Development of a Multi-Source, Radially Confining Drift Cell: Alternative Configurations for SLIM

Kelsey A. Morrison, Brian H. Clowers

Department of Chemistry at Washington State University, Pullman, WA, USA

INTRODUCTION

- With the progress in ion confinement technology such as Structures for Lossless Ion Manipulations (SLIM) systems,[1] radial diffusion of ion swarms can be minimized and even directed through 90° turns.[2]
- This permits the arrangement of SLIM boards so that the ions are directed through pathways amenable to laser irradiation and addition of a second ion source.
- By leveraging the flexibility of SLIM board configurations, we have constructed a ~99 cm-long drift tube compatible with further modifications that will provide additional dimensions of information from ion mobility experiments.

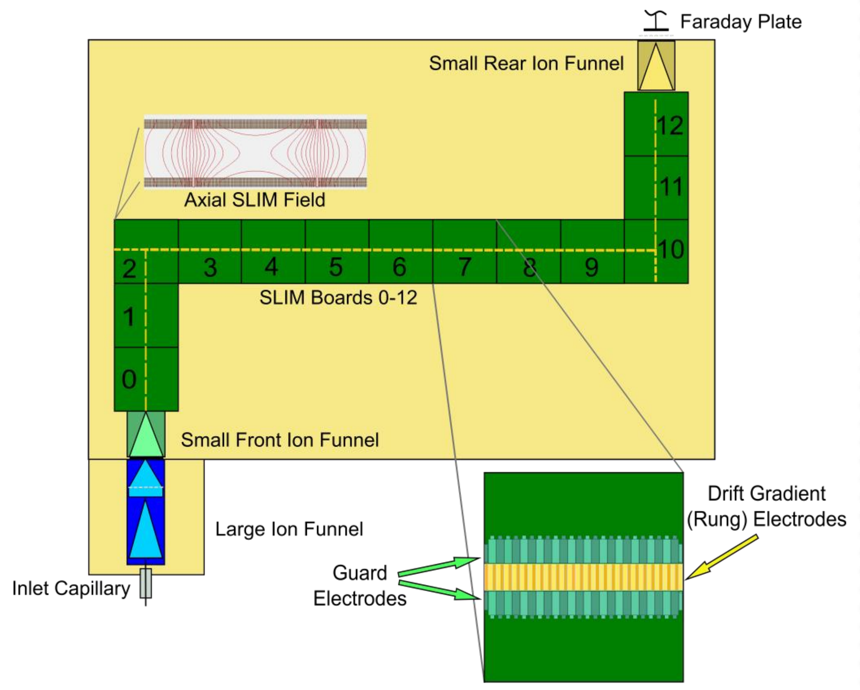


Figure 1. Simplified diagram of the SLIM ion mobility spectrometer design used to obtain the spectra presented within the results section.

AIMS

- Construct a RF-confining ion mobility spectrometer based upon the SLIM architecture that allows for the addition of optical ion manipulations—for dissociative experiments and otherwise—as well as the input of a second ion stream for investigations of ion-ion reactions.
- Evaluate the separation capabilities of the preliminary SLIM design based upon changes in drift time resolving power as a function of gate pulse widths and via analysis of select biomolecules.

METHODS

- Thirteen drift tube SLIM board were arranged with two 90° turns to create a long central path for system flexibility.
- A mixture of seven tetraalkyl ammonium salts (TXAs) at concentrations between 1-10 µM was prepared in a 50:50 acetonitrile:water with 0.1% formic acid solvent was electrosprayed into the standalone SLIM drift tube to assess the system's resolving power as a function of gate pulse width at an electric field of ~10 V/cm and pressure of ~4 Torr.
- Additionally, solutions of 50 µM bradykinin and 10 µM ubiquitin were analyzed to demonstrate the system's applicability to bioanalysis.

RESULTS

- The system performance as a standalone IMS was characterized quantitatively (Figure 2) using a tetraalkyl ammonium salt (TXA) mixture at different gate pulse widths (GPWs).
- A rough maximal resolving power range of ~35-40 was observed at the 150 µs GPW, and baseline separation is achieved for all but the 750 µs GPW (Figure 3).

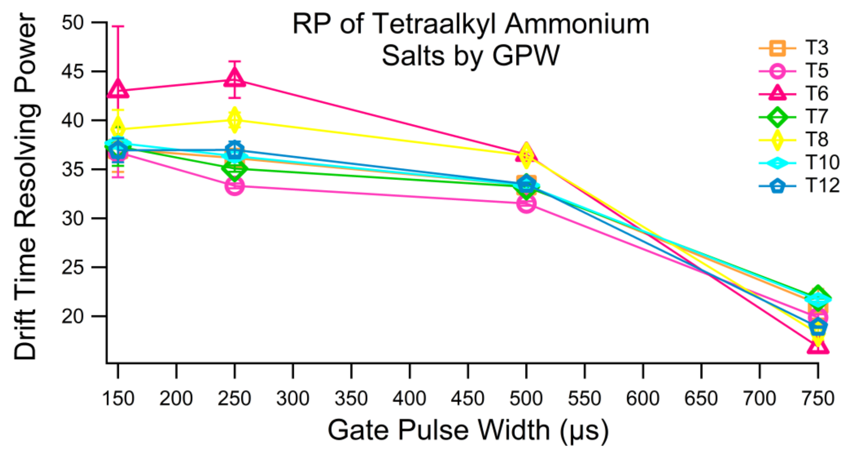
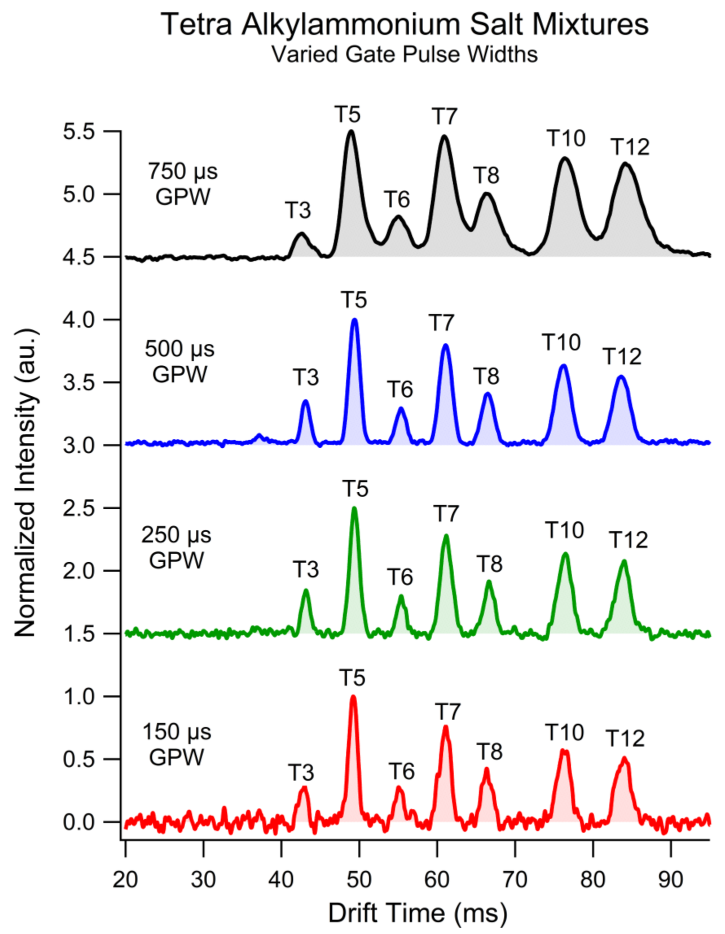


Figure 2. (Above) Using a mixture of seven homologous tetraalkyl ammonium salts (TXAs), the standalone SLIM drift tube's resolving power (RP) was assessed at four different gate pulse widths (150, 250, 500, and 750 µs). Resolving power is maximized using a 150 µs gate pulse width at ~37, and RP is maintained above ~30 up to a GPW of 500 µs.

Figure 3. (Right) Example arrival time distributions for each TXA mixture at the four GPWs used.



- In addition to the TXA mixtures with varying gate pulse widths, solutions containing bradykinin as well as ubiquitin were analyzed (Figure 4).
- The SLIM standalone IMS was able to capture finer features of the arrival time distributions for bradykinin (Figure 4a) and ubiquitin (Figure 4b) within reason; the addition of post-ion mobility mass analysis will enhance the information obtained.

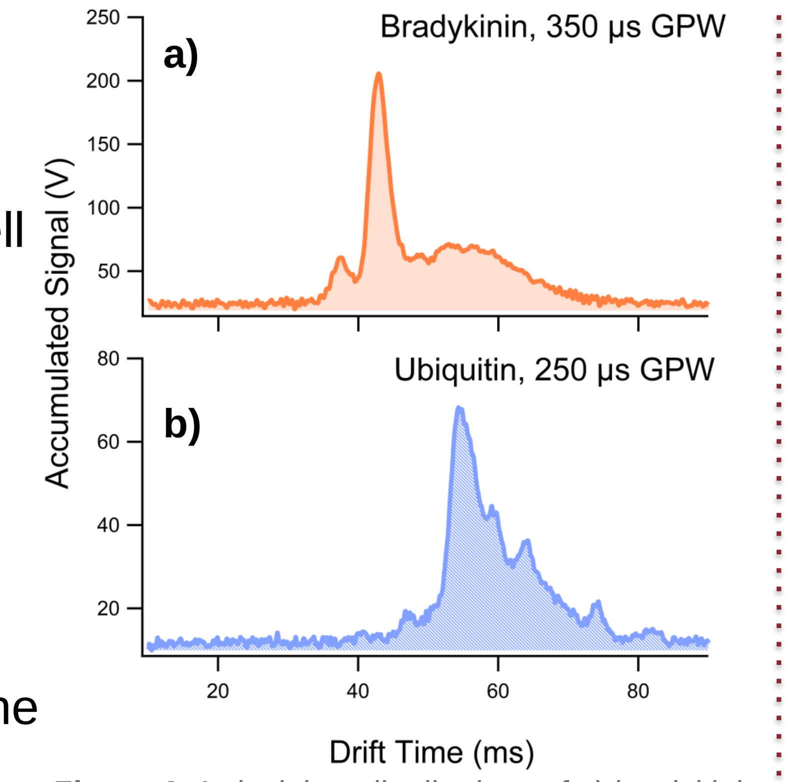


Figure 4. Arrival time distributions of a) bradykinin and b) ubiquitin obtained using the standalone SLIM drift tube as a demonstration of its application to protein mobility separations.

FUTURE DIRECTIONS

Optically-Enhanced Ion Mobility

- The ~61 cm unobstructed drift region allows for optical irradiation of ions for potentially tens of milliseconds (Figure 5).
- Low energy photons, specifically in the infrared spectrum, can be used to manipulate gas-phase clustering behavior.[3]
- Photoisomerization of chromophores can also be assessed.[4]
- Finally, the long path can be irradiated to investigate possible drift time modulation based upon altering effective ion temperature (Figure 6).

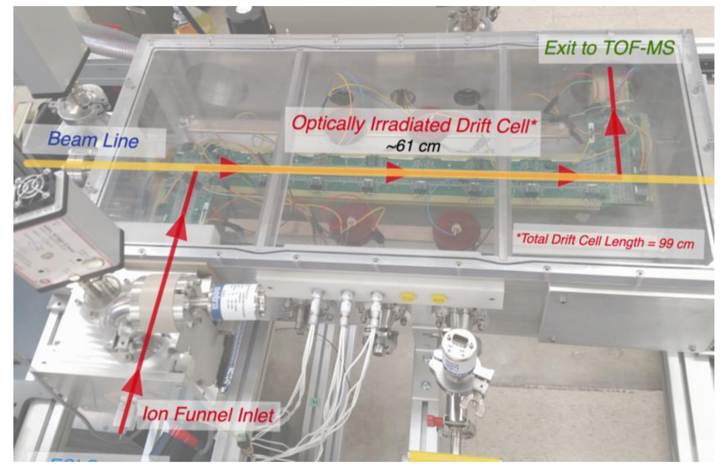
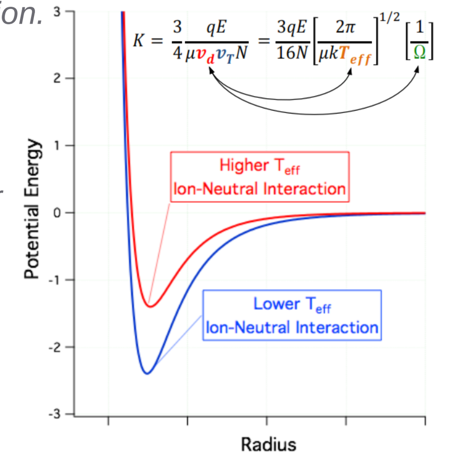


Figure 5. (Above) Image of SLIM drift tube ion mobility spectrometer with labels indicating location for optimal irradiation.

Figure 6.(Right) Predicted changes to Lennard-Jones potentials at higher and lower ion effective temperature, T_{eff}, and its capacity to influence ion mobilities.



Multi-Source SLIM IM-MS

- For enabling ion-ion reactions, a second ion source has been designed to be attached at the second tee-board
- This will permit the investigation of ion-ion neutralization reactions and selective clustering reactions

Figure 7. (Right) Design of the SLIM coupled to a q-TOF-MS with the addition of a second ion source.

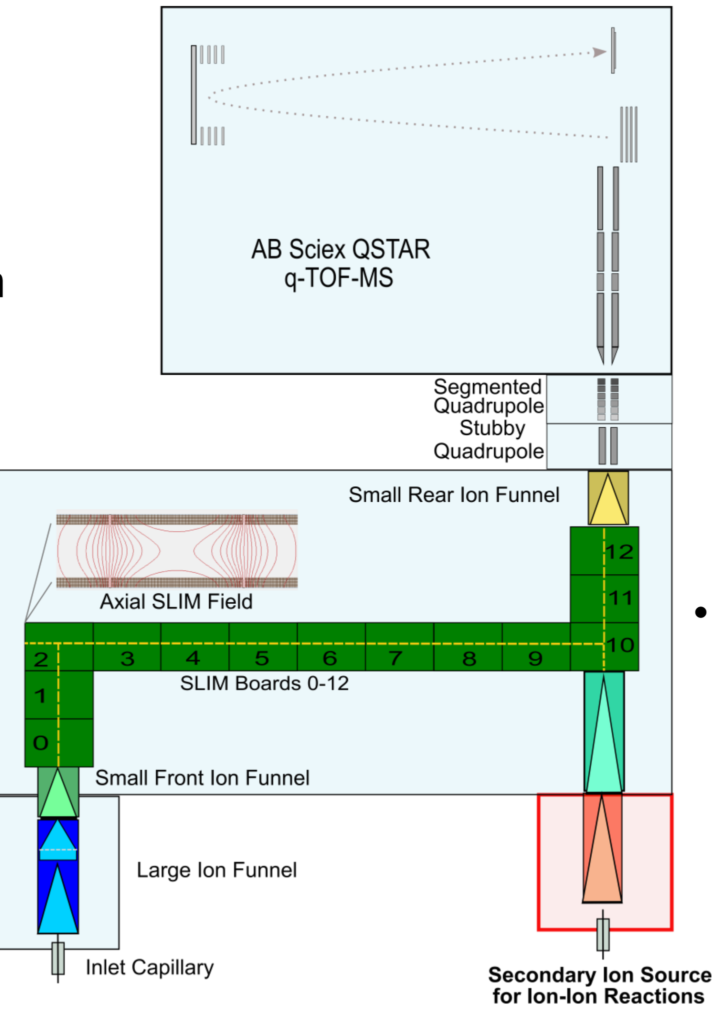
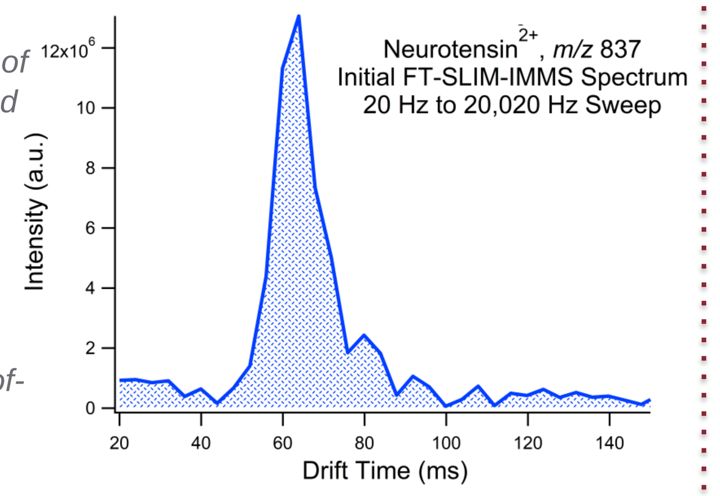


Figure 8.(Right) Preliminary result of Fourier multiplexed arrival time distribution for neurotensin^{2+} obtained via the SLIM drift tube coupled to a quadrupole-time-of-flight mass spectrometer.



Fourier Transform SLIM IM-MS

- Figure 8 shows the first successful Fourier transform[5] spectrum using a SLIM IM-MS. This initial spectrum requires further investigation to identify sources of peak broadening. However, the peak centroid is appropriate for the *m/z*, and correspondingly this demonstrates proof of concept for Fourier multiplexing of a SLIM drift tube IM-MS.

CONCLUSIONS

- A two-turn SLIM drift tube design that can accommodate both long-path laser irradiation as well as a second ion source was successfully constructed.
- Presently, the system is capable of yielding a resolving power of >30 with GPWs of 500 µs or shorter, which is able to easily separate a mixture of species such as the TXAs shown in Figure 3.
- The remaining features to be implemented with this drift tube SLIM are the coupling to a quadrupole time-of-flight mass spectrometer, installation of a laser photon source for optical ion manipulation, addition of the second ion source, and the improved execution of Fourier multiplexing with the SLIM coupled to a mass spectrometer.

BIBLIOGRAPHY

1. Tolmachev et al. Characterization of Ion Dynamics in Structures for Lossless Ion Manipulations. *Analytical Chemistry*, *86*, 2014, 9162-9168.
2. Webb et al. Experimental Evaluation and Optimization of Structures for Lossless Ion Manipulations for Ion Mobility Spectrometry with Time-of-Flight Mass Spectrometry. *Analytical Chemistry, 86,* 2014, 9169-9176.
3. Warnke et al. Protein Structure in the Gas Phase: The Influence of Side-Chain Microsolvation. *Journal of the American Chemical Society*, *135,* 2013, 1177-1180.
4. Coughlan et al. Photoisomerization action spectrum of retinal protonated Schiff base in the gas phase. *The Journal of Chemical Physics, 140,* 2014, 164307.
5. Clowers et al. A two-phase approach to Fourier transform ion mobility time-of-flight mass spectrometry. *The Analyst, 140*, 2015, 6862-6870.

ACKNOWLEDGEMENTS

KAM was supported in part by the Army Research Office under Award #W911NF1510619.

Washington State University

Kelsey A. Morrison
kelsey.morrison @ wsu.edu
www.clowersresearch.com