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Development of a miniature mass spectrometer with in-source desolvation

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ABSTRACT

Miniature mass spectrometers could meet the on-site chemical analysis requirements in applications such as space exploration, homeland security, etc. However, miniaturization of a mass spectrometer would sacrifice its performance due to simplified instrumentation and limitations on power and size. In this study, in-source desolvation capability was developed for a miniature mass spectrometer. Similar to the conventional in-source fragmentation technique, the in-source desolvation is more gentle, which is designed to fragment clusters and droplets other than ions. In-source desolvation could effectively help the desolvation of droplets generated by electrospray ionization, and both signal intensity and signal-to-noise ratio of a mass peak could be increased. As a result, sensitivity improvement could be achieved for the miniature mass spectrometer. Compared to the desolvation techniques used on a lab-scale instrument (heated interface, desolvation gas, for instance), the in-source desolvation method is more suitable and economic for a miniature mass spectrometer.

1. Introduction

The development of miniature mass spectrometers could trace back to the 1960s, in which they were used for space explorations [1,2]. Recently, researchers found miniature mass spectrometers attractive in more applications such as personal healthcare, homeland security and environmental science [3–5]. To meet these demands, different types of miniature mass spectrometers have been developed. Gas inlets that have very limited gas flow rates enable the development of miniature mass spectrometers, which are capable of analyzing volatile samples [6,7]. In these systems, membrane gas inlets and internal ionization sources are typically used [8–10]. Since 2009, the emergence of discontinuous atmospheric pressure interfaces (DAPI) has allowed the development of miniature mass spectrometers, which are capable of analyzing both volatile and non-volatile samples [11,12]. A DAPI could transfer ions from the atmosphere environment to a vacuum chamber, where a mass analyzer (usually an ion trap) was placed. More recently in 2015, a miniature mass spectrometer with a continuous atmospheric pressure interfaces (API) was also developed, in which the effective ion transfer through the API was enabled by the high pressure ion trap operation [13,14] and a differential pumping system design [15,16]. An API with ion transfer capability allows the coupling of miniature mass spectrometers with electrospray ionization (ESI) sources and ambient ionization sources [17,18], which greatly expand the applicability of miniature mass spectrometers.

When designing a miniature mass spectrometer, power consumption and dimensions would be important parameters besides its chemical analysis performances. As a result, its mass analysis capabilities would be affected inevitably. For example, in a conventional lab-scale instrument, several techniques would be applied to help the desolvation of electrosprayed droplets, such as using heated capillary and/or heated sheath gas [19,20]. However, these techniques may not be applicable to a miniature mass spectrometer due to the limited resources of a miniature system. Nevertheless, the distance that a droplet travels from an ESI source to a mass analyzer in a lab-scale instrument is typically much longer than that in a miniature mass spectrometer (less than 20 cm for a DAPI system [21] or even less than 2 cm for a pulsed pinhole API system [18]), which also helps the desolvation process. Experimental evidences have shown the presence of electrosprayed droplets in a DAPI-interfaced ion trap mass analyzer [22,23]. Therefore, the design of an economic desolvation method would allow more

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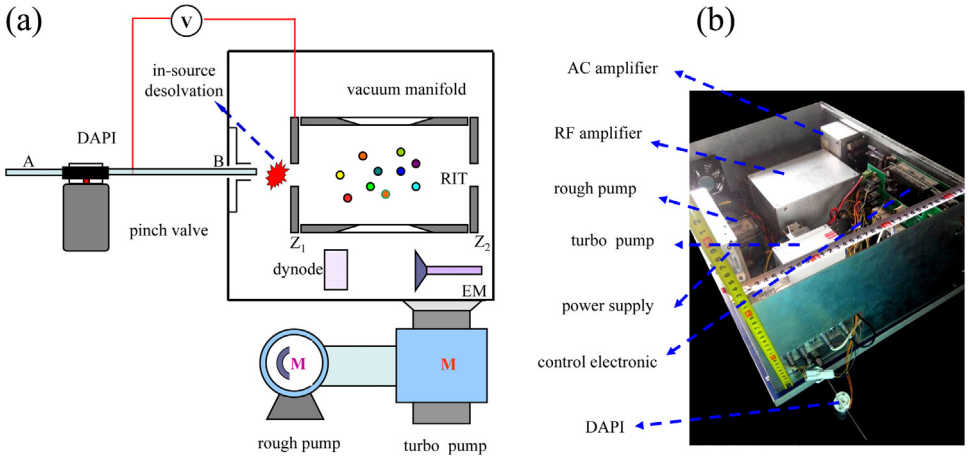

Fig. 1. (a) Schematic structure and (b) a photograph of the min-MS system, including the in-source desolvation module.

efficient couplings of miniature mass spectrometers with electrospray based ionization sources, and enhance their chemical analysis capabilities.

In this study, the in-source desolvation technique was integrated onto a DAPI-interfaced miniature mass spectrometer for improved desolvation and enhanced chemical analysis sensitivity. Similar to the in-source fragmentation technique but more gentle, the in-source desolvation technique is expected to help fragmenting ion clusters and desolving droplets. In a conventional in-source fragmentation process, ions were dissociated during the transfer of ions through the atmospheric interface with multiple differential pumping stages, and dissociations typically happen in the first vacuum stage with a pressure of typically 1–10 Torr. This DAPI-interfaced miniature mass spectrometer has a single vacuum stage, and desolvation of clusters and droplets happens right after they enter the vacuum chamber through the DAPI interface. During the in-source desolvation process, the DPAI was opened for ion introduction, and the pressure in the desolvation region varies, typically around 0.1–10 Torr (or even higher at the exit of the capillary). Without adding additional devices besides a 200 V DC power supply, the in-source desolvation technique could effectively induce the fragmentation of clusters and droplets, which leads to 2–3 times signal-to-noise ratio (SNR) enhancements. More than two-fold limit-of-detection (LOD) improvement was also observed in experiments.

2. Experimental

A DAPI interfaced miniature mass spectrometer was modified and used in this study [24]. Briefly, a single stage vacuum chamber was pumped by a turbo molecular pump (Hipace 10, Pfeiffer vacuum Inc., Germany) and a rough pump (KNF PM25210-84.3, KNF Inc., USA). A rectilinear ion trap (RIT) was applied as the mass analyzer [25]. As shown in Fig. 1, an electron multiplier (Detech 397, Detector Technology Inc., Palmer, MA, USA) with a miniaturized conversion dynode was placed in parallel with the RIT. The DAPI system consists of three components: a normally closed pinch valve (ASCO Valve, Inc., Florham Park, NJ), two stainless steel capillaries A (i.d. 0.25 mm, length 5 cm) and B (i.d. 0.5 mm, length 10 cm). To control the open/close status of the DAPI system, a conductive silicone tube was used to connect these two capillaries. Nano-electrospray ionization (nano-ESI) sources were pulled using a micropipette puller (model P-1000, Sutter Instrument Inc., USA), and the tip diameter of the nono-ESI could be tuned from 1 to 20 μm. With this setup, the miniature mass spectrometer could work in both positive and negative ion modes.

The in-source desolvation was achieved by applying a DC potential between capillary B and front endcap of the RIT during the ion introduction time. Since voltage applied on front endcap of the RIT was set at ground potential during the ion introduction time, a DC voltage tunable from −300 V to +300 V was applied on capillary B to induce the in-source desolvation. The charged droplets sprayed from the nano-ESI tip would turn into ions during the solvent evaporation process; however, the droplet desolvation was usually incomplete. Droplets, clusters and ions sprayed out of the nano-ESI source would be sucked into the vacuum chamber at the same time during the short opening time of the DAPI. Due to the high pressure differences between atmosphere and the vacuum chamber, supersonic expansion exists at the exit of capillary B [26,27]. This supersonic expansion has cooling effects on droplets and clusters, which is not beneficial for desolvations. When a DC potential was applied between capillary B and front endcap of the RIT, droplets and clusters would be accelerated and multiple energetic collisions with neutral gas molecules would happen in this region, which has a relatively high pressure (the pressure could vary from mTorr to tens of Torrs) [28]. These energetic collisions would lead to further explosion of the droplets and/or cleavage of clusters (please refer to Supplementary Information for details).

Vitamin B_1, PEG 600, rhodamine B, MRFA, ampicillin trihydrate, penicillin G potassium salt, atenolol were purchased from Sigma Aldrich (St. Louis, MO, USA). $UO_2(NO_3)_2$ solution was prepared in the following way: uranium oxide powder was first dissolved in 6 mol L^{-1} HNO_3, and allowed to stand overnight; then diluted for further experiments. Methanol/water 1:1 (v:v) were prepared to dilute the samples.

3. Results and discussion

Due to the lack of sophisticated desolvation methods, the chemical noise in a mass spectrum would decrease the SNR and sensitivity of a miniature mass spectrometer, especially when coupling with electrospray type of ionization methods. Accelerated in the in-source desolvation region, charged droplets and clusters from an ESI source would have multi-collisions with neutral molecules before reaching and being trapped in the ion trap. These collisions could help the desolvation process, which increases the number of ions that could be trapped and analyzed in the ion trap and decreases the number of clusters and charged droplets. Fig. 2 shows the effects of this in-source desolvation process. Fig. 2 displays the SNRs of the mass spectra of 5 μg/ml MRFA, 5 μg/ml rhodamine B, 10 μg/ml $UO_2(NO_3)_2$ (negative model), 100 μg/ml PEG 600, with respect to the voltage applied on capillary B. With increased