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Characterization of a discontinuous atmospheric pressure interface. Multiple ion introduction pulses for improved performance

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Dedication in celebration and appreciation of the intellectual career of Michael Bowers, with best wishes for continued success.

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ABSTRACT

Discontinuous atmospheric pressure interfaces (DAPI) are used to match the rate of sample introduction to the pumping capacity of miniature mass spectrometers. In this study, the influence of the interface flow conductance and the mass spectrometer pumping speed on ion introduction into a handheld mass spectrometer is investigated. Results show that an intermediate flow conductance (2.6×10^{-3} L/s) gives the best ion introduction efficiency whereas the pumping speed has no influence in the range studied (0.35–7.1 L/s) except that a minimum pumping speed of 0.35 L/s is required. The linear dynamic range decreases with increasing interface open time, a result that corresponds to observations made using standard electrical gating of ion introduction a method that is not available at the high pressures involved in API into miniature systems where ions are transported through pneumatic flow. However, the mechanical opening of the interface with DAPI can be used for automatic gain control (AGC) using an external ion source. Software modifications to allow the use of multiple ion introduction pulses before mass analysis of the trapped ion population improve the detection limits. This method was validated by comparing the results obtained from the same sample using a single ion introduction pulse and multiple ion introduction pulses. In conjunction with this method, a broad-band waveform can be applied to selectively accumulate analyte ions, allowing essentially the entire ion trapping capacity to be devoted to one or more ions of interest.

1. Introduction

The development of miniature ion trap mass spectrometers has been an active research topic, fueled by the promising analytical capabilities resulting from the broad applicability, high sensitivity, high specificity and the convenience of fast in situ analysis with portable instruments [1]. Progress has been made in refining miniature ion trap instruments [2–12], but their applications are still confined to a few areas [13–17]. A key issue is efficient ionization of the sample of interest. Towards this end, various atmospheric pressure ionization (API) sources have been developed to ionize samples in different physical states and from different sample matrices [18–32]. Ions are readily generated by external atmospheric pressure ionization (API) sources but are difficult to transfer into the vacuum manifold efficiently with the limited pumping speed available from miniature mass spectrometers since large quantities of gas are introduced with the ions. As a result, API sources were difficult to use in conjunction with miniature mass spectrometers until the development of the discontinuous atmospheric pressure interface (DAPI) [33].

The DAPI consists of a series of capillaries directly connecting the atmospheric pressure region to the ion trap. Contrary to standard practice in traditional continuous interfaces, ions are introduced into the vacuum manifold discontinuously. Gases carrying ions are pulsed into the ion trap for short periods at flow rates which are too high to be used in the continuous mode. This procedure allows a sufficient number of analyte ions to pass through the DAPI and enter an ion trap fitted with a low pumping speed vacuum system. DAPI has already been demonstrated using the recently developed Mini 11, a 5 kg ion trap miniature mass spectrometer, with only a 3 L/s pumping speed [9]. Samples in the gas phase, liquid phase and solid phase, ionized using API sources including APCI, ESI, and DESI, have been analyzed successfully in the Mini 11 through discontinuous introduction.

Although the DAPI has proven to be an effective ion introduction method, detailed understanding and design consideration have not been reported. It is highly desirable to understand the ion accumulation process inside the ion trap when DAPI is used for ion introduction. Knowledge of the influence of the interface flow

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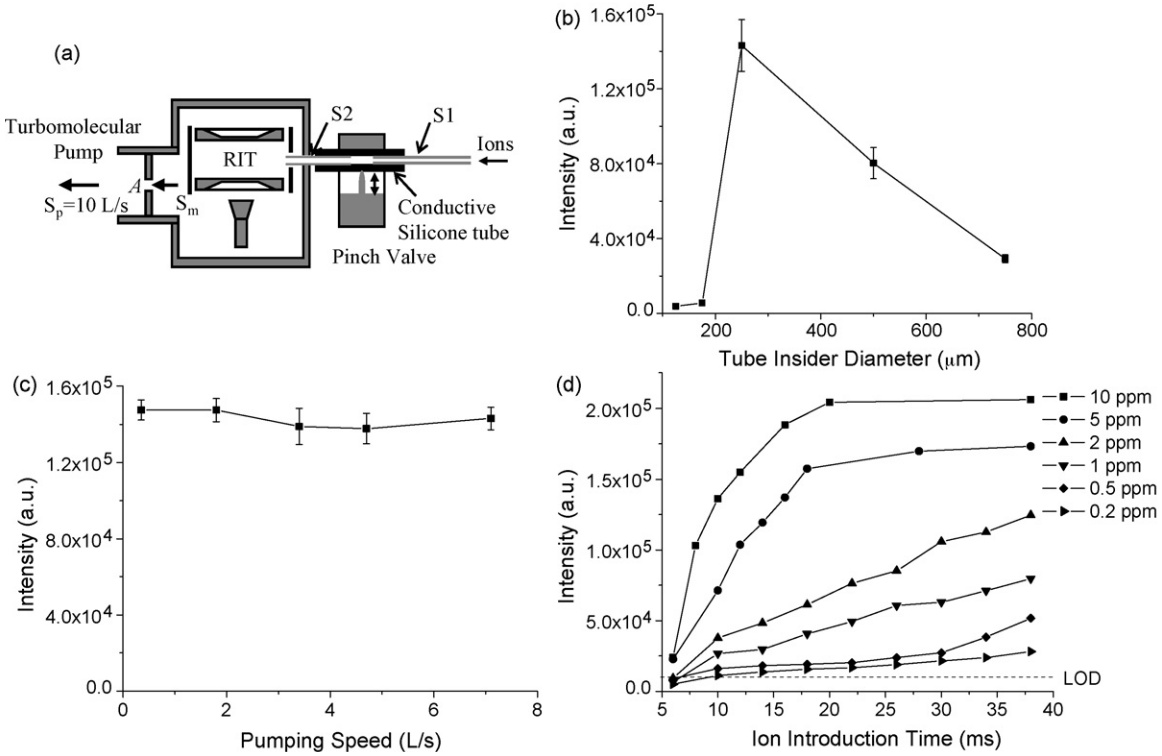

Fig. 1. (a) Instrumentation, including discontinuous interface (DAPI), a rectilinear ion trap (RIT) and electron multiplier. Flange *A* is placed between the turbomolecular pump entrance and the vacuum manifold exit. (b) Ion current at *m*/*z* 443 plotted versus S1 tube inside diameter. (c) Ion current at *m*/*z* 443 plotted versus pumping speed. (d) Ion current plotted versus ion introduction time for Rhodamine B solutions with concentrations of 0.2 ppm, 0.5 ppm, 1 ppm, 2 ppm, 5 ppm and 10 ppm.

conductance and the pumping speed on ion introduction is also important to improve future instrument design. A miniature mass spectrometer was used here to study these aspects of DAPI. Furthermore, a method of multiple ion introduction pulses for DAPI was developed to improve performance.

2. Experiment

A modified Mini 10 mass spectrometer equipped with DAPI was used in these experiments [8,33]. The configuration of the mass analyzer assembly is shown in Fig. 1(a). Ions generated at atmospheric pressure are transferred into the ion trap through the DAPI interface. A standard 5 mm × 4 mm rectilinear ion trap, driven by a 1.3 MHz differential RF signal, is used as the mass analyzer, and an electron multiplier (DeTech 2312, Detector Technology Inc., Palmer, MA) is used to detect ions ejected from the ion trap. The DAPI system consists of two stainless steel capillaries S1 and S2, connected to each other via a conductive silicone tube (i.d. 1.59 mm, o.d. 3.18 mm, length 5 cm). The conductive silicon tube goes through a normally closed pinch valve (390NC24330, ASCO Valve Inc., Florham Park, NJ), which controls the open/closed status of the DAPI. The capillary S1 is the main flow restricting element with an o.d. of 1.59 mm, a length of 10 cm, and an inside diameter as specified herein. The capillary S2, on the vacuum side of the pinch valve, has an i.d. of 1.2 mm, an o.d. of 1.59 mm, and a length of 4 cm. Both stainless steel capillaries, S1 and S2 are electrically grounded at all times.

During operation, a 24 V dc pulse signal lasting for a few milliseconds is applied to the pinch valve at the beginning of each scan cycle to open the DAPI for ion (and gas) introduction; the interface then closes for the remainder of the scan cycle. The manifold pressure rises to $\sim 10^{-1}$ to 10^{-2} Torr after opening of DAPI, then the pumping system slowly restores the vacuum manifold pressure back to $\sim 10^{-3}$ to 10^{-4} Torr for mass analysis in a time period which lasts from hundreds of milliseconds to a few seconds. Next, the multiplier is turned on, and both the RF signal amplitude and resonance ac signal amplitude are scanned to record the mass spectrum. The dc voltages on both ion trap end electrodes are constant at +15 V during the whole scan cycle.

The vacuum system of the instrument consists of a two-stage diaphragm pump (1091-N84.0-8.99, KNF Neuberger Inc., Trenton, NJ), a hybrid turbomolecular pump (TPD011, Pfeiffer Vacuum Inc., Nashua, NH) and a Pirani pressure gauge (MKS 925C, MKS Instruments, Inc., Wilmington, MA). The backing pump with a maximum pumping speed of 5 L/min provides a backing pressure of 3 Torr and the turbomolecular pump provides a pumping speed of 10 L/s. To perform experiments on the effects of pumping speed, a 7.8 mm thick flange *A* with a hole in the center was placed between the turbomolecular pump entrance and the manifold exit, so that the actual pumping speed at the manifold exit could be adjusted by changing the hole size, as calculated using Eq. (1).

$$S_m = \frac{S_P \times C}{S_P + C} \tag{1}$$

In this equation, S_m is the actual pumping speed at the manifold exit, S_P the pumping speed of the turbomolecular pump which is 10 L/s in this instrument, *C* the flow conductance between the manifold and the turbomolecular pump, which can be adjusted by changing the hole size on the flange *A*. The relationship between the flow conductance *C* and the orifice size is discussed in the Supporting Information.

An ESI source with +3 kV ionization voltage and 80 psi sheath gas pressure was used to generate ions in all experiments. All sample solutions were prepared using 1:1 methanol water with 1% acetic acid.