Development of a High-Pressure Electrodynamic Ion Funnel-Mass Spectrometer Interface

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Overview

A new electrodynamic ion funnel was developed for effective ion transmission at high pressure.

Enhanced performance was achieved by reducing the ion funnel capacitance and increasing the RF drive frequency (1.7 MHz) and amplitude (100-170 V peak-to-peak).

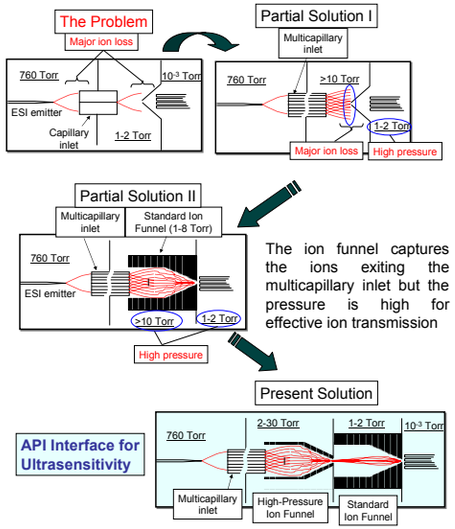
No degradation of ion transmission was observed for pressures up to 30 Torr.

When combined with a multicapillary inlet, the interface provided more efficient introduction of ions, resulting in a significant enhancement in MS sensitivity and detection limits.

Introduction

The quest for higher sensitivity in electrospray ionization mass spectrometry (ESI-MS) is open-ended. While ion transmission efficiency in high-vacuum stages of MS is approaching physical limits, the overall ion utilization efficiency remained <1% because of major ion loss in ESI/MS interfaces. An electrodynamic ion funnel interface was developed previously to overcome this problem[1]. However, the operating pressure of the funnel was limited to be <10 Torr, which severely constrained the maximum aperture of MS inlet and overall MS sensitivity.

We present a new high-pressure ion funnel interface that operates at a pressure of ~30 Torr and significantly improves sensitivity when implemented in a multicapillary and tandem ion funnel interface configuration.



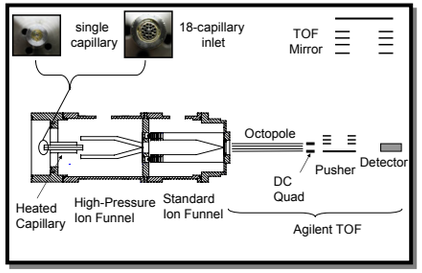
The ion funnel captures the ions exiting the multicapillary inlet but the pressure is high for effective ion transmission

Methods

Instrument

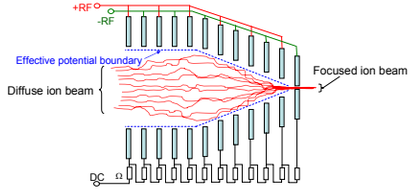
The standard capillary-skimmer interface of Agilent Time-of-Flight (TOF) was replaced with a heated capillary-tandem ion funnel interface.

1. Heated inlet capillary:
   - Single capillary (430 μm i.d.)
   - 18 capillaries (430 μm i.d. each)
2. Tandem ion funnel configuration: a high-pressure ion funnel (1.7 MHz, 100-170 Vp-p) followed by standard ion funnel (560 KHz, 70Vp-p)



How does the ion funnel work?

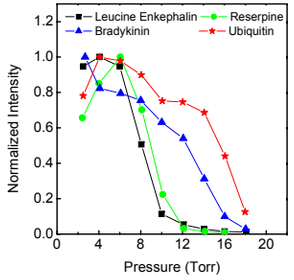
- The electrodynamic ion funnel is a special ion guide consisting of a stack of ring electrodes.
- RF voltages of opposite signs are applied to adjacent ring electrodes to confine ions.
- Ion focusing and transmission are achieved by gradually reducing the inner diameter of the ring electrodes and applying a DC gradient across the funnel.



- The high-pressure ion funnel operates at a higher RF frequency and amplitude.
- The capacitance of 6 nF for the standard funnel is reduced to 1.6 nF in the new funnel by removing the excess material from ring electrodes.

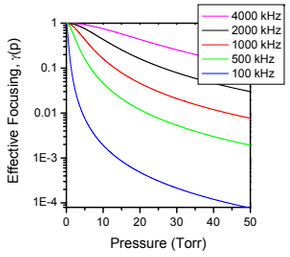
Results

Effect of Pressure on Transmission for a Standard Ion Funnel (F = 560 kHz, A = 70 Vp-p)



- The ion transmission drops for all ions as pressure is increased above 6-8 Torr.
- the ion transmission drops to <10% at 18 Torr
- The loss of transmission is due to the decrease in effective potential and focusing at high pressure.

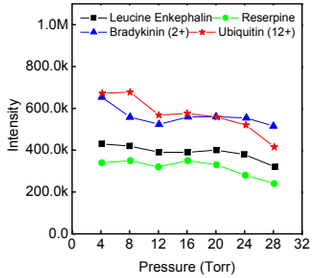
Calculated Effect of Pressure on the Effective Focusing[2]



- This figure indicates that the effective focusing decreases as the pressure increases.
- The effective focusing at high pressure can be realized by increasing the RF frequency.
- The effective potential can be increased by increasing the RF amplitude (V_{RF})

$$V^*(r,x) = \frac{q^2 E_{RF}^2(r,x)}{4m\omega^2} \sim \frac{z^2 V_{RF}^2}{f^2}$$

Effect of Pressure on Transmission for a High-Pressure Ion Funnel (F = 1.70 MHz, A = 100-170 Vp-p)

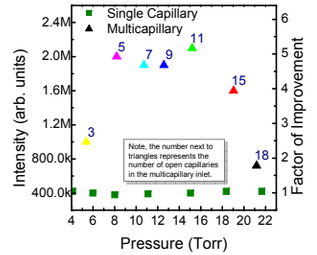


- Constant ion transmission efficiency was maintained at elevated pressures.
- No loss of ion transmission was observed at low pressure compared to the standard ion funnel confirguration.
- Highly charged species require lower RF amplitude relative to singly charged ions because of higher effective potential.

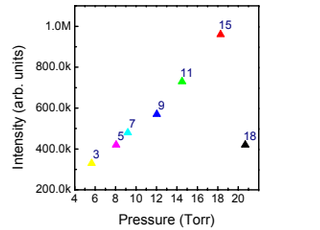
Multicapillary Inlet

- The multicapillary inlet allows more ions to be sampled into MS.[3]
- The increased gas load into the MS requires higher pumping speed to keep the pressure appropriate for standard ion funnel operation.
- The multicapillary inlet does not provide any advantage if coupled with conventional skimmer since ion transmission is limited by the skimmer orifice diameter.
- The new funnel can handle high pressures without the need for increased pumping speed.
- The new funnel also effectively captures all the ions exiting the multicapillary inlet because of its 2.54 cm entrance aperture.

Sensitivity of Multicapillary Inlet *vs.* Single Capillary Inlet (Reserpine)



- The sensitivity obtained using a multicapillary inlet is 5-fold greater than that using a single capillary inlet.
- The plateau in the above figure is due to maximized sampling of ESI ions by using 5 capillaries.



The number next to triangles represents the number of open capillaries in the multicapillary inlet.

- In this figure the ESI emitter was moved further from the multicapillary inlet to provide a more diffuse electrospray.
- This is equivalent to distributing the ESI ions into a larger area.
- The sensitivity increases linearly as a function of number of sampling capillaries.

Implication

The multicapillary inlet is expected to provide > 5-fold improvement in sensitivity when coupled with multi-electrospray emitters.

Conclusions

- We developed an ion funnel that maintains high ion transmission at ~30 Torr.
- The new funnel operated at RF frequency of 1.7 MHz and amplitude of 100-170 Vp-p.
- High RF frequency and amplitude required reducing the funnel capacitance (e.g., by removing the excess material from funnel electrodes).
- The initial implementation with a multicapillary inlet resulted in 5 fold improvement in signal intensity compared to single capillary inlet.
- We showed that the sensitivity can be improved further if not limited by the available ESI current.
- We are planning to extend further the pressure regime in which the funnel works by further reducing the capacitance and increasing the RF frequency and amplitude.
- We are also planning evaluation of an ESI multi-emitter with the multicapillary inlet interface.

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