recorded at 00:14 (China Standard Time) on 7 March 2015, when the intensity of the benzene peak was the maximum during measurement. In the spectrum, a series of strong mass peaks are observed at m/z 19, 37, 55, 73, and 91, corresponding to H_3O^+, $(H_2O)_2H^+$, $(H_2O)_3^+$, $(H_2O)_4H^+$, and $(H_2O)_5H^+$,

respectively. Mass peaks are also observed at m/z 43, 47, 61, 69, 78, 92, 106, 120, 128, and others with comparatively lower intensities (See the magnified plot in Fig. 4), corresponding to VOCs. Based on the measurement results of atmospheric VOCs by GC–MS in the same area from 2000 to 2005 (Jiang, 2006), the mass peaks at m/z values of 78, 92, 106, 120, and 128 can be attributed to benzene, toluene, xylene/ethylbenzene, C_3-alkylated benzene derivatives, and naphthalene, respectively. In urban environments, benzene, its alkylated derivatives, and naphthalene mainly originate from automotive exhaust. They are potential carcinogens and are involved in photochemical reactions (Lee et al., 2005). The mass peaks at m/z 43, 47, 61, and 69 are speculated to be protonated VOCs because of the presence of a large amount of H_3O^+ observed in the mass spectrum. Atmospheric formic acid, acetic acid, and isoprene may form these ions via PTR (de Gouw and Warneke, 2007). Other mass peaks are not assigned in this study.

A magnified image of the mass spectrum around mass peaks at m/z 78 and 79 is shown in Fig. 4. From the magnified image, the signal intensities at m/z 78 and 79 represent 4957 counts and 1212 counts, respectively; i.e., their intensity ratio (I_{78}/I_{79}) is 1 : 0.24. However, according to the carbon isotope ratio of $^{12}C/^{13}C$, the theoretical I_{78}/I_{79} should only be 1 : 0.067. Thus, the PTR may contribute to the formation of the mass peak at m/z 79. By deducting the isotopic contribution ($^{13}C^{12}C_5H_6^+$), ~ 874 counts can be assigned to $^{12}C_6H_7^+$. Hence, the 874 count signal is estimated to be contributed by PTR.

The presence of protonated water and water clusters complicates the mass spectrum. A metal mesh piece was attached to the side of the photoionizer connecting to the VUV lamp to abate ion formation. However, this phenomenon cannot be absolutely eliminated under the current design of the instrument.

Figure 5a–d show the variations in the concentrations of benzene, toluene, xylene/ethylbenzene, and C_3-alkylated benzene derivatives by continuous monitoring by the VUV-PIMS, respectively, and Fig. 5e shows the real-time wind speeds as measured by a meteorological station at a distance of $\sim 200\,\mathrm{m}$ from the laboratory for 6 days. The concentration variation of benzene and its derivatives exhibit similar characteristics. In addition, they exhibit a remarkable opposite trend to the wind speeds. The concentrations of benzene (m/z 78) are quantified by the abovementioned calibration and are found to range between 0.1 and 3.2 ppbv, which is consistent with the reported average level of the benzene concentration in the same area from 2000 to 2005 (4.0 ppbv) (Jiang, 2006). The concentrations of benzene from 10:00 CST on 8 March 2015 (3/8, 10:00) to 17:00 on 10 March 2015 (3/10, 17:00) are in the range of 0.1–0.3 ppbv. A calibration with the 10 ppbv sample of benzene was conducted at 13:00 on 8 March 2015 (3/8 13:00) to check the instrument. The results indicated that the instrument operates normally during this time.

4   Conclusions

A lamp-based VUV-PIMS was developed in our laboratory. The photoionizer with an optical baffle significantly reduced the background noise. An LOD of 3 pptv was achieved for benzene. The PIMS developed herein exhibited sensitivity for VOCs better than that exhibited by VUV photoionization MSs reported previously (Kuribayashi et al., 2005; Muhlberger et al., 2007; Muhlberger et al., 2005a; Muhlberger et al., 2005b). A satisfactory linear response ($R^2 = 0.997$) was obtained. The initial atmospheric measurement demonstrates that the instrument can be used for the real-time monitoring of trace-level VOCs in the atmosphere.
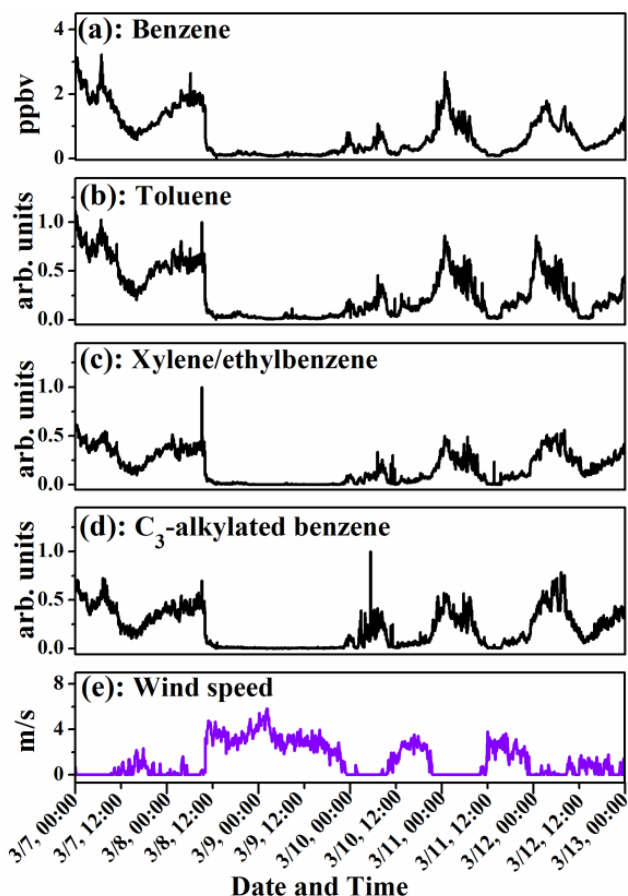
Figure 5. Outdoor measurements for 6 days: concentration variation of benzene **(a)**, toluene **(b)**, xylene/ethylbenzene **(c)**, and C_3-alkylated benzene derivatives **(d)** monitored by the VUV-PIMS. Data for wind speeds **(e)** were obtained from the Beijing Urban Ecosystem Research Station.

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