A High Efficiency Ion Source for GC/MS

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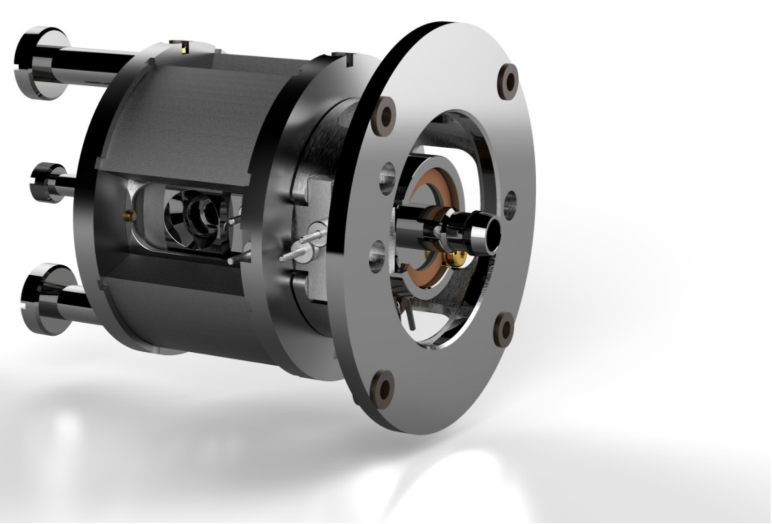
Introduction

GC/MS Electron Impact (EI) ion sources typically introduce an electron beam orthogonal to the "effective" design axis of the ion beam. Agilent's High Efficiency Source (HES) defines the electron beam *[and resulting ion beam]* to be coaxial to the entrance of the mass analyzer. Up to an order of magnitude increase in the number of ions ultimately transmitted through the mass analyzer is realized compared to conventional EI sources designs.

EI source designs typically require a well defined magnetic field to constrain the electron beam. Decades ago, with improvement in electronics, an electron target was no longer required to control and regulate emission current. This allowed for an improvement in design where the electron beam could be reflected back and forth between the active (emitting) and opposing electrostatic filament reflectors thus achieving multiple reflections. The electrons undergo a magnetically induced spiral trajectory where multiple reflections increase the electron flight path thus increasing the ionization probability of the incoming analyte. However, this electron beam was still orthogonal to the axis of the mass analyzer and as such inefficient in delivering ions generated in the source to the mass analyzer.



The challenge for the HES design was to utilize electron reflections while transmitting the maximum number of ions to the mass analyzer. This was accomplished by optimally designing an axial magnet configuration and incorporating an electron reflecting lens element in the design of the source.

Experimental

Prior Art and Unique Design Considerations

There have been several works cited in the literature showing ion source designs generating very intense ion beams using very large axially configured magnetically constrained electron beams starting with Theodore A. Finkelstein, Rev. Sci. Inst., 11 (1940) 94-97

While very intense ion beams have been described in these papers, many of these ion beams had very high energies with large ion energy distributions not suitable for ideal introduction into a quadrupole mass filter (functioning more as "ion guns").

This early work and subsequent work however suggested that with some ion optics design effort it should be possible to design a similar concept ion source based on an axially constrained electron beam which could produce a significant ion beam suitable for integration with existing quadrupole mass filtering technology.

SIMION modeling was employed to compare the electron and ion trajectories on both Agilent's orthogonal electron beam Standard and Extractor Sources to the axial electron beam High Efficiency Source. Both 2D and 3D models were employed. For modeling the HES, the trajectories of ions from various starting locations in the ion source volume were done to evaluate quad acceptance as a function of the location of ion creation and to illustrate why the source is much more efficient. Chromatograms of OFN would be acquired on a tandem quad mass spectrometer using both source designs at a variety of concentrations, down as low as 100 attograms /µL, to show the performance differences.

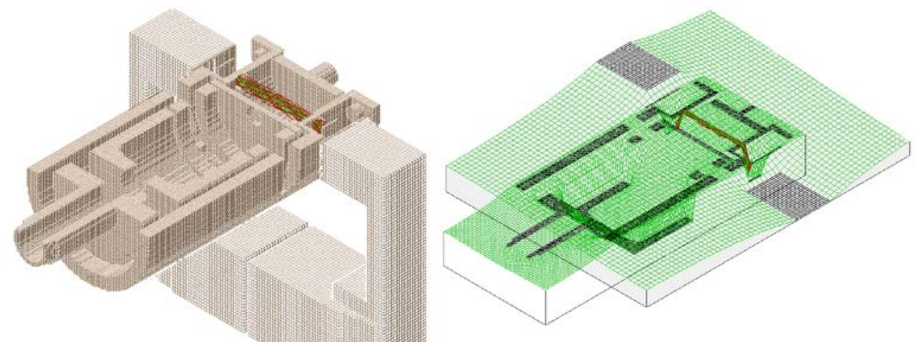
Upfront concerns to address in this design were determined to be as follows:

- Electron beam space charge issues
- Ion beam space charge issues
- Ion energy and ion energy distribution
- Utilizing a reflected electron beam for improved electron beam efficiency
- Potential dynamic range issues
- Increased helium metastable noise
- Source reactivity (inertness and source volume surface area)
- Undesirable ion trapping resulting in ion beam instabilities and possible non-linearity

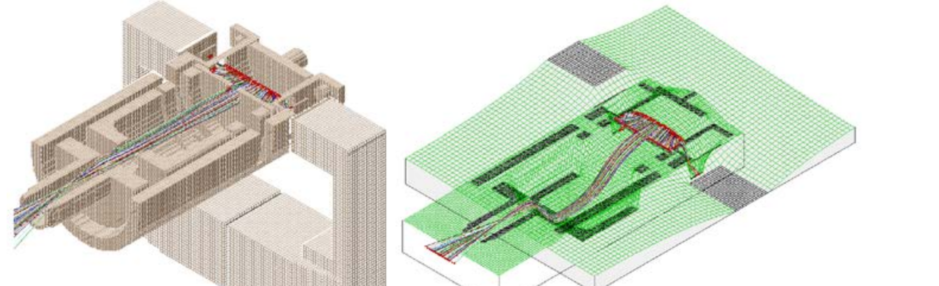
Results and Discussion

SIMION Source Modeling: Orthogonal Design

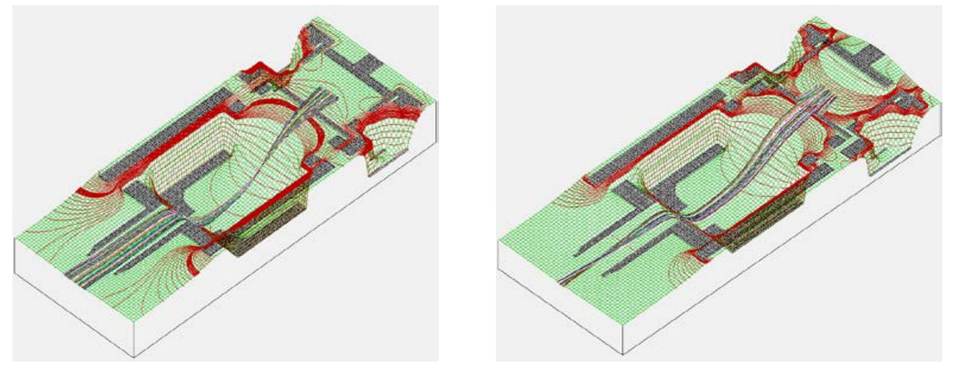
SIMION models are often created to aid in visualizing and optimizing ion optic designs. The SIMION model cross-section and the Potential Energy (PE) view (below) shows a quick snapshot of a reflecting orthogonal electron beam as constrained by a magnetic field.



The SIMION model Cross-Section and the (PE) view (below) of Agilent's Standard Source show the fate of the resulting ions generated from a reflecting orthogonal electron beam. The inefficiency in directing ions out of the source volume toward the mass filter (emittance) in this design should be apparent, where most of the ions generated end up colliding with the internal surfaces of the ion volume or exiting out to the filaments.

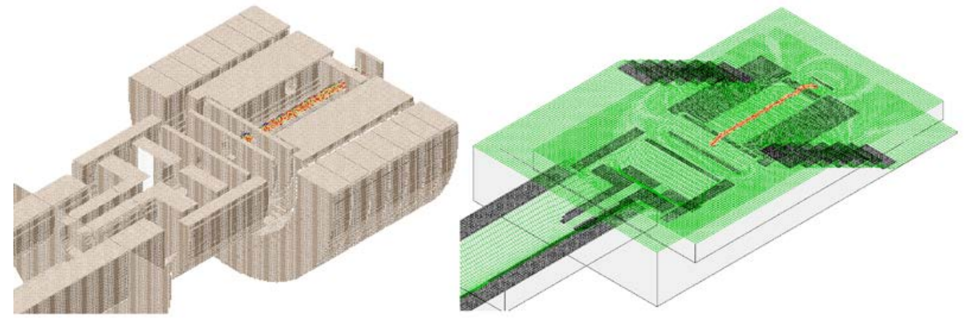


The PE views of the Extractor Source (below left) show an improvement in emittance as compared to the Standard Source (below right) "flying" the identical relevant starting ion population. While there is a measurable increase in emittance with the Extractor Source compared to the Standard Source, the overall losses to the walls of the ion volume and out to the filament are still quite measurable.

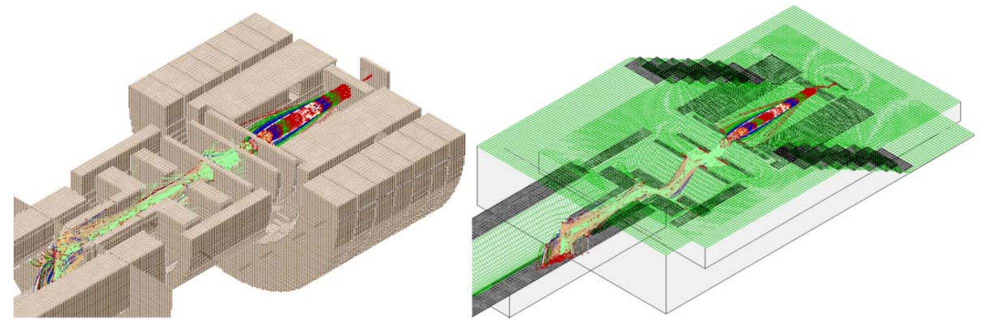


SIMION Source Modeling: Axial Design

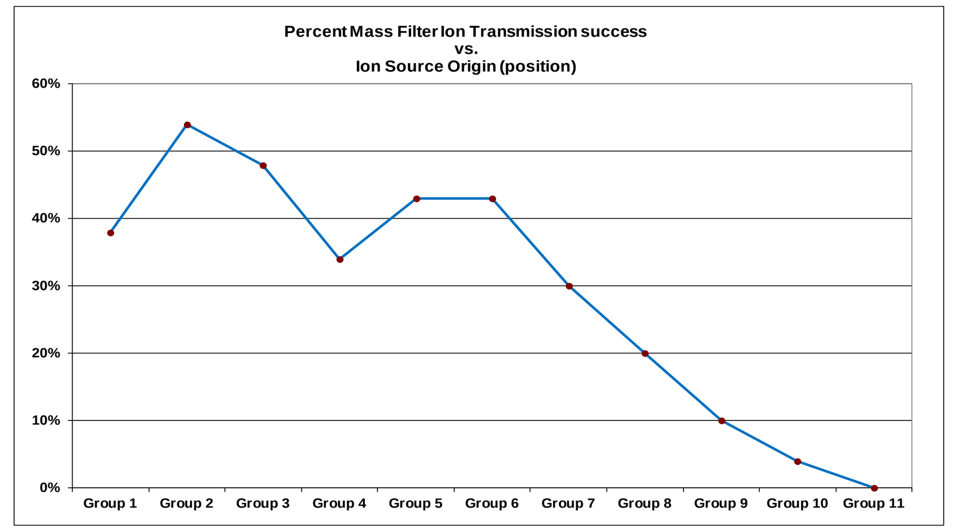
The SIMION model Cross-Section and the PE view (below) shows a quick snapshot of a reflecting axial electron beam constrained by the axial magnetic field.



The SIMION model Cross-Section and the PE view (below) shows the greatly improved fate of the resulting axial ion beam.



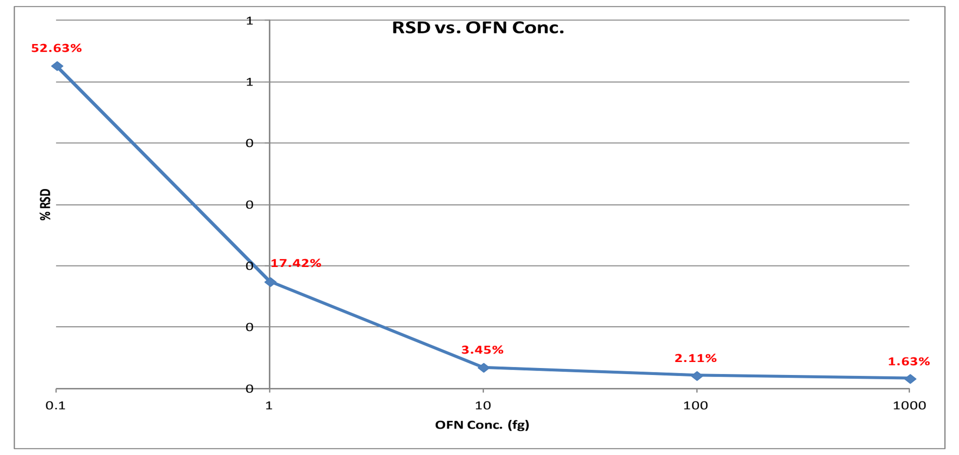
The higher the magnetic strength, the tighter the spiral trajectories of the electron beam. From the electron beam simulations, ions populations were modeled as originating from the same volume as defined by the electron beam. In this study, the SIMION ion beam was broken down into a series of 11 spherically generated ion groups having low energy (thermal) distributions along the axis in order to evaluate the success / failure of ion transmission all the way through a resolving quadrupole for each ion group position (origin). Group 1 is closest to the filament. The ions were created at random times so they would cover 1 rf cycle, in order to better represent the varying quadrupole phase space acceptance ellipses.

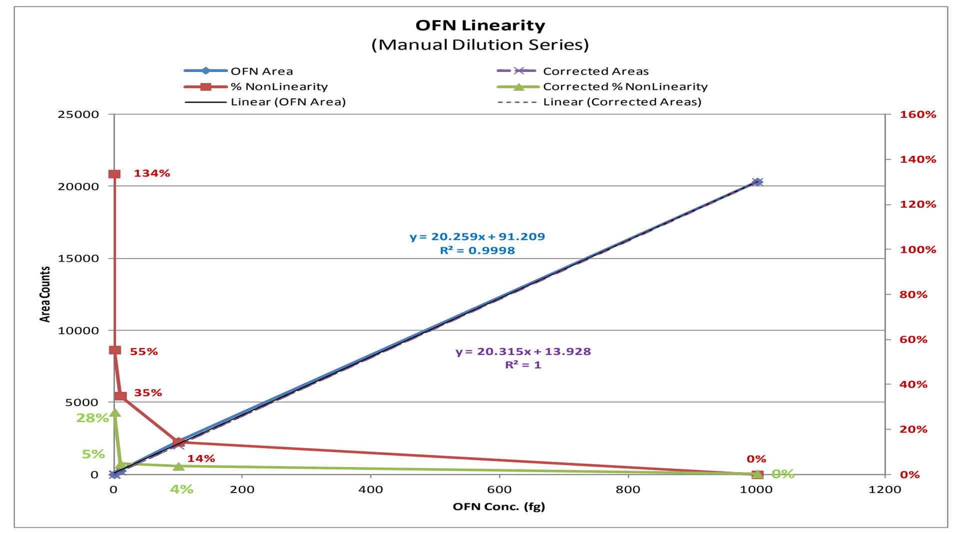


Results and Discussion

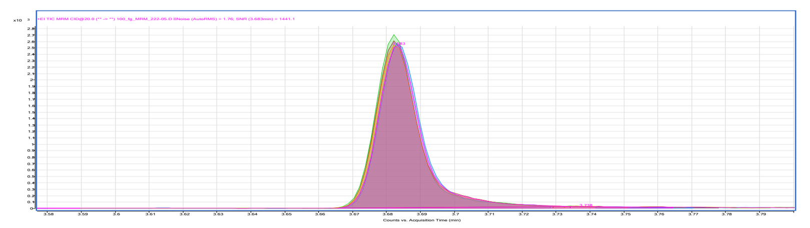
The ion modeling indicated that designing and testing a "technology demonstrator" prototype was worth pursuing. Many options were actually modeled in SIMION, which led to several ion optic embodiments to test. As usual, moving from SIMION models to a viable hardware design posed several constraints that did not exist in the SIMION models evaluated.

The following is a plot of % RSD as a function of concentration for the best physical embodiment. It should be noted that these data are based on 5 replicate injections for each concentration. Better RSD's have since been demonstrated. For these first assessments of the "technology demonstrator", issues with our automated sample preparation system forced us to prepare the dilution series (Octafluoronaphthalene (OFN) in isooctane) manually, which led to an approximately 14% systematic dilution error (acceptable for evaluation at this stage).

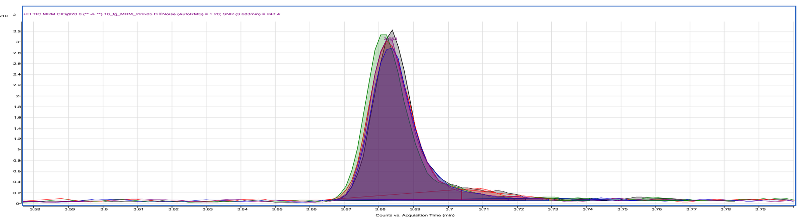




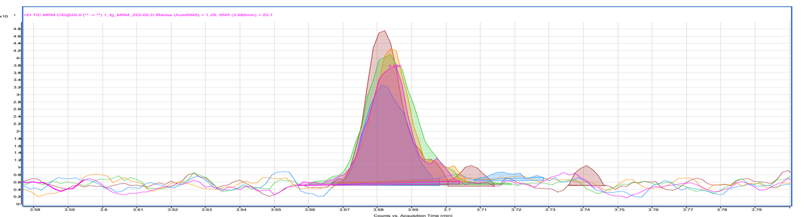
Chromatograms:



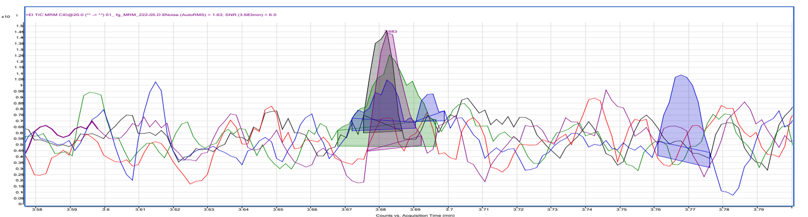
Chromatograms of 5 consecutive injections of a 100 fg OFN sample (MS/MS; 272:222 transition).



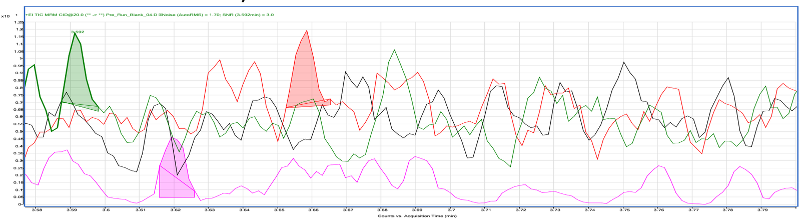
Chromatograms of 5 consecutive injections of a 10 fg OFN sample (272:222 transition).



Chromatograms of 5 consecutive injections of a 1 fg OFN sample (272:222 transition).



Chromatograms of 5 consecutive injections of a 0.1 fg OFN sample (272:222 transition).



Isooctane blanks run prior to the 0.1 fg OFN sample show that the result immediately above is not an artifact of carryover or contamination due to the prior, higher concentration samples (272:222 transition).

Conclusions

- The work described in this poster shows how ion modeling assisted in the design of a new ion source technology
- Preliminary results demonstrated a potential of 10 to 20X increase in ion current, in this case for OFN MRM (272:222) as measured at the detector
- From this "technology demonstrator", further optimization yielded a new source design, currently available in the Agilent 5977B MSD and 7010 Triple Quadrupole Mass Spectrometer, that achieves a significant increase in ion current over the existing orthogonal EI source designs. This is best demonstrated by a measurable improvement in %RSD's / IDL's, especially at low concentrations

Acknowledgements

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