Development of a Portable Single Photon Ionization-Photoelectron Ionization Time-of-Flight Mass Spectrometer

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1. Introduction

Mass spectrometry has been widely employed for detection of environmental pollutants, illegal drugs, and explosives for its rapid, high sensitivity, and accuracy in qualitative analysis [1]. However, traditional mass spectrometry used in lab can barely be applied for in situ detection due to its size and weight. The technology of portable mass spectrometry has been recognized as one of the most promising and widely used techniques in environment monitoring, field diagnosis, and process monitoring.

Researches on miniaturization of magnetic mass spectrometry, quadrupole mass spectrometry, ion trap mass spectrometry, and time-of-flight mass spectrometry (TOFMS) all have been reported in the literature [2–8]. Compared with other types of mass spectrometry, TOFMS provides rapid scanning speed, full range scanning of the mass to charge, and simpleness in structure. Particularly, TOFMS can give a satisfying performance with moderate mechanical accuracy. Hopkins et al. have achieved remarkable approaches in developing and application of field detecting TOFMS [9–11]. A tiny TOFMS analyzer was developed with a length of 20 cm and 500 g in weight. A coaxial reflecting TOFMS with MALDI ion source was also developed, and the mass range is as high as 10,000 m/z; sensitivity of picomole and resolution of 300–1000 (m/Δm) were achieved. Cornish and Cotter [12] designed an end cap miniature TOFMS, this TOFMS featured with a laser ion source and a resolution of 210 at 1061 m/z. Brinckerhoff et al. [13] explored a laser-focusing micro TOFMS with coaxial structure and a length of 20 cm, and multifield energy focusing technique was applied to this micro TOFMS. The micro TOFMS has a resolution of 1000 m/Δm with an upper mass range to 1000 m/z and was used for elemental and organic analysis on the surface of a planet. White et al. developed a mini TOFMS with membrane inlet and EI ion source [14]. The mini TOFMS
2. Description of Spectrometer

2.1. Instrument Description. A schematic diagram and photograph that illustrate the features of the portable TOFMS are presented in Figure 1. The dimensions of the TOFMS are $40 \times 31 \times 29$ cm, and it weighs about 27 kg including the battery and all the pumping system. Power consumption is approximately 70 W at working condition. The portable TOFMS consists of an ionization source, an orthogonal acceleration reflection mass analyzer, two sampling inlets, the pumping system, and the electronics for the TOFMS timing and data acquisition. The ions generated from ionization source are accelerated from the source region to orthogonal repelling region through a set of electrodes. The repeller then was applied with pulse voltage to converge the ions into acceleration region, and then the ions enter a field-free region. A cylindrical reflectron is used for focusing the ion beam and directing it back along the flight tube. When the ion beam reaches the detector, it is detected by a micro-channel-plate detector. The electronic signal from the detector is sent to a time-to-digital converter (TDC) based data acquisition system. Mass spectrum histogram with 100 ps resolution is then passed to a laptop PC. Data analysis and processing including data reduction are performed using home-made data processing software.

The portable TOFMS employs a three-stage differential pumping system with an 80 L/s split-flow turbomolecular pump and a 10 L/s turbomolecular pump; both of the turbomolecular pumps are backed by a 5 L/min diaphragm pump. The 10 L/s turbomolecular pump is used for the first-stage differential pumping of ion source and held the pressure at 1.5 Pa. The split-flow turbomolecular pump provides about 3 L/s pumping for second stage of ion transmission region and 80 L/s pumping for the third stage of mass analyzer (kept below $5 \times 10^{-4}$ Pa at working condition). Vacuum gauges (MKS 925) were used to monitor the pressure of ion source, and a MKS 972 vacuum gauge was used for mass analyzer.
2.2. Sampling Inlet. The portable TOFMS is equipped with two kinds of sampling inlet: a fused silica capillary (150 μm in i.d., 1.7 m in length) based direct sampling inlet for high concentration analytes and a sheet PDMS membrane (with thickness of 50 μm and 150 mm² in area) inlet for trace analytes. A stainless steel mesh was set under the membrane to keep the sheet membrane flat. Volatile organic compounds (VOCs) in the sample diffuse faster than air when passing through the membrane into the ionization region; therefore, the VOCs are relatively enriched. The flow rate of the samples through the surface of the membrane was optimized as 1 L/min and was controlled by a mass flow controller (Seven Star Electronics Co., Ltd., Beijing, China).

2.3. Ionization Source and Ion Transmission Region. The electrodes configuration inside of the ion source and ion transmission region is shown in Figure 2. The ionization source consists of three parts: a VUV lamp, permanent magnetic ring, and DC voltage lens including electrode 1, electrode 2, and skimmer electrode. The VUV lamp is a commercial low-pressure krypton discharge lamp (10.6 eV, Cathodeon Ltd., Cambridge, UK), with a flux of about 1 L/min and was controlled by a DC voltage applied on electrodes inside of ionization source. When 20 V, 17 V, and 5 V were applied to electrode 1, electrode 2, and skimmer electrode, respectively, the ionization source operates under SPI mode, and voltages on electrode 3, electrode 4, and electrode 5 were changed to 9 V, and 40 V. The PEI mode was activated when voltages on electrode 1, electrode 2, and skimmer were changed to 22.5 V, 21 V, and −44.5 V. The energy of the photoelectron was calculated as 67 eV by subtracting the voltage on the skimmer from the voltage on electrode 1, and the voltages on electrode 3, electrode 4, and electrode 5 were changed to 9 V, −120, and 0 V, accordingly.

The ion source was operated at two modes: single photonoization (SPI) mode for analytes with ionization energy (IE) lower than 10.6 eV and photoelectron ionization (PEI) mode for analytes with IE higher than 10.6 eV. The two different modes were controlled by the DC voltage applied on electrodes inside of ionization source. When 20 V, 17 V, and 5 V were applied to electrode 1, electrode 2, and skimmer electrode separately, the ionization source operates under SPI mode, and voltages on electrode 3, electrode 4, and electrode 5 were −20 V, −120, and 40 V. The PEI mode was originated from the electrons generated on the surface of skimmer by the photoelectric effect when VUV light irradiated on electrodes. The PEI mode was activated when voltages on electrode 1, electrode 2, and skimmer were changed to 22.5 V, 21 V, and −44.5 V. The energy of the photoelectron was calculated as 67 eV by subtracting the voltage on the skimmer from the voltage on electrode 1, and the voltages on electrode 3, electrode 4, and electrode 5 were changed to 9 V, −120, and 0 V, accordingly.

The total power consumption of the present ionization source was only 1.5 W with the VUV lamp, much lower than 50 W with traditional EI ionization source.

The mass analyzer of TOFMS consists of four parts: the ion repeller region, ion accelerator region, field-free region, and the reflectron with a length of 6 mm, 23 mm, 210 mm, and 58 mm, respectively. Typical parameters of the portable time-of-flight mass spectrometer were shown in Table 1.

2.4. Methods Used for Gas Preparation. The two standard gas mixtures of 1 ppmV benzene, toluene, and p-xylene (BTX) and 50 ppm SO₂ diluted with N₂ (99.9993% purity) were purchased from Dalian Special Gas Company (Dalian, China). The samples of BTX and SO₂ with different concentrations used in the experiments were obtained by diluting standard gas with pure N₂ within a PTFE sampling bag. The dilution process was as follows: a measured amount of N₂ was blown

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**Table 1: Typical parameters of the portable time-of-flight mass spectrometer.**

| Parameters                        | SPI mode | PEI mode |
|----------------------------------|----------|----------|
| Pressure inside of ion source    | 1.25 Pa  | 1.25 Pa  |
| Electrode 1                       | 20 V     | 22.5 V   |
| Electrode 2                       | 17 V     | 21 V     |
| Electrode 3                       | 5 V      | −45.5 V  |
| Electrode 4                       | −20 V    | 9 V      |
| Electrode 5                       | −120 V   | −120 V   |
| Electrode 6                       | 40 V     | 0 V      |
| VUV lamp voltage                  | −1400 V  | −1400 V  |
| Repeller voltage                  | 400 V    | 400 V    |
| Accelerator                      | 1800 V   | 1800 V   |
| Reflector 1                      | 1000 V   | 1000 V   |
| Reflector 2                      | 420 V    | 400 V    |
| MCP detector                     | 2600 V   | 2600 V   |
| Pressure inside of mass analyzer  | 5 × 10⁻⁵ Pa | 5 × 10⁻⁵ Pa |

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The ion lens in the ion transmission region includes three cylinders: electrode 3, electrode 4, and electrode 5. Electrode 1, electrode 2, and skimmer are all tubular steel stainless electrodes; the size is 5.5 mm in length, 16 mm i.d., 28 mm o.d., and with 4 mm central hole (1 mm central hole for skimmer electrode). These three electrodes are separated by insulator rings, and the distance from the VUV lamp light window to the surface of orifice electrode is only 20 mm. The permanent magnetic ring locates between electrode 2 and skimmer, the dimensions were 31 mm in inner diameter, 19 mm in outer diameter, and 6.5 mm in thickness, and it offered a maximum energy product (BHmax) of 1200 kJ/m³.

The ion transmission region consists of three circular electrodes with inner diameter of 10 mm and thickness of 2 mm, 1 mm, and 2 mm, respectively. The insulated spaces among the skimmer, electrode 3, electrode 4, and electrode 5 are all 2 mm.
into a PTFE sampling bag, and then a desired amount of sample was added to the bag. The amount of N₂ and sample was controlled by 3 L/min and 100 mL/min calibrated mass flow controllers.

3. Performance of the Instrument

The detection of 10 ppb benzene, toluene, and xylene (BTX) was achieved in SPI mode with the membrane inlet. The spectra shown in Figure 3(a) were collected during 50 s at a repetition rate of 20 kHz. The linear response curve for benzene, toluene, and xylene range is in the concentration range from 5 ppb to 400 ppm, and the linear dynamic ranges are greater than four orders of magnitude with a good linear correlation coefficient ($R^2 > 0.9900$). Based on the criteria of signal-to-noise ratio ($S/N = 3$), the limit of detection for BTX is calculated to be 1 ppbv. This sensitivity is even much better than the reported results in the literature with more powerful VUV light source [22].

$SO_2$ can rarely be ionized in SPI mode for its high ionization energy (12.5 eV); therefore, PEI mode was selected for its analysis. The concentrations of $SO_2$ used in the experiment were 1 ppm, 2 ppm, 5 ppm, 10 ppm, 20 ppm, and 50 ppm, respectively. The samples were introduced to the TOFMS by the capillary inlet. The spectra were collected.

**Figure 3:** Spectra and the linear response curve for (a) benzene, toluene, and xylene and (b) $SO_2$. 
4.2. Discharging Products of Sulfur Hexafluoride (SF₆). Sulfur hexafluoride (SF₆) is widely used in gas-insulated switchgear (GIS) and transformers due to its excellent insulating and arc-suppression properties. However, in the presence of partial discharge, SF₆ decomposes into various byproducts, which leads to a significant decrease in the electric property of SF₆. These byproducts are often used to detect and identify partial discharge. For instance, SO₂, SOF₂, SO₂F₂, SF₄, OF₂, and SF₅F₁O could be present in SF₆ insulating devices with discharging fault. The main characteristics of these discharging products were given in Table 2. All of these compounds have higher ionization energies than 10.6 eV. Therefore, PEI mode was selected for the analysis. The capillary inlet was used and the analysis time was 13 s. The spectrum of the discharging products of SF₆ is shown in Figure 5(a). Peaks of discharging products, SO₂F⁺ (m/z, 83), SF₃⁺ (m/z, 85), SOF₂⁺ (m/z, 86), SO₂F⁺ or SF₃⁺ (m/z, 102), and SOF⁺ (m/z, 105), can be observed clearly in the figure. And the fragments and reaction products of SF₆ such as SF⁺ (m/z, 51), SF₂⁺ (m/z, 54), SF₃⁺ (m/z, 70), SF₄⁺ (m/z, 127), SF₅⁺ (m/z, 108), and SF₈⁺ (m/z, 89) can be observed as well. Peaks of O₂⁺ (m/z, 32) and N₂⁺ (m/z, 28) can be observed due to the air mixed with SF₆. The portable TOFMS was used for in situ detection of the real decomposition products of SF₆ which were sampled from an insulation fault of a GIS. The spectrum is shown in Figure 5(b); the peaks of m/z 64 and m/z 86 can be ascribed to SO⁺ and SO₂⁺, which originate from gaseous byproducts of SO₂ and SO₂F, separately. The concentration of SO₂ is calculated as 400 ppm from the linear curve, and this result indicated that serious discharging has occurred inside the GIS.

5. Conclusion

A VUV lamp based portable TOFMS has been developed for field analysis of gas analytes. The portable TOFMS is equipped with two sampling inlets and dual ionization operating mode for different requirements. The TOFMS is 40 × 31 × 29 cm in size and 27 kg in weight with a favorable power consumption of 70 W. Instrument performance was assessed using BTX and SO₂, a mass resolution of 1100 at m/z 64 has been obtained, and, under optimized conditions, the detection limits for BTX were 0.005–400 ppm by volume with linear dynamic ranges greater than four orders of magnitude. The portable TOFMS was used to detect SO₂, the typical decomposition product of SF₆, for diagnosis of potential
fault in SF$_6$-insulated switchgear. The results reported here indicate that compact, high-performance TOFMS is ready for field development.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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