Supporting Information

Study of Discontinuous Atmospheric Pressure Interfaces for Mass Spectrometry Instrumentation Development

Deleted: Mass Spectrometer with Discontinuous Atmospheric Pressure Interfaces

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Pumping Process for a DAPI-MS system

The pressure inside the vacuum chamber increases rapidly (to >>10 mTorr) when the pinch valve is opened for a short time, e.g. 13 ms. The time for pressure to decrease from P_{2max} to P_{2min} (Figure 1b) is a function of the effective pumping speed of the pumping system (S) as indicated in Equation S1.

$$t = \frac{V}{S}\ln\left(\frac{P_{2max}}{P_{2min}}\right)$$

Equation S1

Faster pumping system can shorten the duration which is required between each of DAPI openings.

Different pumping systems were tested. Two rotary vane pumps were available for selection, including a 19.8 m^3/h Leybold Trivac D 16B and a 307 m^3/h Edwards E2M275; two turbomolecular pumps were used in the test, including which were a 345 l/s Leybold TurboVac 361 and a 210 l/s Pfeiffer TMH262P. Different combinations of rough and turbomolecular pumps were made for the pumping a 35 cm x25 cm x25 cm vacuum manifold. A DAPI with a specification of DAPI (I) (Figure 2a) was used in these tests and opened for 13 ms each time. The pressure inside the vacuum manifold was monitored using a MKS 925C microPirani transducer (MKS Instrument, Andover, MA). The analog output of the MKS 925C was recorded using a Fluke 199C Scopemeter. The pressure variations measured with three pumping systems are shown in Figure S1 and all show very similar curves, regardless the difference in the specified pumping speeds of the pumping systems. After the pinch valve was closed, it took about 300 ms to pump the pressure down to 2 mTorr, and the pressure drop was much slower after reaching 2 mTorr in all cases.

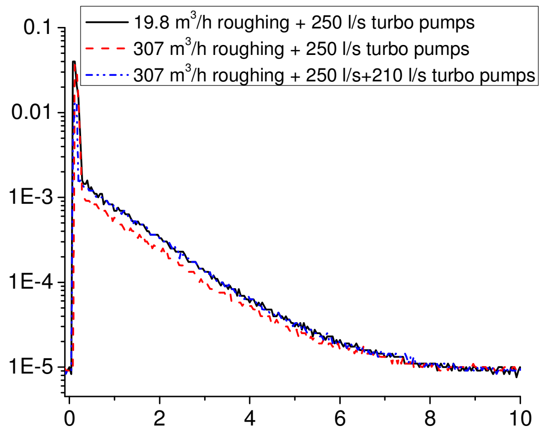

Figure S1. Pressure variation inside the vacuum manifold pumped with different pumping systems, DAPI open time of 10 ms.

Protein Analysis Using DAPI-MS Instrument with Extended Mass Range

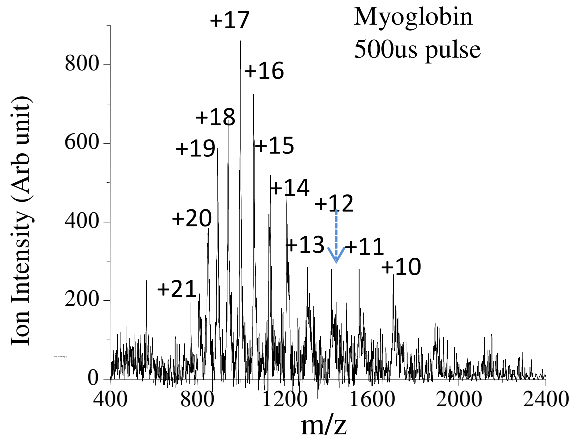

Figure S2, Mass spectrum of 50ng/µL myoglobin with a 500 µs nano-ESI pulse. The mass range of the instrument was extended to 2400 with ejection at a low q =0.35 (resonance ejection AC at 115kHz).

Mass Spectral Resolution of DAPI-RIT Configuration

Figure S3 shows the mass spectra of electrosprayed methamphetamine and MRFA with unit resolutions. The mass analysis is performed with resonance ejection at q~0.82 (AC=340 kHz) and at the gas pressure (air, ~ 1 mTorr). The open time of the pinch valve was 9.3 ms.

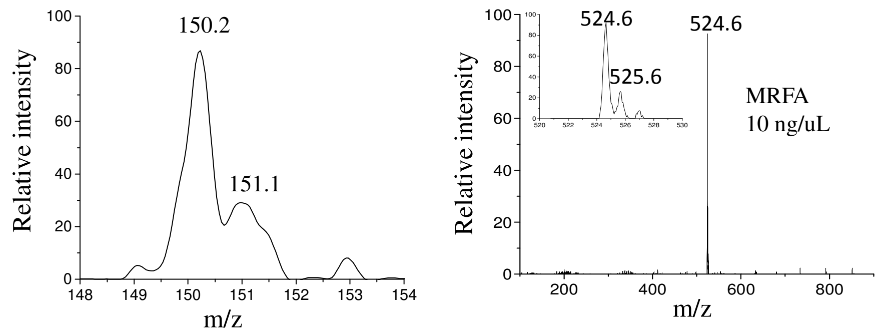

Figure S3. Mass spectra of methamphetamine (a, 5 ng/uL) and MRFA (b, 10ng/uL) with unit resolution, using nanoESI.

Gas Dynamic Simulation

The 3D model of the API interface was created in the software ANSYS (ANSYS Inc., Canonsburg, PA), as shown in Figure S4. Exact geometries of Capillary 1 and RIT were used for the model. The vacuum manifold was modeled by a circular cylinder with open boundary. In this way, the vacuum manifold can be well simulated while keeping the effective simulation volume minimized.

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Due to the high pressure difference between the inside and the outside of the vacuum manifold, the simulation was performed in a descrete step procedure to achieve a converged solution for low pressure gas expansion. The pressure in the vacuum chamber first was set at a relatively high value, e.g. 400 Torr; after a converged gas dynamic simulation was obtained, the simulation results were used as the initial condition to get a converged solution at a lower pressure, e.g.100 Torr. By repeating this process, a converged simulation can be performed for our model where a very large pressure differential exists between atmosphere and the vacuum manifold at ca. 400 mTorr.

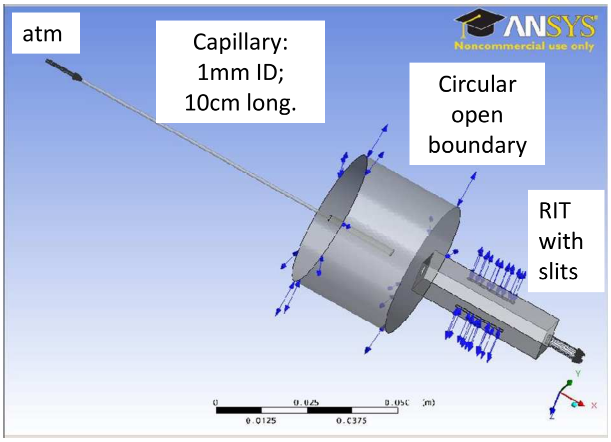

Figure S4. The model for the gas dynamic simulation using ANSYS.

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Calculation of Sample Consumption.

A very small amount of solution containing analyte was sprayed each time for the pulsed nanoESI. To estimate the sample consumption for pulse of different width but at the same voltage, the sample consumption at a 100 µs pulse was first measured using the same spray tip at the same voltage and then a linear function of time was assumed for estimation. The 100 µs pulsed spray with 2.4 kV applied voltage was repeated at 10 Hz for 4 hours and 4.2 µL solution was consumed, corresponding to 29 pL per pulse of 100 µs. The 4.2 µL consumption includes the amount loss by evaporation between the pulses, which makes the amount calculated larger than that consumed for each pulse.

Comparison of Different Pulse Modes of nanoESI

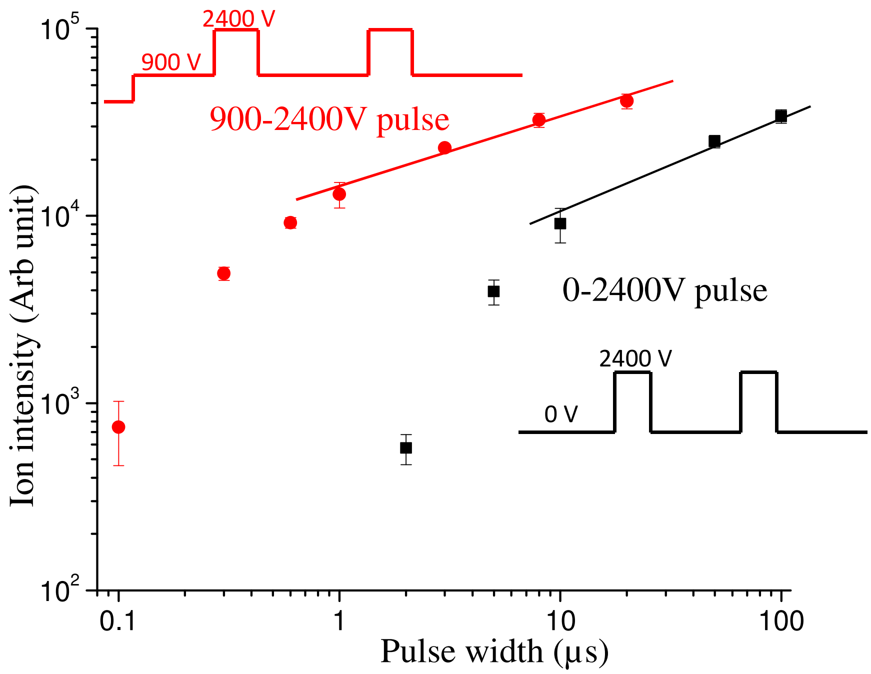
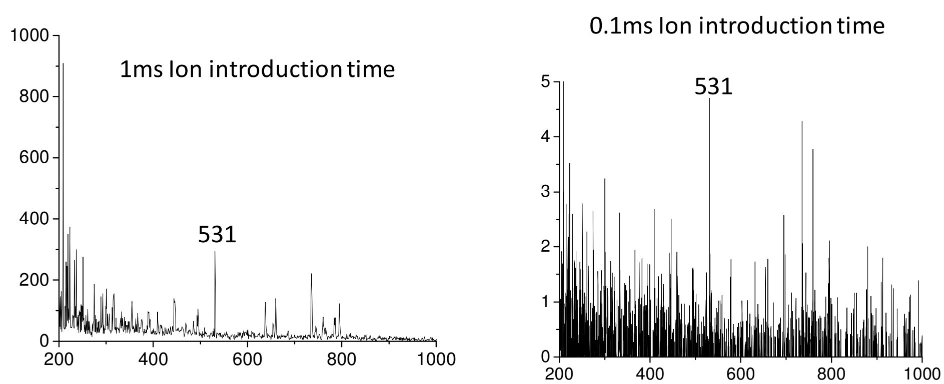


Figure S5. Pulsed nanoESI with spray voltage pulse 0V – 2.4kV (black) and 900V – 2.4kV (red), 13 ms ion introduction with DAPI.

Analysis of Bradykinin Using LTQ



(a) **(b)**

Figure S6 Single-scan spectra recorded for 10 ng/μL bradykinin using LTQ at (a) 1 ms and (b) 0.1 ms ionization time, AGC off.

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Counter Flow Effect for Ion Introduction

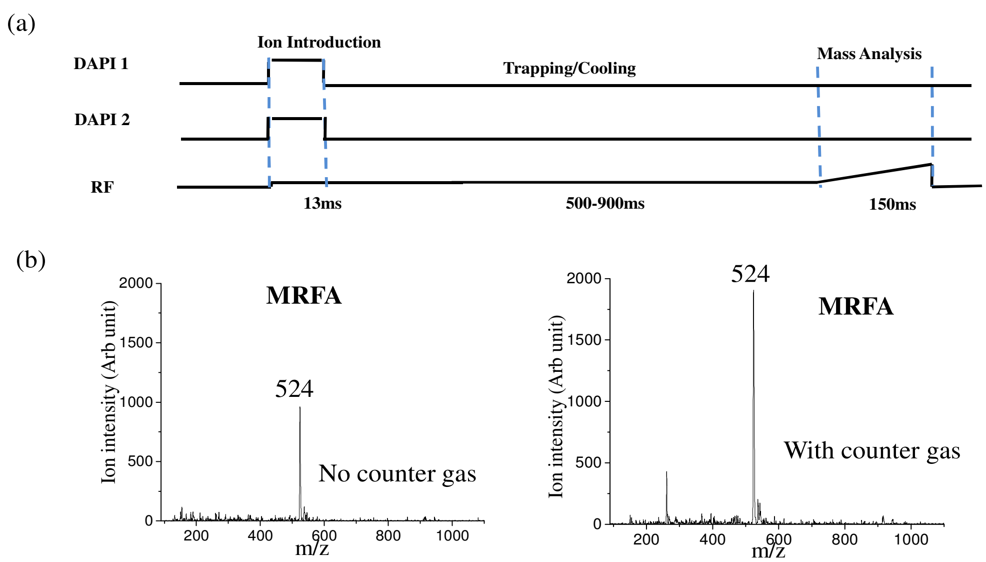

Figure S7. (a) Scan function with a counter gas flow introduced through DAPI (II) during ion introduction. (b) Mass spectra of 100 ng/μL MRFA with and without counter gas flow. A 2 time increase in signal intensity was observed.

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