High Capacity Electrostatic Ion Trap Mass Spectrometer and its Signal Processing

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Overview

Apart from the Kingdon trap/Orbitrap, the electrostatic ion trap (EIT) can be built with various form. The traditional electrostatic beam ion trap (EIBT) possesses a limited dynamic range due to the low space charge tolerance as well as low efficiency detection of image charge signal.

A planar type of EIT is designed where a rotational symmetrical trapping field is created between two layers of concentric round and ring electrodes. The ions are trapped and oscillating around the centre plane between the electrodes. The oscillatory motion of ion is simulated and the field distribution was optimized to achieve isochronous motion against energy spread in R, z and φ directions. The recorded image charge signal can base-line resolve ions of 609 and 609.12 Da within 12 ms transient.

Traditional Fourier transform to the image charge signal from EIT generates many harmonic components therefore it is not suitable. Using wavelet transform the mixed peaks of different mass and different harmonics can be separated.. The WT coefficient for each scale represents a range of mass to charge ratio, and its distribution is subjected to further Fourier transform. The resulted frequency spectrum are less crowded and may be de-convoluted to mass spectrum.

Unwanted harmonic peaks can also be eliminated by linear combination of image charge signals from multiple pick-up electrodes. Test with simulated image charge data gives satisfactory result.

References

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2.Golikov, Soloyev, Sudakov, Kumashiro: WO2009001909A21

3.A Verentchikov, a Path from Multi-reflecting ToF to Electrostatic Trap, 10th European FTMS workshop, 2012

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5.Q Sun, C Gu, L Ding, J. Mass Spectrom (2011), 46, 417-424

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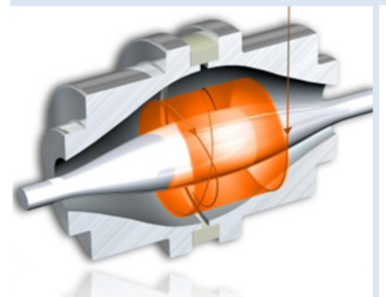
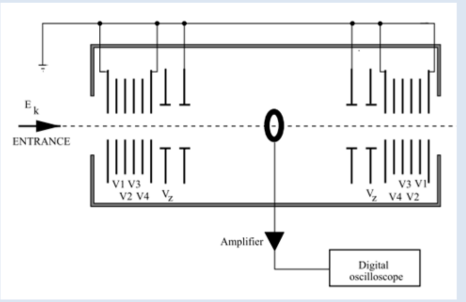
7.L Ding, R Badheka, An Electrostatic Ion Trap with Planar Rotational Field Structure, 10th European FTMS workshop, 2012

Available EITs



Kingdon/Orbitrap



EIBT /Linear EIT[1]

The problems of the LEIT

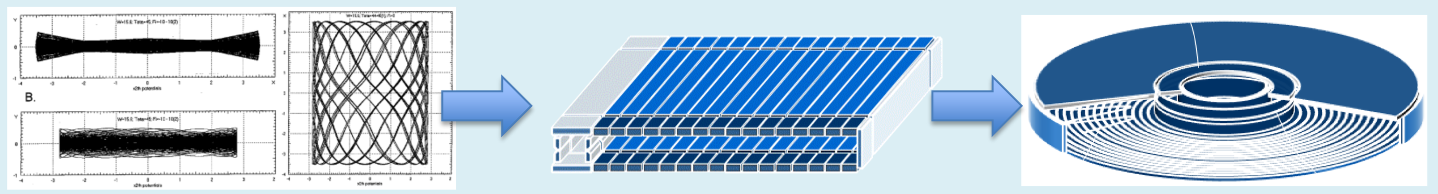
- Linear flight path, space charge → coalescence →low dynamic range
- Multiple harmonic components in image charge signal → overlapping → Badly convoluted spectrum

Limit mass range? example: if using H5, mass range < 0.5M

On increasing charge capacity of EITs

There have been increasing attempts to make use of larger space for ion trapping and measurement of the image charge signals[2,3,7]

Isochronous-Traps



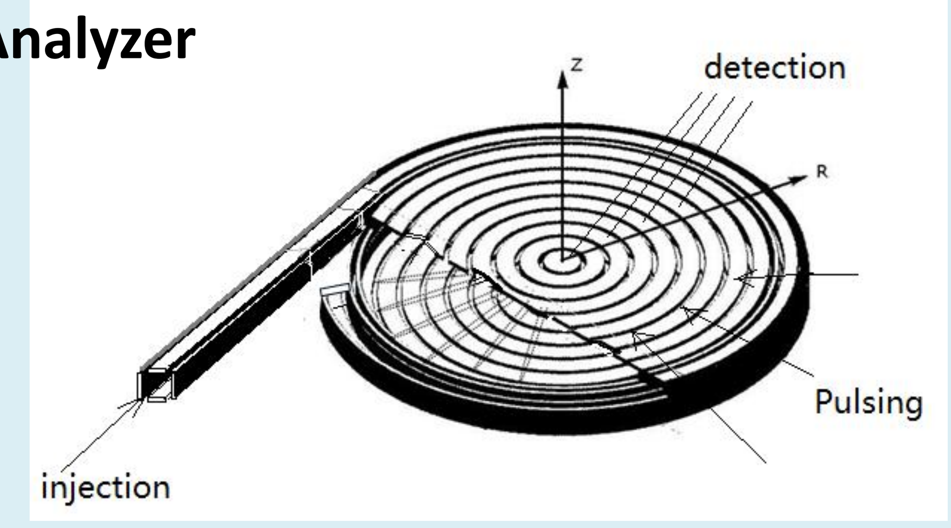
Planar EIT Mass Analyzer

Dimension:

diameter 180mm excl. injection ion guide, 200 mm inc.

Thickness 20 mm

9 -10 ring electrodes (may be reduced)



- Ions are trapped arround the center plane , radially orbital fly between 2 planar ring arrays →very large trapping capacity
- Using long perimeter ion guide (or toroidal IT) for injecting ion → high efficiency
- All ions pass the center region, small pick up electrode generate high signal → high S/N
- Multiple ring pick-ups detecting radial motion component, may be used, getting signal of 4f of ion oscillation → higher mass resolution or faster measurement
- Rotational symmetrical structure → easy to make

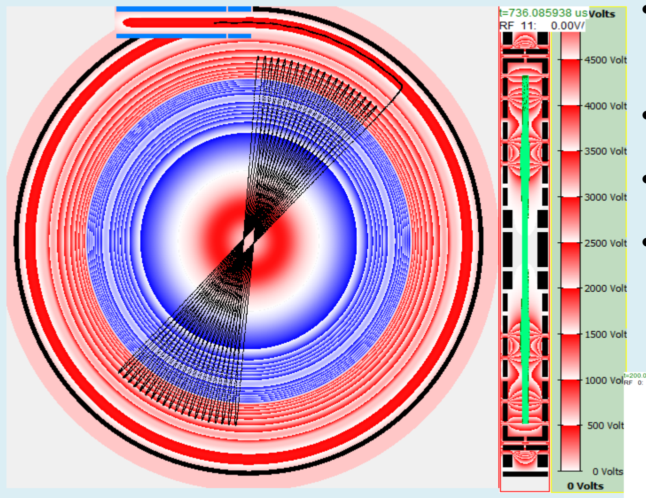
Field Structure

$$\Phi(\rho,\vartheta)=\sum_{n=0}^{\infty}\frac{A_n}{r_0^n}\rho^n P_n(\cos\theta)$$ Where P_n are the Lagrange polynomials

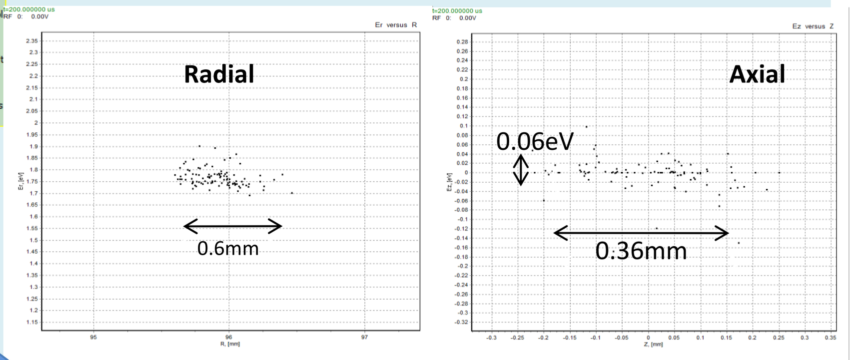
$$\rho=\sqrt{z^2+r^2},\quad \cos\theta=\frac{z}{\sqrt{z^2+r^2}}$$

Design and Simulation

SIMION + AXSIM used



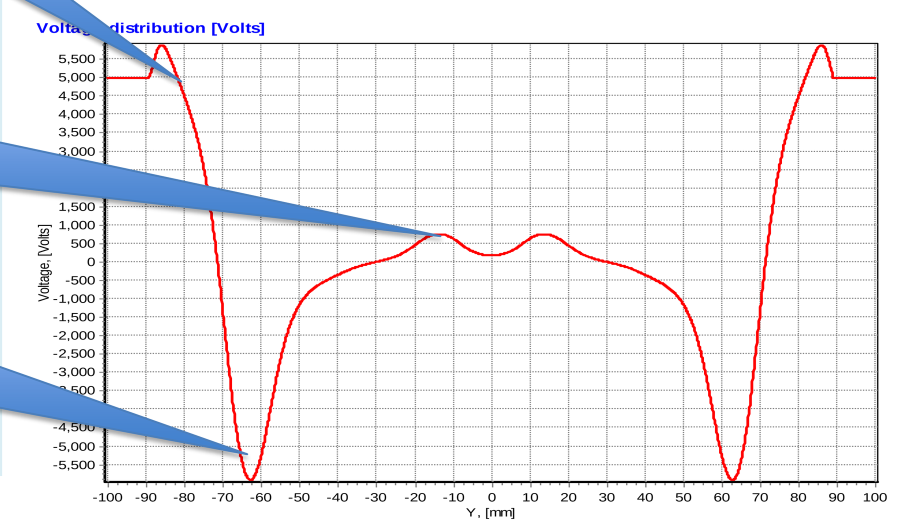
- Ions are injected from perimeter ion guide with initial spatial and energy spread
- Lateral Focusing (z)
- Precession motion (φ)
- Isochronous motion against the energy spreads in radial (R), axial (z) as well as tangential (φ) directions



Reflecting field
Slope here is adjusted to satisfy energy focusing in radial direction

Centre field region
Control the precession speed and satisfy energy focusing in tangential direction

Lateral/axial z focusing field
Focusing ions to the central plane and is optimized to satisfy energy focusing in axial z direction



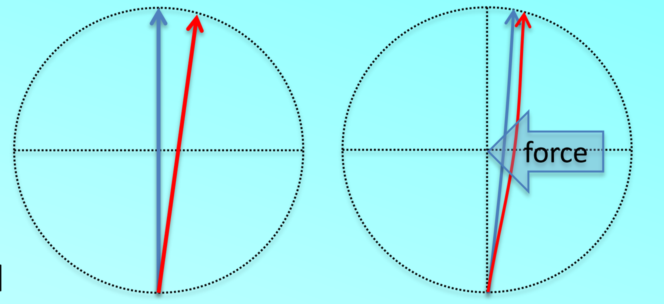
Why central field ?

Initial tangential velocity causing spread Δt(φ)

The field around the centre bend the ion trajectory so to correct the time difference

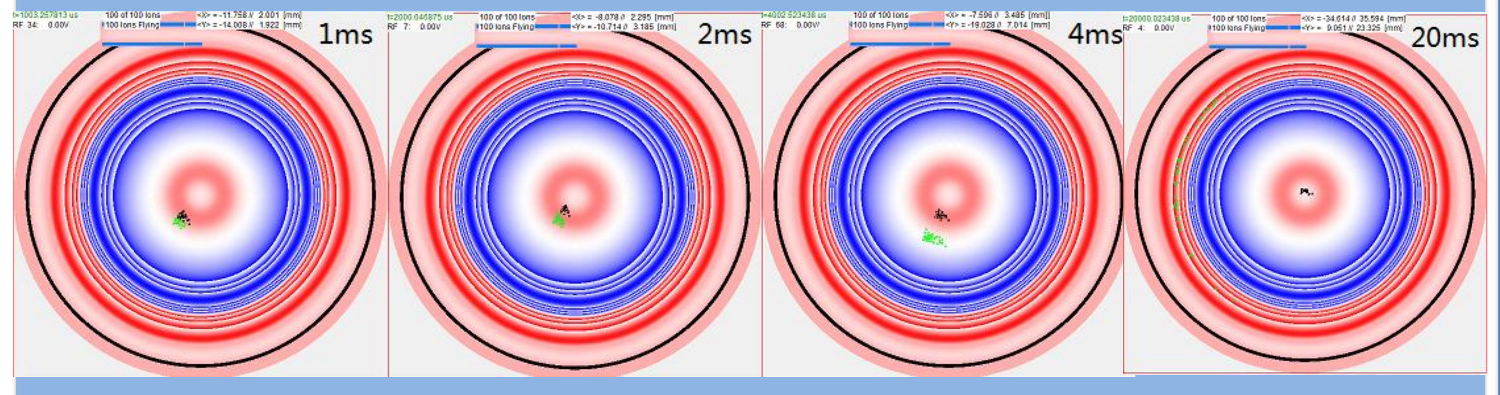
No central field

t2 < t1 with central field and offset in V_φ, t2= t1



Fly Test and Resolving Power

M=609, 609.12, 50 ions for each mass



Ions are pre-cooled in the linear ion guide, taking 100μs to fuse into the perimeter ion guide driven by digital square wave of 1MHz and +/-500V (z plates only), before injected into the PEIT with -300V pulse

Image Charge Signal

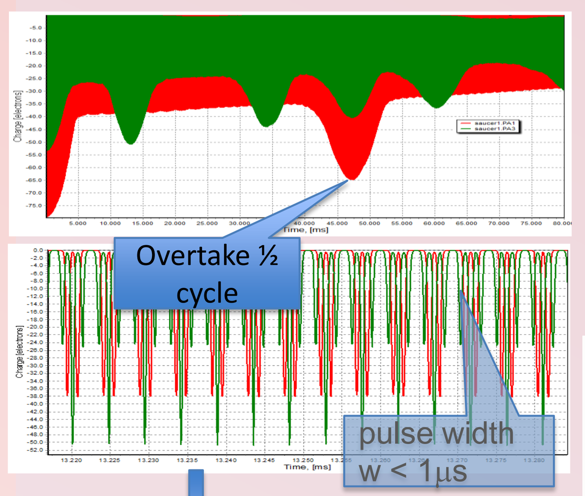
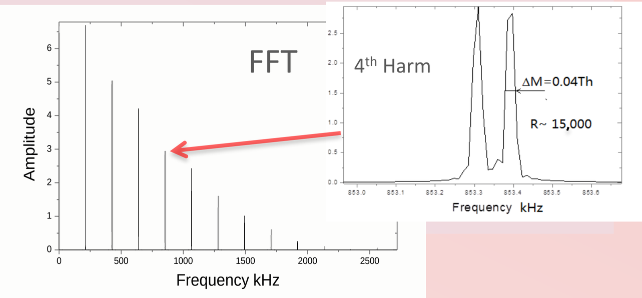


Image charge or current signal reflects the radially orbital motion and can be recorded with AXSIM

In 80 ms transient (red from centre pick-up and green from the 3rd ring pick-up electrode), the ion group of 609 Da has overtaken 609.12Da nearly one whole cycle! At 12ms, image charge signal of 609 and 609.12 are baseline separated.



WT + FFT Algorithm

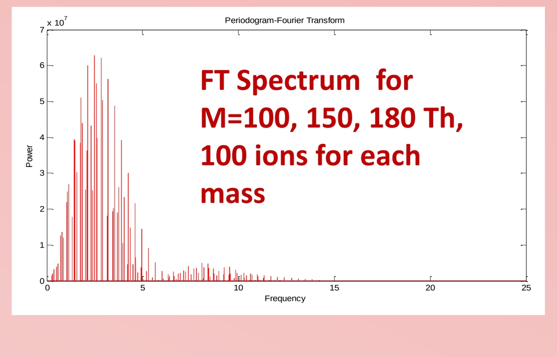
Using wavelet transform, the peaks at the scale coefficient are identified which give a coarse mass position of the mass peak without overlap with different high tunes. A further Fourier transform for particular scale coefficient gives precise mass peak for every small mass range associated with the scale coefficient.

Results

The FFT for each scale coefficient looks much simpler than FFT of original data. However there are still frequency components from other masses embedded in the spectrum. Algorithm for subsequent spectrum de-convolution is under the development.

Converting Image Charge Signal to MS

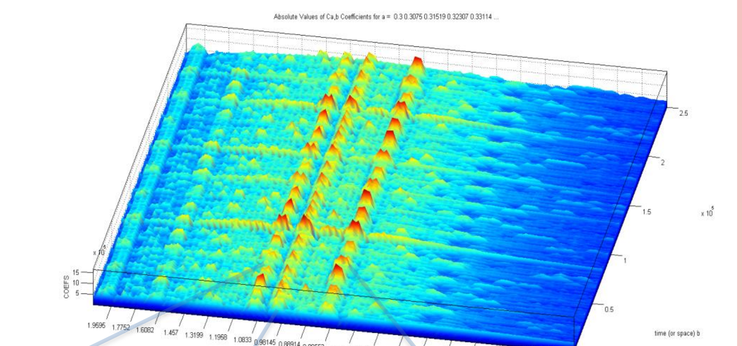
- The frequency spectrum by FFT includes too many high harmonics and they are mixed together when multiple masses exist.
- The problem exist also for FTICR[4]
- Orthogonal projection method[5] and Comb-sampling methods[6] for signal conversion have been developed in recent years

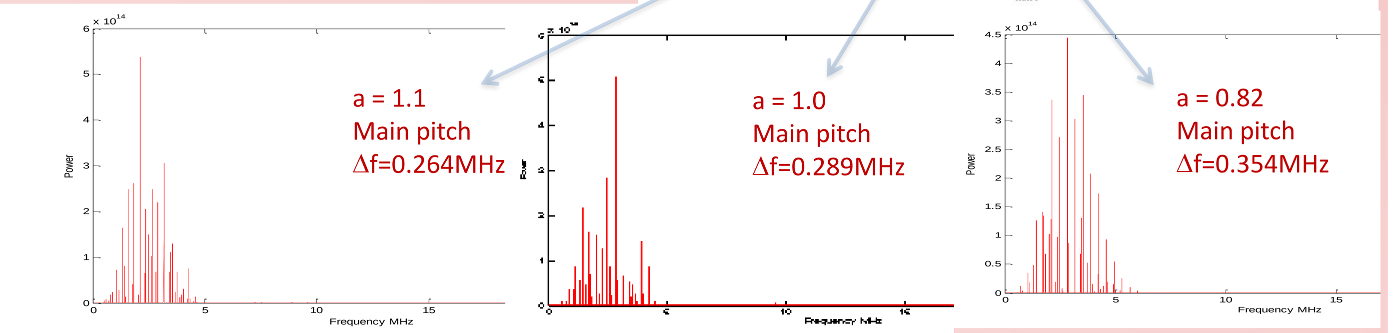


Wavelet Transform

$$C(\text{Scale, position})=\int_{-\infty}^{\infty}f(t)\psi_{a,b}(t)dt$$

$$\text{where}\quad \psi_{a,b}(t)=\frac{1}{\sqrt{a}}\psi\left(\frac{t-b}{a}\right)$$





The Elimination using Multiple Image Charge Pick-ups

The distribution of Harmonic components are different for different pick up electrodes. Therefore it is possible to make a linear combination of signal from different pick up electrodes with a set of pre determined coefficients, to eliminate a number of unwanted harmonic peaks.

Using 5 Pick-ups and eliminating 2nd to 5th harmonic and keep the fundamental frequency

$$\mathbf{C}=\begin{pmatrix}C_{11}(m/z) & C_{21}(m/z) & C_{31}(m/z) & C_{41}(m/z) & C_{51}(m/z)\\ C_{12}(m/z) & C_{22}(m/z) & C_{32}(m/z) & C_{42}(m/z) & C_{52}(m/z)\\ C_{13}(m/z) & C_{23}(m/z) & C_{33}(m/z) & C_{43}(m/z) & C_{53}(m/z)\\ C_{14}(m/z) & C_{24}(m/z) & C_{34}(m/z) & C_{44}(m/z) & C_{54}(m/z)\\ C_{15}(m/z) & C_{25}(m/z) & C_{35}(m/z) & C_{45}(m/z) & C_{55}(m/z)\end{pmatrix}\quad \mathbf{X}=\begin{bmatrix}x_1\\x_2\\x_3\\x_4\\x_5\end{bmatrix}\quad \mathbf{CX}=\mathbf{L}=\begin{bmatrix}1\\0\\0\\0\\0\end{bmatrix}$$

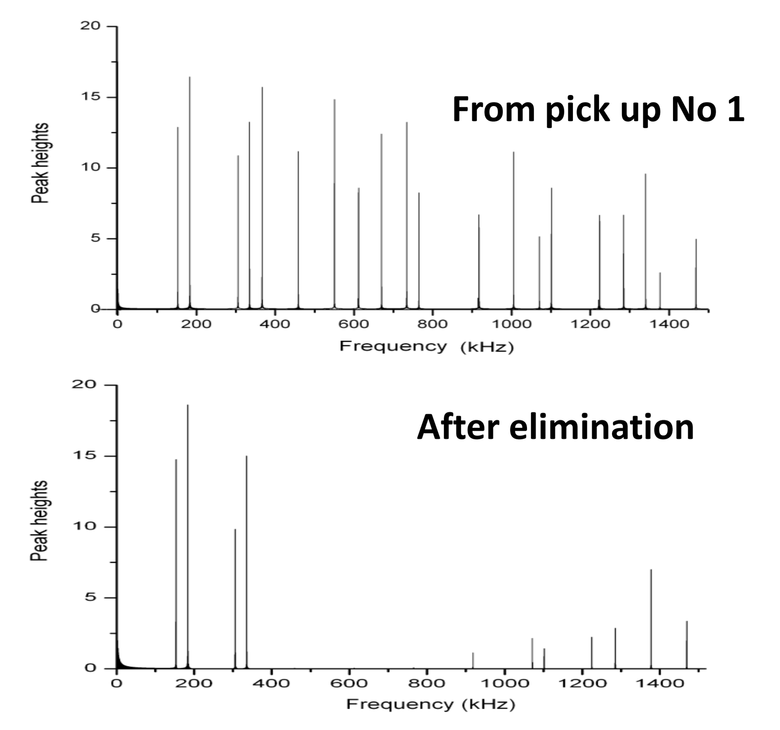
3rd Harmonic component in the signal from 4th pick up electrode

Test with 6 masses

mass (Th)	ion number	frequency (kHz)
720	15	153.07
500.5	12	183.49
500	20	183.66
181	1	305.53
180	10	306.14
150	15	335.31

Determine Coefficients

$$\mathbf{X}=[x_1,x_2,x_3,x_4,x_5]^T=\begin{bmatrix}-1.6263+4.1715i\\-3.1495+8.0828i\\-3.8622+9.9077i\\-2.9562+7.5850i\\-1.7743+4.5537i\end{bmatrix}$$



Conclusions

•Planar Electrostatic Ion Trap can be designed with a rotational symmetrical structure

•Compared with other electrostatic trap, PEIT employing radial orbital trapping and image charge detection allows higher ion capacity and signal intensity , thus the dynamic range can be improved without sacrifice the mass accuracy

•Field optimization using ion optical simulation achieves energy focusing in radial, lateral and tangential directions and mass resolution (FWHM) over 15,000 is obtained in simulation.

•The Wavelet transform + FFT gives chance to utilize a single channel transient in mass analysis but still has difficulty to deal with complex mixture of ion.

•The multiple image charge signals can be linearly combined to eliminate the unwanted harmonics, and the algorithm has been tested with simulated data.

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