



## Full Length Article

## A dual-source miniature mass spectrometer with improved sensitivity

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## ABSTRACT

Previously, we have reported the development of a miniature mass spectrometer with a continuous atmospheric pressure interface, whose sensitivity was sacrificed due to the limited gas flow rate. In this study, a circular lens was designed and integrated on the ion transfer pathway between the two pumping stages, and a ten-fold sensitivity improvement could be achieved when coupling with external ionization sources. Besides the capability of working with ionization sources in the atmosphere, there is also an in-vacuum plasma ionization source, so that both volatile and non-volatile samples could be analyzed. A 10 ppbv detection sensitivity was achieved for dimethyl methyl phosphonate (DMMP) in air using the plasma ionization source. Furthermore, the miniature mass spectrometer was also demonstrated for the direct analyses of progesterone in drinking water and atrazine in soil samples using paper spray and syringe spray, respectively.

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## 1. Introduction

With high sensitivity, resolution, and accuracy, mass spectrometry (MS) has been widely used in various fields, including clinical diagnosis [1], food industry [2,3], forensic science [4–9], etc. Conventional lab-scale mass spectrometers enable the analysis of various compounds, from polar to non-polar molecules, by coupling with different ionization sources [10–12] or combining with chromatography techniques [13,14]. The relatively large size of mass spectrometer often limits its application for on-site or in-situ chemical analysis. Also, the complex instrumental operation procedures require professional knowledge and skills, retarding MS from being broadly used, e.g., in physician's office. Over the past decade, miniaturization of the MS system has been demonstrated in different aspects, and miniature mass spectrometers have emerged [15,16].

As the major parts in a MS system, the mass analyzer [17] and vacuum system are key factors for reducing the size of a mass spectrometer. With outstanding analysis performance under relatively high pressure, ion trap has been selected as the analyzer for miniature mass spectrometers [18–20]. Typically cylindrical quadrupole

ion trap (CIT) [21–23] and rectilinear ion trap (RIT) [24,25], at cubic centimeter scale, were utilized based on their simplified geometry and compact size. On the other hand, the design of vacuum systems is highly dependent on the type of atmospheric pressure interface (API) of the MS device. Conventional membrane gas inlet, with extremely low gas flow rate, is generally coupled with internal ionization sources to detect volatile compounds [26,27]. Discontinuous atmospheric pressure interface (DAPI) [28,29] allows for the analysis of liquid or solid samples with ambient ionization sources [30–32]. Recently, miniature MS system with continuous atmospheric pressure interface (CAPI) has been reported for analyzing both volatile and non-volatile compounds using in-vacuum plasma source or nano-electrospray (ESI) [33]. However, the limited ion transfer efficiency in CAPI-MS system [34,35] resulted in relatively low detection sensitivity. With reduced size and power consumptions, performances of miniature mass spectrometers were usually sacrificed, which in turn greatly limited their applications. Therefore, performance improvements of a miniature mass spectrometer (MS) with minimum or no instrument scaling up are even more important towards their practical applications in real life.

In this study, we reported an improved CAPI miniature mass spectrometer with a circular lens incorporated behind the capillary between the two pumping stages. The use of a DC lens is a simple but effective way for sensitivity improvement. By adjusting the voltage supplied on the electrostatic lens, performance of the miniature mass spectrometer was optimized. A limit of detection of 0.1 ppm MRFA was achieved with 3 V voltage applied on the lens, ~10 times higher than the previous MS model. Internal

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plasma source and external ambient ionization sources, including nanoESI, paper spray, and syringe spray, have been used in conjunction with the miniature MS system. Stable and robust signal was obtained from gas, liquid, and solid samples. The detection of progesterone in drinking water and atrazine in soil samples has also been demonstrated using this miniature mass spectrometer.

## 2. Methods and materials

### 2.1. Chemicals and materials

Clenbuterol (CLE), methotrexate (MTX), progesterone, atrazine, and Met-Arg-Phe-Ala (MRFA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dimethyl methyl phosphonate (DMMP), a warfare agent simulator, was obtained from Beijing chemical reagent co., LTD (Beijing, CN). Deionized water was purchased from Wahaha Company (Hangzhou, CN). All chemicals were diluted in 50% methanol, except MTX, atrazine and progesterone. MTX was diluted in menthol (HPLC grade), atrazine was diluted in deionized water, and progesterone was diluted in tap water. Soil samples were collected on the campus of Beijing Institute of Technology.

A glass capillary with a tip diameter of  $\sim 5 \mu\text{m}$ , used for the nanoESI source, was fabricated by pulling a glass capillary (i.d. 0.8 mm, o.d. 1.5 mm) using a micropipette puller (model P-1000, Sutter Instrument Inc., USA). A swagelok (0.25 inch), PFA tubes (o.d. 0.25 mm, length 1 m), glass sampling bottles (500 mL), enameled wires (o.d. 0.20 mm), and a syringe needle (1 mL, i.d. 0.25 mm, o.d. 0.45 mm) were purchased from an instrumental retailer.

### 2.2. Instrumentation

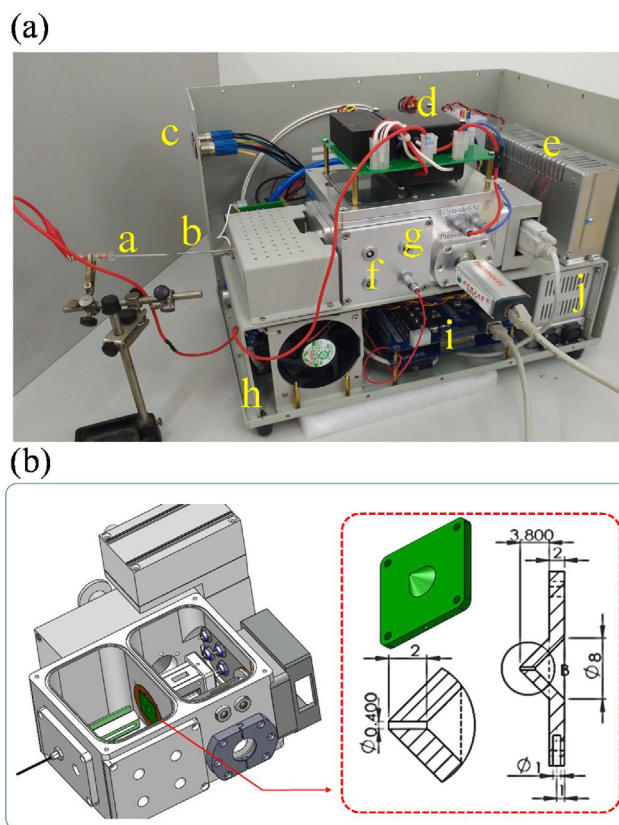
All experiments were performed using a miniature mass spectrometer ( $40 \times 26 \times 30 \text{ cm}$ , length  $\times$  width  $\times$  height) modified based on the previously reported miniature MS model. [33] In this work, an electrostatic lens (I.D. 0.4 mm) with voltage supplied was mounted behind the metal capillary (I.D. 0.25 mm) outlet to connect the two vacuum stages, as shown in Fig. 1. The spectrum signal was optimized by adjusting the supplied voltage, ranging from 0 to 10 V. A linear ion trap (LIT) with rod length of 40 mm and field radius of 4 mm was used as the mass analyzer. The distance between the capillary outlet (i.d. 0.25 mm, length 20 cm) and the electrostatic lens was manipulated to accommodate different ionization sources. All mass spectra were collected in positive ion mode.

With the in-vacuum plasma source as described before [36], samples were injected using a micro syringe pump through the PFA tubing and exposed under the plasma in the first vacuum chamber. In nanoESI, the pulled capillary was filled with  $10 \mu\text{L}$  sample solution, and a high voltage power supply (Tianjin Dongwen High Voltage Power supply Co. Ltd, Tianjin, CN) applied 1000 V voltage on the solution to generate an electrospray. For paper spray, a piece of filter paper (isosceles triangle with bottom side length of 1.5 cm and apex angle of  $30^\circ$ ) and a DC voltage (+3.5 kV) power supply were utilized. With  $10 \mu\text{L}$  sample solution loaded, the filter paper (apex angle tip) was kept  $\sim 5 \text{ mm}$  away from the inlet capillary and the bottom side of the filter paper was connected to a high-voltage power supply.

## 3. Results and discussions

### 3.1. Characterization of the modified miniature mass spectrometer

In the CAPI interfaced miniature mass spectrometer, the gas flow rate was reduced to enable an acceptable vacuum pressure within the vacuum chamber using miniature sized vacuum pumps. There-



**Fig. 1.** (a) Schematic description of the miniature mass spectrometer: a. ion source, b. inlet, c. pump switch, d. direct current amplifier (DC), e. power supply, f. vacuum chamber, g. plasma ion source, h. rotary pump, i. control system, and j. radio frequency system (RF). (b) Internal assembly of the vacuum chamber and the linear ion trap. The inset shows the feature of the skimmer (i.d. 0.4 mm).

fore, the ion transfer efficiency was limited, leading to reduced detection sensitivities especially when coupling with ionization sources in the atmosphere pressure [36]. To solve this problem, an additional circular lens was mounted between the two pumping stages in the MS system (the green part in the inset of Fig. 1(b)). The circular lens was electrically isolated from the chamber, and there is a skimmer (I.D. 0.4 mm) in the middle of the circular lens to separate the two vacuum stages while allowing ion transfer. In this setup, the metal capillary, the circular lens and the front endcap of the linear ion trap could form an electrostatic lens. During the ion introduction period, the metal capillary and the front endcap of the linear ion trap would be grounded; while a DC voltage could be applied on the circular lens. This setup would have similar performance as an Einzel lens, which would focus ions into the second vacuum chamber (or the linear ion trap) through the pinhole.

The DC voltage applied on the circular lens was critical for optimizing the performance of the miniature mass spectrometer. A MRFA solution at concentration of 100 ppm was analyzed with nanoESI using this MS device. With the lens voltage increased from 0 V to 10 V, the abundance of MRFA signal increased significantly at the beginning and saturated at  $\sim 3 \text{ V}$ , then slowly decreased with the voltage, as shown in Fig. 2a. In the formed positive electrical zone around the lens, the ions were slowed down from traveling through, and focused towards the center of the lens. With a voltage below a threshold value of 3 V, ions were able to pass through. While at a voltage above 3 V, the electrical field was too intense to reverse the moving direction of some ions and resulted in a decreased detection signal. Therefore, the threshold voltage of 3 V was the optimal lens voltage, and all the following experiments were conducted using this parameter. A limit of detection

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