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Communication

## Radiofrequency field enhanced chemical ionization with vacuum ultraviolet lamp for miniature time-of-flight mass spectrometer

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### ABSTRACT

It is difficult to rapidly and on-line detect trace volatile organic compounds for miniature mass spectrometry due to its limited sampling volume at slow pumping speed. In this paper, we developed a new radiofrequency field enhanced chemical ionization source (RF-ECI) with vacuum ultraviolet (VUV) lamp by coupling radiofrequency electric field and direct-current field together. The experiment results showed that the sensitivity of benzene, toluene, hydrogen sulfide and other compounds increased by 2–3 orders of magnitude under the introduction of RF-ECI comparing to traditional single photon ionization (SPI). At the same time, the reagent ion of  $O_2^+$  realized the charge transfer reaction chemical ionization, and the RF-ECI effectively expanded the detection range of the VUV lamp based SPI. The VUV lamp has inherent advantages in the on-site analytical instrument for its small size and low power consumption, and the VUV lamp based RF-ECI miniature time-of-flight mass spectrometer (TOFMS) has a limit-of-detection for  $H_2S$  as low as  $0.0571 \text{ mg/m}^3$ , and it is expected to be used widely in the field of on-site rapid analysis.

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It is imperative to develop on-line or on-site analytical instrument for industrial processes and environmental monitoring due to the huge number of samples and the need for continuous monitoring [1]. Mass spectrometry has become the “gold standard” in the field of chemical qualitative analysis. More and more Chinese national standards use mass spectrometry as analytical detector, and a lot of attention has been given to the development of sensitive portable/miniature mass spectrometry for on-site rapid analysis in the literature [2]. The ionization source, which determines the analytical sensitivity, spectral characteristics and detection scope of the compounds, has become an increasingly important technique on the scope of mass spectrometer [3]. Soft ionization has become the dominant method for online mass spectrometry due to its relative low degree of fragmentation and straightforward spectral interpretation [4,5].

Recent innovations in soft ionization of mass spectrometry for the direct analysis of various volatile organic compounds [6], e.g., proton transfer reaction ionization (PTR) [7–9], extractive

electrospray ionization (EESI) [10,11], direct analysis in real time (DART) [12] and ultraviolet single photon ionization (SPI) [13], facilitate the applications of online or on-site analysis. However, the miniaturized vacuum system of the portable mass spectrometer dramatically reduces the injection volume of the analyte and thereby leads to the low sensitivity. The commercialized low pressure Kr gas VUV lamp (photon energy is 10.6 eV), which is small size, low cost and low power consumption, has been widely used in the single photon ionization mass spectrometer for on-site environmental pollutant analysis. However, the photon flux of the Kr-VUV lamp is limited to  $10^{11}$  photons/s which is not high enough for trace analysis, and the photon energy of 10.6 eV also limits the detection scope to the analyte with ionization energy (IE) lower than 10.6 eV. Therefore, for the VUV lamp based ionization source portable mass spectrometer, only by improving these two most important specifications, i.e., sensitivity and detection scope, can it be widely applied to on line or on-site analysis.

In order to improve the performance of VUV-SPI ionization sources, Zimmermann *et al.* [14] designed a high photon flux VUV lamps up to  $10^{14}$  photons/s, known as electron-beam pumped rare-gas excimer light sources (EBELs). And an SPI-MS LOD of 35 ppb was achieved for toluene with a measurement time of 0.65 s by a

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EBELs-TOFMS. But, the on-site application for this EBELs-TOFMS is limited due to the weight and volume of the high-vacuum system required by the EBELs. Shu *et al.* [15] designed a microwave discharge induced high-power VUV lamp SPI source with an optical baffle for preventing VUV light from entering the ion-migration lens assembly, and with this baffle, the baselines of the mass spectra decreased from  $263.6 \pm 15.7$  counts to  $4.1 \pm 1.8$  counts. Pan *et al.* [16] designed a pair of aluminum-coated disk electrodes with circular center cavities for Kr-VUV lamp. VUV light can be reflected back and forth in the photoionization region between the aluminum-coated electrodes, thus the signal amplification of VUV lamp can be enhanced around 4-folds comparing to uncoated electrodes. Li Haiyang's group, from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, has designed a series of soft ionization sources based on VUV lamp for on line mass spectrometer since 2003 [17–21]. The summarized soft ionization sources can be found in Table S1 (Supporting information). Gao *et al.* developed a single photon ionization time-of-flight mass spectrometer combined with membrane, the LODs of toluene and xylene are 0.5 ppbv and 0.4 ppbv, respectively, with scan frequency of 10 kHz [22]. These VUV lamp soft ionization sources mentioned above are almost based on laboratory bench-top mass spectrometer, which is not used in miniature mass spectrometer.

Presented here is a novel, radiofrequency field enhanced chemical ionization source on the base of Kr-VUV lamp for miniature time-of-flight mass spectrometer (TOFMS). The miniature TOFMS uses a three-stage differential vacuum system, and the pressure inside of ionization pressure increased to 90 Pa. The radiofrequency electric field was used to modulate photoelectron and enhance the chemical ionization for improving the sensitivity and extending the detection range of organic compounds of miniature TOFMS.

Fig. 1 shows the schematic diagram of miniature TOFMS and radiofrequency field enhanced chemical ionization source (RF-ECI). The RF-ECI ion source consists of a commercial 10.6 eV krypton discharge lamp (PKS106, Cathodeon Ltd., Cambridge, U.K., 19.6 mm in diameter, 52 mm in length) and an ionization region. The VUV lamp with photon flux of  $1 \times 10^{11}$  photons/s is set outside the ionization chamber and sealed with an O-ring. The ionization region comprises eight circular steel stainless electrodes: one repelling electrode (6 mm length, 14 mm i.d., 38 mm o.d.), six focusing electrodes (named SE1–SE6, with 5.5 mm length, 14 mm i.d., 38 mm o.d.), and one orifice electrode (with a central hole of 0.5 mm diameter). These electrodes are separated by the PTEF insulation washers, and the distance from the VUV lamp light window to the surface of orifice electrode is 17.4 mm. DC voltages of V1, V2, and V3 were applied to the repelling electrode, SE6, and orifice electrode separately with three individual DC power

supplies. The electrodes from repelling electrode to SE6 electrode are connected one by one with 2 M $\Omega$  resistors to produce a uniform DC field, while the voltage of V3 applied at orifice electrode was controlled independently. A two-channel radio-frequency (RF) voltage  $V_{rf}$  with 180° phase difference is applied separately to the adjacent focusing electrode by a 10 nF capacitor, respectively.

The ion source could work at two different operation modes, *i.e.*, the SPI and RF-ECI modes, by simply switching  $V_{rf}$  on and off. At SPI mode, the  $V_{rf}$  was turn off and the V1 was set to 36 V DC voltage, and there is only uniform DC field inside of the ionization source. At RF-ECI mode, the  $V_{rf}$  was turn on and the V1 was set to 36 V DC voltage and the radiofrequency field and DC field coupled together inside of the ionization source.

A miniature orthogonal acceleration reflection TOFMS was used in the experiments, which was home-made and described in detail in the literature [23]. Gaseous analytes were directly introduced into the ionization source through a fused silica capillary 100  $\mu\text{m}$  i. d. from sample bag, and the pressure inside of the ionization source was controlled by adjusting the length of the silica capillary. The operating parameters of the miniature TOFMS are listed in Table S2 (Supporting information) and all the mass spectra were accumulated for 50 s.

Benzene and toluene were used to explore the efficiency of RF-ECI. Sample preparation is shown in the S1 section in Supporting information. Mass spectra in SPI mode and RF-ECI mode for 34.8 mg/m<sup>3</sup> benzene and 41.1 mg/m<sup>3</sup> toluene are shown in Fig. 2. The characteristic peaks at both SPI and RF-ECI mode for benzene and toluene are  $\text{C}_6\text{H}_6^+$  ( $m/z$  78) and  $\text{C}_8\text{H}_{10}^+$  ( $m/z$  92) respectively. The  $\text{C}_6\text{H}_6^+$  and  $\text{C}_8\text{H}_{10}^+$  are all molecular ions, so the RF-ECI is also a soft ionization source. The ion intensities for benzene and toluene

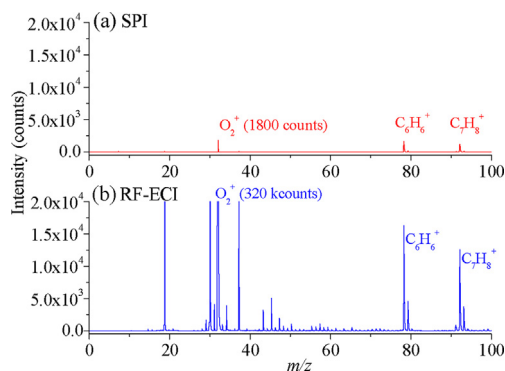


Fig. 2. Mass spectra in SPI mode (a) and RF-ECI mode (b) for 34.8 mg/m<sup>3</sup> benzene and 41.1 mg/m<sup>3</sup> toluene. The actual value in (a) was magnified 10 times.

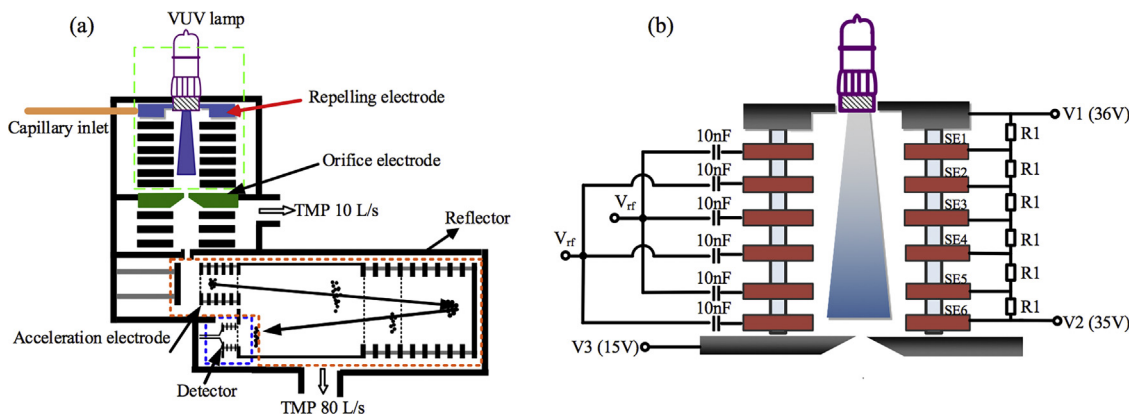


Fig. 1. Schematic diagram of miniature TOFMS (a) and RF-ECI source (b).

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