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Achieving High Resolution Ion Mobility Separations Using Traveling Waves in Compact Multiturn Structures for Lossless Ion Manipulations

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Abstract

We report on ion mobility (IM) separations achievable using traveling waves (TW) in a Structures for Lossless Ion Manipulations (SLIM) module having a 44 cm path length and 16 90° turns. The performance of the TW-SLIM module was evaluated for ion transmission and IM separations with different RF, TW parameters, and SLIM surface gaps in conjunction with mass spectrometry. In this work, TWs were created by the transient and dynamic application of DC potentials. The module demonstrated highly robust performance and, even with 16 closely spaced turns, achieving IM resolution performance and ion transmission comparable to a similar straight path module. We found an IM peak capacity of ~31 and peak generation rate of 780 s⁻¹ for TW speeds of ~80 m/s using the current multi-turn TW-SLIM module. The separations achieved for isomers of peptides and tetrasaccharides were found to be comparable to those from a ~0.9-m drift tube-based IM-MS platform operated at the same pressure (4 Torr). The combined attributes of flexible design, low voltage requirements and lossless ion transmission through multiple turns for the present TW-SLIM module provides a basis for SLIM devices capable of achieving much greater IM resolution via greatly extended ion path lengths and using compact serpentine designs.

Ion mobility separations in conjunction with mass spectrometry (IM-MS) represent a versatile technique for analytical separations, detection, and characterization of biomolecules.^{1–6} IM has been used to detect chemical warfare agents, explosives, drugs, and

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Notes

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environmental pollutants,^{7–10} and has broad potential for separation of structural isomers and in resolving conformational features of macromolecules.^{1,11–16} The benefits and the applicability of IM is enhanced with improvement in the achievable resolution. The resolving power (R_p) of drift tube ion mobility spectrometers is typically determined using eq 1^{17,18}

$$R_p = \frac{t}{\Delta t} = \frac{1}{4} \left(\frac{zeLE}{k_B T \ln 2} \right)^{1/2} \quad (1)$$

where t represents the drift time measured at the peak apex, while Δt is the full width at half-maximum (fwhm), T is temperature, L is the drift tube length, E is the electric field, z , e , and k_B are the charge state, fundamental charge, and Boltzmann's constant, respectively. Equation 1 indicates R_p can be improved by increasing E and L or decreasing T .^{19,20} However, achieving high IM resolution via increasing E or decreasing T is technically challenging and ultimately feasible gains are limited.¹⁹ To this point, significant extension of L is usually accompanied by both sensitivity losses and increasingly challenging voltage requirements. More successful recent attempts to increase IM resolution have involved the construction of devices where the drift path is increased by multiple passes (e.g., through a cyclic ion path).^{21–23} One approach involved operation of multipass separation in a frequency scanning mode wherein a very narrow mobility range is effectively selected.^{24,25} Thus, the lapping phenomenon (i.e., the faster ions approaching/overtaking the slower ions) is minimized to enable high-resolution separations over a limited range. Such approaches are ultimately limited by the gradual expansion (e.g., by diffusion) of the peak widths, and the point at which a single component will span most of the path.

Recently our laboratory introduced Structures for Lossless Ion Manipulations (SLIM) and initially reported their use for a range of efficient ion manipulations and that constitute building blocks for future more complex devices.^{26–30} Although IM has been demonstrated using SLIM with similar performance to drift tube separations, the high voltage constraint and practical limits on drift length remain.^{21,23,28,29} We have recently reported the use of traveling waves (TW) for mobility separations^{31,32} in SLIM. TW-SLIM circumvents the voltage limitations with uniform fields used in drift designs, providing a basis for extending IM path lengths.³³ TW-based IM separations utilize a preset and repeating voltage profile or waveform (i.e., to define the wave) to create electric waves moving along the intended direction of ion motion. A characteristic of TW is that the fields applied are essentially independent of path length, that is, the voltages applied are the same at both ends of the ion path; avoiding voltage related limitations for development of much longer path length designs.

Changing ion path direction in IM devices is crucial for the design and development of future SLIM devices allowing much more complex manipulations, as well as capable of achieving greater resolution. Of particular interest also is to do this in compact (and thus more practical) implementations. Approaches for conducting effective turns (i.e., with minimal loss of ion current and resolution) have been accomplished previously under high vacuum conditions using “bent” quadrupoles,^{34,35} reflectron TOFs,³⁶ curved ion guides,³⁷

etc.^{38,39} The turning of ions under these conditions is challenged by the need to avoid the excitation of ion motion that can potentially lead to collisions with surrounding electrodes. A related challenge for such manipulations is the generally long ion paths required, particularly at higher ion energies where otherwise better performance can be achieved. However, the challenges associated with turns in IM are different than under high vacuum as ion motion in IM is highly damped, generally conducted in a static gas, and is thus more comparable to turns in condensed phases, e.g. capillary electrophoresis separations. Ion turns in static gases as well as for IM separations were, to our knowledge, first used in Clemmer and co-workers in the development of a cyclical IM separator,²⁴ where four ion funnels were utilized to focus ions before each of four turns to minimize variation in ion path, and thus loss of resolution. In previous SLIM studies, wherein effectively lossless ion turning were demonstrated for use in drift field IM separations,³⁰ the ions on the inside of the turn travel shorter distances than those ions on the outside, causing some degradation of the resolution achievable.⁴⁰ This “race track” effect, a general issue in condensed phase separations, decreased the achieved IM resolving power when compared to an ideal drift tube of comparable drift path length. In such ion mobility separations, a well-defined ion path or ion transport mechanism that minimizes the “race track” effect is crucial.

In this work, we explore the use of IM turns in highly compact designs that do not incur significant variations in ion path. The use of traveling waves provides an alternative approach for performing ion turns and that can potentially circumvent the need for complex fields and electrode structures. The development of a TW IM approach with SLIM can enable ion paths providing dramatic increases in L by making multiple “U” turns in a compact IM module. Unlike SLIM operating on static DC gradients⁴⁰ the factors that could contribute to peak broadening at the turns with the TW-SLIM are different: ions move predominantly within “traveling traps” or bins, with a periodic “rollover” into preceding bins with a mobility-dependent rollover probability.

We have developed and evaluated a simple and effective approach for making turns in TW-SLIM, and additionally evaluated the impact of the turns upon achieved resolution. Using a separation module having sixteen 90° turns, we show it is feasible to achieve higher resolution by significantly extending L in a compact design. In addition, we found the TW-SLIM module demonstrated similar resolution as a drift tube ion mobility platform but with much shorter path length.

EXPERIMENTAL SECTION

Chemicals used in this work include the Agilent low concentration ESI tuning mix (Agilent, Santa Clara, CA), the peptides with sequences GPFRPRFPS and RRGPFSPF were purchased from Sigma-Genosys while RPPGFSPFR (Bradykinin) was purchased from Sigma-Aldrich (St. Louis, MO) and tetrasaccharides (cellotetraose, maltotetraose, and mannotetraose) were purchased from Sigma-Aldrich (St. Louis, MO). The chemicals have been used without further purification. The peptides were prepared in 1 μ M solutions of 50/50/0.1 (vol/vol/vol) water/methanol/formic acid. Ten micromolar solutions of tetrasaccharides were prepared in 50/50/0.1 (vol/vol/vol) water/methanol/formic acid.

The instrumentation has been described elsewhere.³³ Briefly, ions were produced by nanoelectrospray ionization source (3000 V), infused by a syringe pump (Chemyx, Stafford, TX) with a flow rate of 300 nL/min. Ions were introduced into the first stage of vacuum through a 500- μ m i.d. stainless steel capillary heated to 140 °C (Figure 1A). After exiting the heated capillary, ions were focused then stored for 10 ms in an ion funnel trap (1.3 MHz and $\sim$ 160 V_{p-p}) at 3.95 Torr.^{41–43} Ions were released from the ion funnel trap by lowering the voltage applied to the exit gate for 324 μ s and then directed into the TW-SLIM module (4 Torr N₂). Ions exiting the TW-SLIM were collimated by an 18 cm long “rear” ion funnel (830 kHz and $\sim$ 350 V_{p-p}) and then guided to an Agilent 6538 QTOF mass spectrometer equipped with a 1.5-m flight tube (Agilent Technologies, Santa Clara, CA). Data was recorded with a U1084A 8-bit ADC digitizer (Keysight Technologies, Santa Rosa, CA) and processed using in-house developed control software written in C#.

The TW-SLIM module consisted of a pair of parallel 30.5 cm $\times$ 7.6 cm printed circuit boards (PCBs).^{28,29,43} As shown in Figure 1B, the electrode layout included sixteen 90° turns forming a multiturn ion path (Figure 1B), thus the path length of the straight and the multiturn configurations is different (30.5 cm vs 44 cm measured at the center of the path). As displayed in Figure 1C inset, the TW-SLIM used 5 arrays of TW DC electrodes, separated from adjacent RF electrodes by 0.13 mm gaps, with each electrode having a length of 1.98 mm and width of 0.43 mm. The use of 6 RF and 5 DC electrodes was found well suited for the present experiment. For a smaller number of RF electrodes, ion transmission becomes increasingly sensitive to the guard electrode potential. For a larger number of RF electrodes (e.g., 12 RF, 11 DC) the detrimental effect of the guard electrodes is eliminated, but results in less compact designs and with somewhat greater fabrication cost (because of the approximate doubling of the number of electrodes). The 6 RF 5 DC design provides effective RF confinement (as will be seen below) for lossless ion transmission while providing a small footprint for the ion path, allowing it to be maximized on a given surface.

The SLIM DC guard electrodes were 5.08 mm wide.³³ RF waveforms (at 1 MHz, 180° out-of-phase for adjacent electrodes) were applied to the six 44 cm long RF electrodes on each surface to create a confining pseudopotential preventing loss of ions to the two SLIM surfaces. In this work, the TW was created by switching the DC (on and off) to individual electrodes of each eight electrode set.³³ The TW sequence was varied between 10000000 and 11111100, where 0 corresponds to 0 V and 1 to the application of the TW amplitude (e.g., 30 V) to the electrode set, and stepped one electrode at a time in the direction of ion motion. The gap between the two TW-SLIM surfaces was varied by changing the size of aluminum spacers (McMaster-Carr, Los Angeles, CA). The gaps studied in the present work are 2.2, 3.2, and 4.75 mm.

RESULTS AND DISCUSSION

A key development in this work is a conceptual arrangement by which ions make turns in TW-SLIM without ion losses or significant loss of IM resolution, providing a foundation for much longer path length designs capable of much higher IM resolution. The simple approach developed allows the use of the same TW sequence (e.g., voltages and power supplies) as the linear path designs. In this approach the TW path in one direction is

terminated at the intersection with the orthogonal path and ions are effectively “pushed” into a “bin” on the new path at the appropriate point in the TW sequence (e.g., 11110000). Previously, we have utilized ion simulations to understand the ion motion in SLIM operating with static and transient fields to drive the ion motion.^{26,27,33} In this study, ion trajectory simulations were also performed using Statistical Diffusion Simulation (SDS) collision model in SIMION 8.1 (Scientific Instrument Services Inc., Ringoes, NJ, USA).^{26,33} Simulations utilizing a portion of the 44 cm multiturn TW-SLIM module with 6 RF electrodes and 5 interspersed DC electrodes have been performed; Figure 1C shows an example of the ion trajectory simulation viewed from above (i.e., perpendicular to) surfaces, utilizing a TW speed of 84 m/s, a TW amplitude of 30 V, and 15 V applied to the guard electrodes, and showing efficient ion confinement and lossless transmission.

Importantly, the simulations indicated that the race track effect was effectively avoided using TW-SLIM where the orthogonal path at a turn effectively captures ions coming from the previous section (Figure 1D left panel shows the potential surface in the device); ions from a set of traveling traps are transferred to corresponding traps moving in an orthogonal direction. Thus, if electrodes are arranged such that the wave continuity is maintained in the orthogonal channel, then ions in one bin are transferred efficiently to the orthogonal bin, assuming the plume width is on the order or less than the width of the traveling trap. The plume width is influenced by the guard electrode potential as well as the gap between the SLIM surfaces. Figure 1C shows the plume width in the short multiturn SLIM to be ~2 mm, similar to the length of the TW electrodes, and less than the width of the traveling trap (created by 4 electrodes with the present sequence, i.e., ~8 mm, as shown in Figure 1D right panel). The IM resolution from simulations for straight and multiturn configurations was comparable; i.e. the turns had no effect on resolution or significant effect on IM peak width.

Unlike constant drift field IM, R_p can be a misleading metric in dynamic conditions (where, e.g., the field, gas composition, temperature, or collision cross sections change during the separation).^{18,33,44} At TW speeds lower than a threshold only very narrow peaks with no separation are observed due to ion confinement in traveling traps (sometimes referred to as “surfing”). In this work, we use the resolution of m/z 622 and 922 ions ($R_{622-922}$) obtained from Agilent low concentration tune mix to evaluate separation quality³³ using eq 2

$$R_{622-922} = \frac{2(t_{922} - t_{622})}{\Delta t_{922} + \Delta t_{622}} \quad (2)$$

where t_{922} and t_{622} represent the arrival times of m/z 922 and 622 ions while Δt_{922} and Δt_{622} are the fwhm of the m/z 922 and 622 peaks, respectively. The factors that affect the resolution in the TW-SLIM multiturn module included TW sequence, TW amplitude, guard bias, RF amplitude, TW speed, and SLIM surface gap spacing. TW sequences, the voltages applied in a repeating pattern to each set of eight electrodes (Figure 2A), included two up and six down (11000000) to six up and two down (11111100) yielded similar ion mobility resolutions of 10.4 ± 0.1 which were also similar to those previously reported results for a straight TW-SLIM module.³³ A symmetric TW with a sequence of 11110000 at a TW speed of 90 m/s was used at TW amplitudes from 15 to 60 V, with the optimum resolution of 10.4

± 0.1 at 30 V (Figure 2B). The guard bias and the applied RF had no significant effect on the resolution over a wide range (Figures 2C and 2D). The observed effects of the guard and RF voltages are similar to those reported previously for other SLIM arrangements.^{27,29,33}

Figure 3A shows the effect of TW speed on the resolution for the 44 cm multiturn module, at different SLIM surface gaps. The gap affects the position of the ions and the net fields they experience, leading to subtle differences in resolution at different TW speeds. With a 4.75 mm gap, at slower TW speeds (2–52 m/s) ions can move with the TW, and no significant IM separations are achieved.⁴⁵ Significantly improved resolutions were observed as the TW speed increased from 52 to 63 m/s, where ions begin to occasionally fall over the tops of the waves.^{33,45} Upon further increasing the TW speed, a plateau was observed in the measured resolution upon varying the TW speed from 80 to 126 m/s, showing that good IM resolution can be achieved over a broad range of TW speeds. The maximum resolution of 10.7 ± 0.1 was achieved at a TW speed of 90 m/s. Upon further increasing the TW speed from 126 to 210 m/s, the resolution decreased to 7.8 ± 0.3 at 210 m/s, where the overall IM separation is reduced and simulations show that ions oscillate slightly with minimal axial displacement as waves pass.^{45,46} As shown in Figure 3A, maximum resolution values of 9.6 ± 0.4 , 11.5 ± 0.1 , and 10.7 ± 0.1 were obtained for gaps of 2.2 mm, 3.2 mm, and 4.75 mm, respectively. Interestingly, the TW speed for the transition from traveling trap to separation mode increased with a decreasing gap. For example, the transition occurred at ~ 63 m/s for a 4.75 mm gap (Figure 3A), and occurred at higher speeds with smaller gaps. This can be explained by the effect of the net TW field (E_{TW}) experienced, which is inversely dependent on the gap (d) and the width of electrodes (w):

$$E_{TW} \propto \sqrt{\frac{1}{d^2 + w^2}}$$

Since this TW transition speed (s) is proportional to E_{TW} , a simple theoretical consideration arises that the speed and SLIM surface gap are related as $s \sqrt{d^2 + w^2} = \text{constant}$. On the basis of the 63 m/s transition speed for a 4.75 mm gap, theoretical expectation for transition speeds for 2.2 and 3.2 mm gaps were 85 and 109 m/s respectively, in good agreement with experimental observations (Figure 3A).

The m/z 622 and 922 ions resolution ($R_{622-922}$) for the straight TW-SLIM module (30.5 cm) was 9.6 ± 0.1 and 10.7 ± 0.1 for the multiturn TW-SLIM (nominal 44 cm) at TW speed of 90 m/s (Figure 3B).³³ If the entire added path length contributes to improving the resolution achieved (i.e., is proportional to the square root of the length) the maximum resolution expected (considering a 44 cm path length provided by the present device) to be achievable is $[9.6 (44/30.5)]$ or ~ 11.5 . The observed resolution was $\sim 7\%$ lower. This is potentially due to either the reduced separation events at the intersections of the turn or the position of injection into the orthogonal TW. To elaborate, at the intersection region, the ions are deposited into the region with orthogonally directed traveling wave. Since the turn region is confined by a guard electrodes, the ions do not have the freedom to execute a rollover immediately upon entering the orthogonal TW, at least while they are still in the intersection region. Thus, this region (corresponding to about 2 TW electrode widths, or 3.96 mm for the

present design) does not contribute to the separation capacity of the device. For the present device with 16 turns the effective separation path can be estimated to be (44 cm – 16*3.96 mm = 37.7 cm). Thus, the theoretically expected resolution is 9.6 (37.7/30.5) or ~10.8, very close to what was experimentally observed (10.7). Thus, the present results provide no evidence for loss of resolution at turns but also suggest that turn regions contribute less to increasing the resolution than might be expected. As future modules would have much longer straight sections between turns, these results indicate that TW-SLIM incorporating turns provide an effective route for significantly extending ion path length and achieving higher IM resolution in a compact format.

In addition to resolution, the separation peak capacity, and peak generation rate serve as useful metrics of performance. The separation peak capacity is a dimensionless measure of overall resolution; it is defined as a measure of the range over which features are separated divided by the peak width associated with the selected species and calculated using eq 3:^{17,33,47}

$$\text{peak capacity} = \frac{t_{1822} - t_{622}}{(\Delta t)_{\text{average}}} \quad (3)$$

In the current study, the peak capacity is calculated by dividing the separation range ($t_{1822} - t_{622}$) where t_{1822} and t_{622} represent the apexes of the arrival times of m/z 1822 and 622 ions, respectively by $(\Delta t)_{\text{average}}$ which is the average fwhm of m/z 622, 922, 1222, 1522, and 1822 ions.³³ Ions of m/z 2122 were not considered in the estimation of peak capacity as they had very low signal intensities. Peak generation rate, the number of the peaks generated per separation time, is defined here as the ratio of the peak capacity to the full separation time or across multiple separations. In a single separation, this can be defined by eq 4^{33,48}

$$\text{peak generation rate} = 1/(\Delta t)_{\text{average}} \quad (4)$$

The maximum peak capacity and peak generation rate of 31 ± 1 and $782 \pm 25 \text{ s}^{-1}$ were achieved at a TW speed of 80 m/s, for a TW amplitude of 30 V, a symmetric TW sequence, and a 3 mm gap. We note that this peak generation rate is approximately 3 orders of magnitude greater than typical of condensed phase separations.^{47–52}

Separations using the multiturn TW-SLIM module (3 mm gap and 30 V TW amplitude) were also compared with those from drift tube IM-MS platform at 4 Torr nitrogen.¹ The collision cross sections for each ion were measured using drift tube IM-MS (Table 1) and were consistent with literature reported values.^{6,53} The arrival time distributions of the doubly charged peptides, RPPGFSPFR (bradykinin), GPFRPRFPS and RRGPFSPF, obtained by the multiturn TW-SLIM module at a TW speed of 126 m/s and by a drift tube IM-MS with 17.3 V/cm are shown in Figure 4. Bradykinin and RRGPFSPF display a slightly shorter arrival time than GPFRPRFPS, where another longer arrival time feature is evident. Although the drift tube IM analysis provided narrower peaks, comparable separation power was observed. As illustrated in Figure 4A and B, there is a minor feature

(A) with a lower arrival time in addition to the major feature (B) for bradykinin, which can be attributed to another conformer, consistent with previous work.^{19,54} The collision cross section of the major feature (B) was measured using drift tube IM and shown in Table 1 (the signal for the minor species was too low to obtain a reliable collision cross section). In addition, GPFRPRFPS isomer gives rise to two distinct peaks by both drift tube and TW-SLIM analyses which can be attributed to different coexisting conformers (C and D). The two conformers have different collision cross sections of $349.6 \text{ \AA}^2$ and $359.4 \text{ \AA}^2$ for structures C and D, respectively (Table 1). An additional minor species (E) with a lower arrival time was observed for GPFRPRFPS peptide isomer when analyzed by drift tube IM (Figure 4B). Similarly, the effects of ion mobility separation of three tetrasaccharide isomers (cellootetraose, maltotetraose, and mannotetraose) achieved by the multiturn TW-SLIM module and the drift tube IM-MS platform were compared.¹ As shown in Figures 4C and 4D, the three tetrasaccharides display distinct IM peaks, with the order of arrival times = cellootetraose < maltotetraose < mannotetraose. The collision cross section for each tetrasaccharide was measured and shown in Table 1. It is noteworthy that cellootetraose shows a wider IM peak than the other two isomers, especially upon IM analysis by TW-SLIM module (Figure 4C), suggesting the existence of multiple coexisting conformers not resolved by either multiturn TW-SLIM module or the drift tube IM. Again, IM separations of the peptide and tetrasaccharide isomers using the 44 cm multiturn TW-SLIM and 89 cm drift tube IM platforms provided similar resolution.

CONCLUSIONS

In this work, we have described for the first time the concepts, their investigation by simulation, and experimental validation of an approach for lossless 90° turns in TW-SLIM, and doing so without significant impact on IM resolution. The effect of TW speed, TW amplitude, TW sequence, RF amplitude, guard bias, and SLIM surface gap have been investigated. The present work shows the capability of TW-SLIM modules for essentially lossless ion transmission without significant loss of ion mobility resolution through a TW-SLIM module having 16 closely spaced 90° turns. Our results are consistent with previous TW IM reports from both theoretical and experimental investigations.^{11,33,45,55} The maximum resolution for the m/z 622 and 922 peaks of 11.5 ± 0.1 was obtained for a symmetric TW sequence with the speed of 111 m/s, TW amplitude of 30 V, guard voltage of 15 V, and RF amplitude of $300 V_{p-p}$ using a 3 mm gap. The peak capacity and the peak generation rate were estimated to be 30.8 ± 0.8 and $782 \pm 25 \text{ s}^{-1}$ at 80 m/s, respectively. IM resolution obtained utilizing the 44 cm multiturn TW-SLIM module was similar to that obtained using an 89 cm drift tube. Most importantly, the present work provides the foundation for the development of long ion path multiturn TW-SLIM modules to achieve much higher IM resolution in highly compact designs, and in conjunction with high sensitivity. In a companion manuscript, we report initial results for a 13-m long TW-SLIM device.⁵⁶

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Figure 1.

(A) Schematic diagram of the instrumental arrangement. (B) Illustration of the straight and multiturn TW-SLIM. (C) Simulated trajectories for a thousand ions at a TW speed of 84 m/s and 4 Torr with a detailed view of the electrode geometry shown in the inset below, showing the detail for the RF, traveling wave and guard electrodes in a portion of the simulated geometry of the experimental 44 cm long TW-SLIM module. The TW voltages are applied to subsets of 8 electrodes numbered 1 through 8 forming a traveling wave (see text). (D) Potential energy surface from SIMION 8.1 near a turn at an instant in time (left). The potential values along the axis of ion motion (right). The width of the trap is ~8 mm. The plume width (~2 mm into the plane of paper) is lower than trap width thus allowing complete transfer of ion plume from one trap into the corresponding orthogonal trap at the turn.

Figure 2.

Ion mobility resolution measured at TW speed of 90 m/s as a function of: (A) the various TW sequences considered in the present study at a TW amplitude of 30 V, a guard bias of 15 V, and RF amplitude (V_{p-p}) of 300 V. (B) TW amplitude for a symmetric sequence (11110000), a guard bias of 15 V, and an RF amplitude (V_{p-p}) of 300 V. (C) Guard bias for a TW amplitude of 30 V. (D) RF amplitude for a TW amplitude of 30 V and a guard bias of 15 V.

Figure 3.

(A) Ion mobility resolution based on m/z 622 and 922 as a function of TW speed for: a TW amplitude of 30 V, a symmetric TW sequence of 11110000, guard bias of 15 V, and RF amplitude (V_{p-p}) of 300 V, at three different SLIM surface gaps of 2.2 mm, 3.2 mm, and 4.75 mm. (B) Arrival time distributions using the multiturn TW-SLIM module (44 cm) (left) compared to that analyzed by a straight TW-SLIM module (30 cm) (right) obtained for a TW speed of 90 m/s using a symmetric sequence (11110000), a TW amplitude of 30 V, a guard bias of 15 V, and an RF amplitude (V_{p-p}) of 300 V.

Figure 4.

Arrival time distribution of the doubly charged peptide ions of bradykinin (RPPGFSPFR), GPFRPRFPS, and RRGPFSPSPF analyzed by (A) multiturn TW-SLIM module (44 cm) at TW speed of 126 m/s (B) drift tube IM (89 cm) applying a static field of 17.3 V/cm. Arrival time distributions for singly charged tetrasaccharides analyzed by (C) multiturn TW-SLIM module (44 cm) at TW speed of 84 m/s (D) drift tube IM (89 cm) applying a static field of 17.3 V/cm. The TW-SLIM studies were performed at the following conditions: TW amplitude of 30 V using a symmetric square wave (11110000), a guard bias of 15 V, and an RF amplitude (V_{p-p}) of 300 V.

Table 1

Collision Cross Sections of the Samples Considered in the Current Study Measured by 89 cm Drift Tube IM-MS Platform Using 17.3 V/cm in 4 Torr of Pure Nitrogen Buffer Gas

sample	species	m/z	cross section ($\text{\AA}^2$)
bradykinin	$[M + 2H]^{2+}$	530.79	344.3
RRGPFPSPF	$[M + 2H]^{2+}$	530.79	347.3
GPFRPRFPS (C)	$[M + 2H]^{2+}$	530.79	349.6
GPFRPRFPS (D)	$[M + 2H]^{2+}$	530.79	359.4
cellotetraose	$[M + Na]^+$	689.21	225.3
maltotetraose	$[M + Na]^+$	689.21	232.6
mannotetraose	$[M + Na]^+$	689.21	235.1