SIMULATION OF THE EFFECT OF MECHANICAL MISALIGNMENT ON HIGH M/Z RESOLUTION CDMS TRAP SOLUTIONS

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OVERVIEW

PURPOSE: Examination of the effect of realistic mechanical build tolerances on the performance of high m/z resolution CDMS trap solutions

METHODS: Monte-Carlo approach to electrode misalignment, geometries constructed in SIMION, trajectory simulation using custom GPU code

RESULTS: Demonstration of a high m/z resolution trap solution that is robust with respect to mechanical misalignments

INTRODUCTION

In charge detection mass spectrometry (CDMS) single ions or small ensembles of ions are trapped in an electrostatic linear ion trap (ELIT), the induced charge is detected on a central detector tube as the ions oscillate in the ELIT. The signal is analysed using a Fourier transform (FT), the frequency of the FT peak determines the m/z and the amplitude the charge, hence allowing direct mass measurement for large and heterogeneous ions.

Since charge is quantized, reduction of the charge uncertainty to a sufficiently low level leads to perfect charge accuracy. Mass resolution is therefore limited solely by the m/z resolution of the ELIT. Ideally all ions of a given m/z would oscillate with the same frequency, in reality this is not the case as trapped ions have a spread in axial KE and take differing radial trajectories; for a given geometry the dependence of the frequency on these factors determines the m/z resolution of the trap.

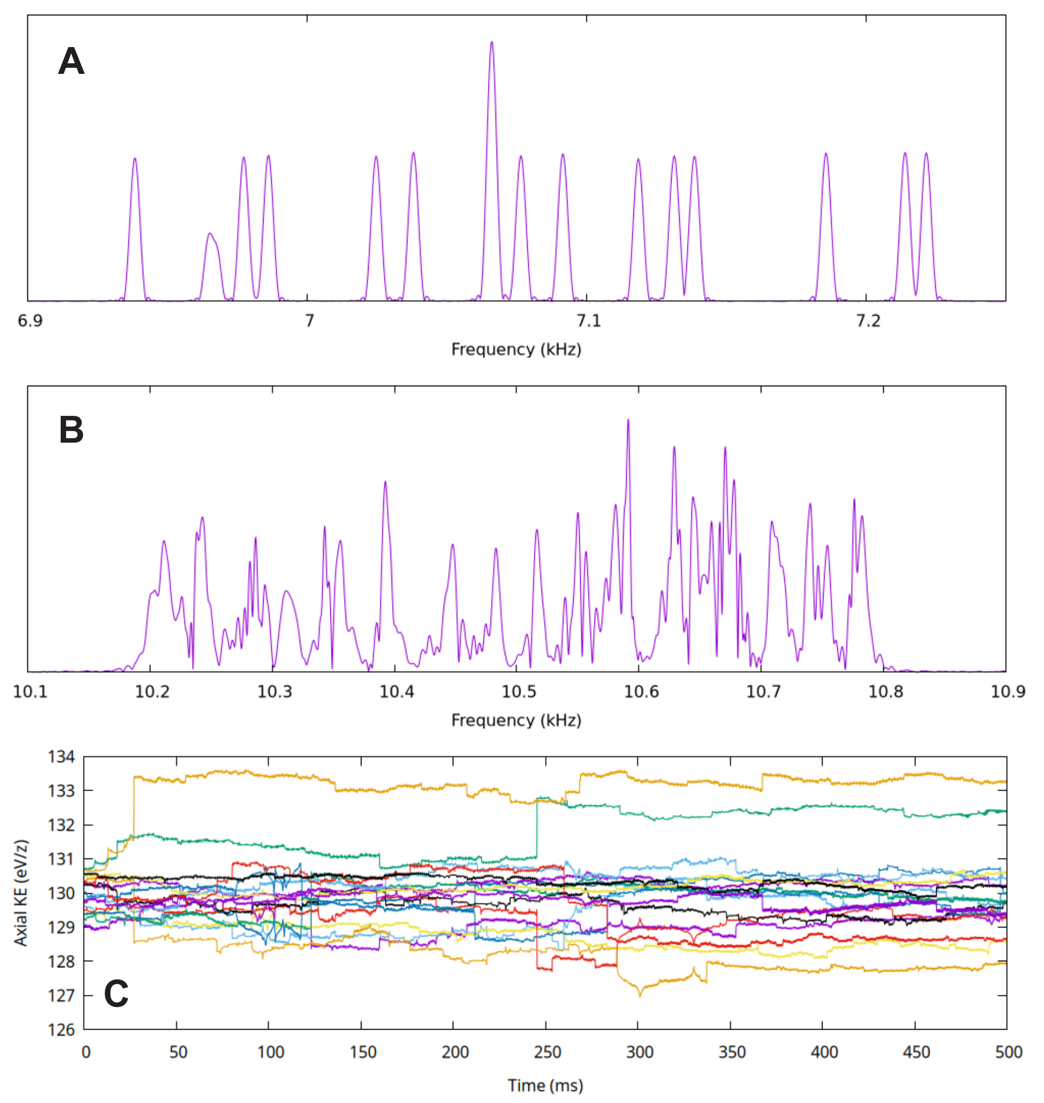

***Figure 1**. Data from trajectory simulations including space charge effects of 17 AAV ion trapping events. A) FT at high m/z resolution (4 electrode trap geometry). B) FT at low m/z resolution (current prototype trap). C) Axial KE of the ions over the 500ms transient for the low m/z resolution FT.*

Our current prototype CDMS trap geometry has m/z resolution in the order of a few hundred. Experimental implementations of higher resolution traps have demonstrated resolution of 14,000 [**1**], while in silico optimisation predicts highly stable trap solutions with resolutions >200,000 for typical input beam conditions [**2**]. A wide range of high resolution trap geometries can be found, however the tolerance of these geometries to mechanical misalignment is unknown. Understanding how these ideal solutions perform when constructed with realistic mechanical tolerances allows us to estimate realistic limits on m/z resolution and avoid the experimental implementation of solutions with poor stability and/or resolution tolerance to mechanical imperfections.

While for many applications the current modest m/z resolution is sufficient, traps with high m/z resolution have an additional advantage in terms of charge capacity. For trapping events with multiple ions space charge interactions lead to changes in axial KE. High m/z resolution traps are tolerant to axial KE changes, while in a low resolution trap both m/z and charge measurement accuracy are degraded.

As an example of space charge effects, **figure 1** shows results from simulated 500ms trapping events of 17 AAV ions (mean m/z 23.3kDa, mean z +159) . **Figure 1A** shows the 1st harmonic peaks from the FT of the simulated transient for the high resolution 4 electrode trap in **table 1**. **Figure 1B** shows an equivalent FT for the current prototype low resolution trap. Space charge interactions cause changes in the ions axial KE during the trapping event, leading to the corruption of the FT peaks in **figure 1B**. Assignment and accurate charge measurement of the corrupted peaks is impossible, incremented short window FTs would reduce the peak distortion at the cost of wider FT peaks leading to overlapping peaks. Due to the high m/z resolution of the 4 electrode trap, the peaks in **figure 1A** are not corrupted by the changes in axial KE. The two peaks with grossly different amplitude are overlaps between ions with similar frequency, excluding these we can accurately assign the m/z and charge of 13 ions from this transient.

Figure 1C shows the axial KE of the 17 ions of **figure 1B** over the 500ms. While this data is an example from a single trapping event the behaviour is typical, ions undergo a range of interactions leading to drift and step changes in axial KE.

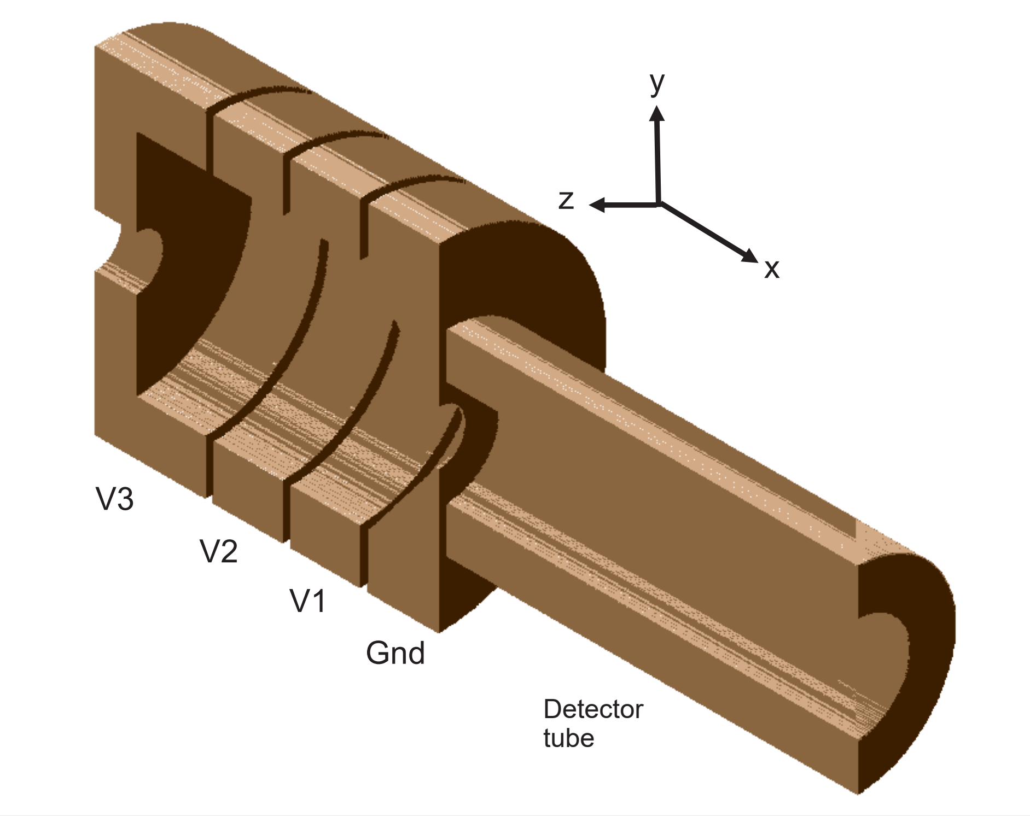

***Figure 2**. Example of a 3 electrode trap geometry. The trap designs in this poster all comprise a detector tube and shield electrode at ground potential and either 3 or 4 electrodes with applied voltages V1 to V4.*

METHODS

Trajectory simulations

PyCUDA was used to implement a 4th order Runge-Kutta trajectory calculation. Electric field dat files for a given physical trap geometry are obtained using SIMION® 2020 [**3**] to solve the Laplace equation, these are then imported into the CUDA® model. The optimisation procedure for new trap geometries is described in [**2**].

Mechanical misalignment of trap electrodes was modelled via a Monte-Carlo approach, we build a number of half trap assemblies where an x-y -z position offset of each electrode is given by a normal distribution with a standard deviation of 16μm. These half trap assemblies are then combined randomly to give a number of full traps. We also examine the case where the trap halves are constructed ideally but are radially offset or tilted with respect to each other. An example 3 electrode trap geometry is shown in **figure 2**.

Initial phase space

The performance of an ELIT is dependent on the initial position and velocity spreads (phase space) of the incoming ion beam. Mean frequency values are determined after 100 passes through the detection tube for each ion, m/z resolution is calculated as $f/(2^*\Delta df)$ where Δf is the width of the frequency peak at 10% intensity. We use 10% peak width resolution to account for peak shape distortion since some high resolution solutions exhibit asymmetric peak shapes. Unless otherwise noted we use ions of mass 340kDa and z=+40, mean axial KE 130 eV/z, standard deviations: axial KE σ= 0.5eV/z, radial (x/y) position σ= 0.2mm, radial angle σ= 0.35°. For the current prototype trap this phase space gives an m/z resolution of 120, in good agreement with that seen experimentally.

RESULTS AND DISCUSSION

Trap solutions

There are a wide range of electrode geometries and voltages for traps that exhibit high stability and m/z resolution. In this poster we examine three candidate high m/z resolution trap solutions: a short and a long 3 electrode trap, with m/z resolution ~25-30k, and a long 4 electrode trap with m/z resolution ~200k. These are listed in **table 1**, referred to by the number of independent electrodes and the axial distance between the inner faces of the end cap electrodes (i.e. the internal axial dimension of the trap).

Trap design	Stability %	Mean freq (kHz)	Resolution
Current prototype 3 elec 88mm	>99%	17.9	120
Short 3 elec 96mm	>99%	16.8	25,000
Long 3 elec 150mm	>99%	12.0	30,000
4 elec 140mm	>99%	11.7	193,000

***Table 1**. Performance metrics of the current prototype trap and the three candidate high m/z resolution traps. Frequency is for an ion of m/z 8500 at the default axial KE of 130 eV/z.*

Monte-Carlo 16μm offsets

Measurement of a limited number of pre-production half trap assemblies suggests the current build method leads to offsets with a standard deviation of 8μm. We use 16μm here as a conservative estimate.

Figure 3A plots stability vs resolution for the long 3 electrode trap. There is performance loss in stability and resolution; at worst stability drops to 60% and resolution to ~14,000. Only one trap assembly performs identically to the ideal result. We also plot the results from applying a V3 voltage retune to the worst (stability and/or resolution) trap assemblies. We can generally recover stability, with the lowest now at 83%. While some trap assemblies can be retuned for both stability and resolution, in many cases we lose resolution when we retune for stability. As an estimate of yield ~25% of the trap assemblies have stability <95% and/or resolution <20,000.

Figure 3B plots stability vs resolution for the short 3 electrode trap. For this trap geometry we see severe loss of stability and resolution. Around 10% of the trap assemblies are completely unstable, no ions survive for 100 passes. Two thirds of the trap assemblies have stability <50%, while only 25% of the trap assemblies have resolution greater than half the ideal. The lowest stability assemblies were retuned using V3; we see an improvement in stability but at a severe cost to m/z resolution. Clearly this geometry is significantly less tolerant than the long 3 electrode trap.

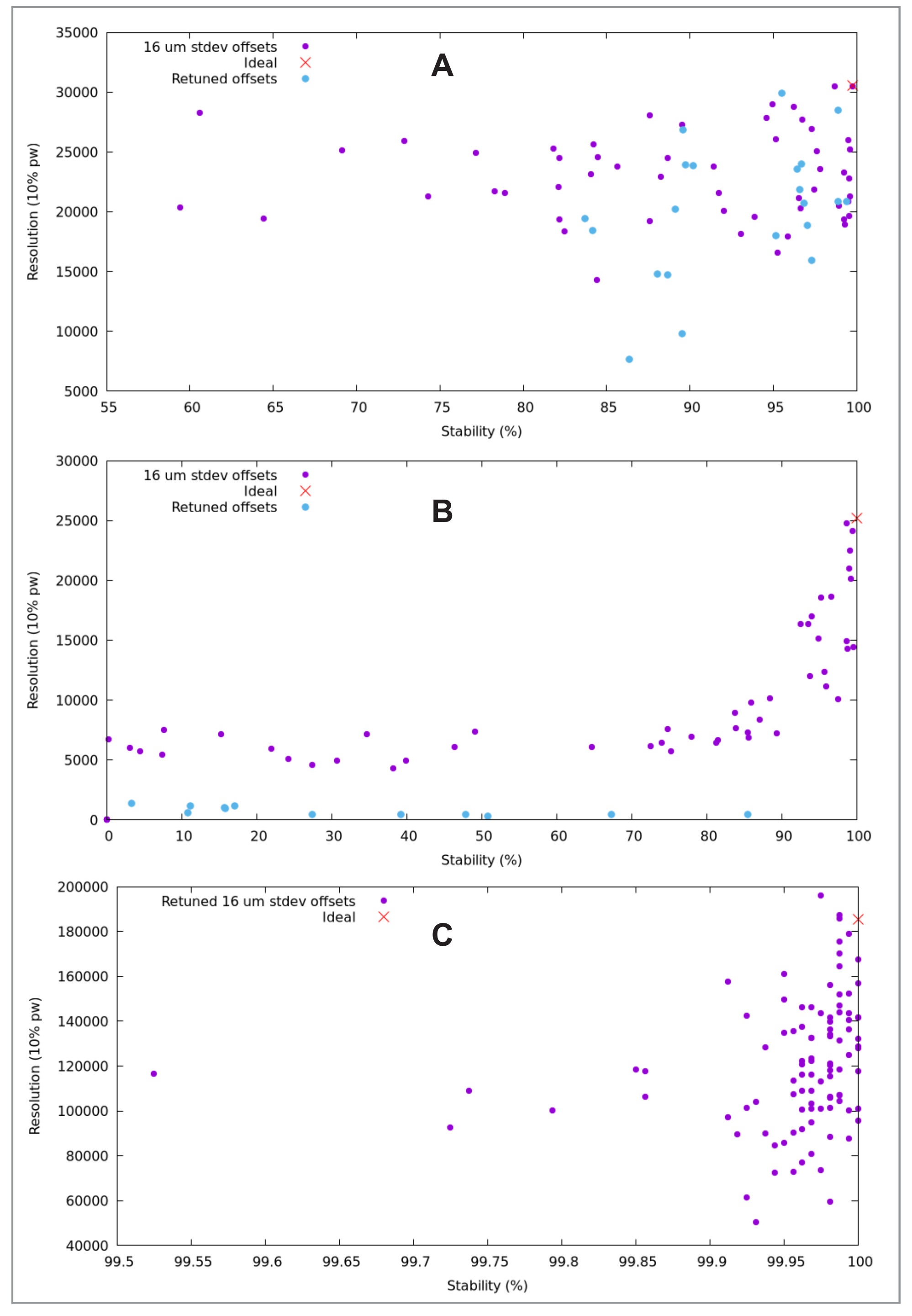

***Figure 3**. Stability vs m/z resolution for the Monte-Carlo offsets ensembles of trap assemblies. A) Long 3 electrode trap. B) Short 3 electrode trap. C) 4 electrode trap.*

Figure 3C plots stability vs resolution for the 4 electrode trap. Remarkably all trap assemblies are >99.5% stable. Since we see no significant loss of stability the plot shows results from a V4 retune for optimal resolution. While there is a clear effect on resolution, only 20% of the trap assemblies have resolution < 100,000, and only 3% have resolution < 70,000.

Tilt and offset of trap half assemblies

We also examine the case where the trap half assemblies are ideally constructed but one is either tilted or offset in the y-axis relative to the other.

Figures 4A and **4B** plot stability and resolution (relative to the ideal) for the case where one half trap assembly is tilted in the y-axis relative to the other. We see differences in behaviour, e.g. the short 3 electrode trap is the most stable vs tilt, while the long 3 electrode trap maintains the best relative resolution. We have to apply gross tilt angles to observe significant effects however, at realistic mechanical tolerances of up to 0.2° we see no loss of stability and at most 5-10% loss of resolution for all trap designs.

Figures 5A and **5B** plot stability and resolution (relative to the ideal) for the case where one half trap assembly is radially offset relative to the other. We see similar behaviour to the tilt case, the long 3 electrode trap being the least tolerant with respect to stability but the most tolerant with respect to relative resolution. Measurement of current trap assemblies indicates radial offsets of up to 0.2mm, which would have no effect on stability for any of the trap geometries, and up to a 10% loss of resolution for the 4 electrode trap.

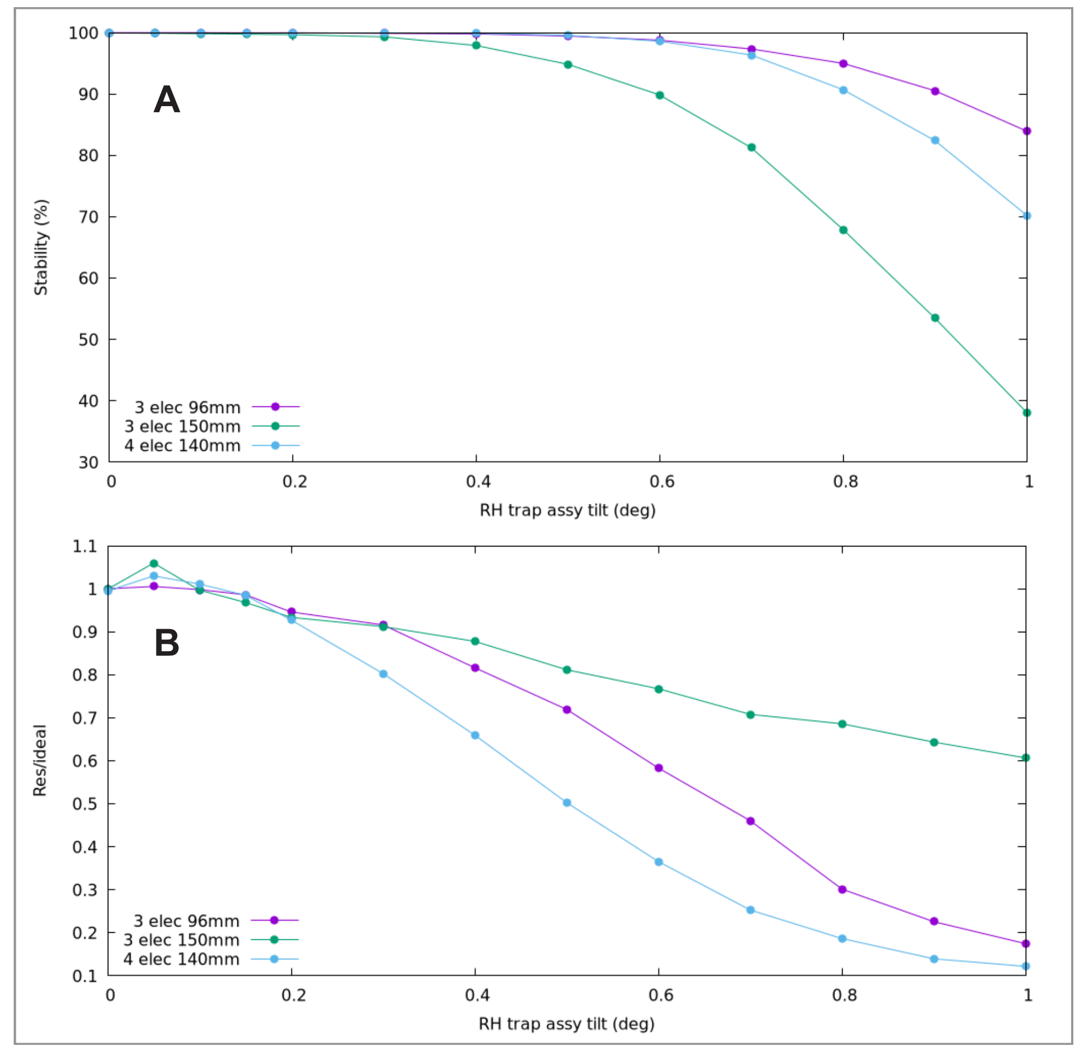

***Figure 4**. Data for a y-axis tilt of the right trap assembly with respect to the left trap assembly. A) Stability vs tilt. B) Relative resolution vs tilt).*

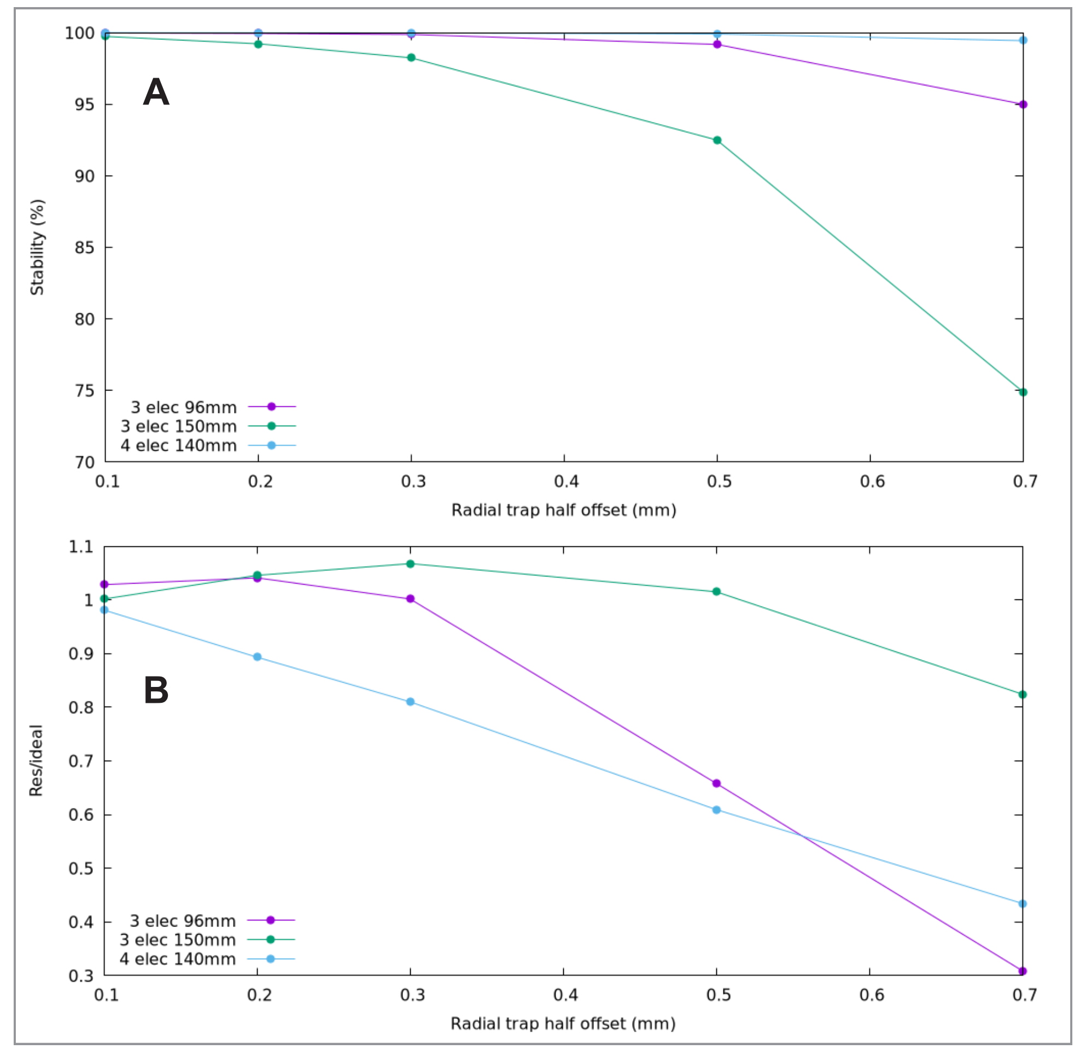

***Figure 5**. Data for a y-axis offset of the right trap assembly with respect to the left trap assembly. A) Stability vs offset. B) Relative resolution vs offset).*

CONCLUSION

- **Three high m/z resolution trap solutions studied: the ideal solutions all have at least 200x higher m/z resolution vs the current prototype.**
- **Monte-Carlo method used to examine build tolerance of trap half assemblies:**
- **Short 3 electrode trap: many trap assemblies exhibit severe stability and resolution loss.**
- **Long 3 electrode trap: stability and resolution loss, although less severe than seen for the short 3 electrode trap, and can be partially recovered by retuning V3.**
- **4 electrode trap: No loss of stability. Resolution loss is seen, partially recovered by retuning V4. Note that the ideal resolution is significantly higher vs the 3 electrode traps.**
- **Tilt / offset of one trap half vs the other: for realistic estimates of current trap construction tolerances none of the trap designs here would suffer significant effects.**
- **Results here suggest the 4 electrode trap geometry would be 100% stable and have m/z resolution > 100k when constructed with our current build tolerances.**

References

1. D. Reitenbach, D Botamanenko, L. Miller, M. Jarrold, *Anal. Chem.* 2024, 96, 14060−14067
2. D. Langridge, K. Richardson, J. Brown, K. Giles, MP 394, ASMS 2023
3. SIMION 2020, Scientific Instrument Services, Inc., www.simion.com

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