A New Electrically Compensated Cylindrical ICR Trap: Procedure for Tuning and Improvements in Mass Resolving Power and Sensitivity

Overview

Purposes
- Evaluate the resolving power and sensitivity achievable with a new compensated trap for FTMS as a function of m/z and develop a protocol for tuning this trap.

Methods
- Employed empirically the cyclotron frequency surface at various cyclotron radii and m/z distributions.
- Compare the resolving power and sensitivity at various m/z with achievable with a compensated trap compared to those achievable with the conventional (uncompensated) trap.

Results
- Compensated trap achieves nearly three fold increase in apparent resolving power and ~15 fold increase in sensitivity.

Introduction

- FTMS offers high sensitivity, high resolving power, and high accuracy in mass measurement (mass accuracies of ±3 ppm [1] and sub ppm with careful recalibration [2][3][4] are achievable. Ultimate performance of the instrument, however, is compromised by imperfections in the electronics, potential well, created by the trapping electrodes, that confines ions.
- To improve performance, we are developing a mass compensator for correcting or compensating the electric trapping fields in the analyzer. Electric compensation of a Penning trap is not new as indicated by the following precedents:
  - Tanimoto, who designed and built Penning traps to study the relationship between cyclotron frequency and m/z [5]
  - Günter Gabrielse, who compensated a cylindrical Penning trap [6], and analyzed the cylindrical and hyperbolic inner ring in 4 quadrants, 4 connections.
- The extent of improvement is masked, in part, by phase locking of ion cloud in uncompensated trap, yielding a higher apparent resolving power than expected from the frequency surface.
- In this work, we compare the mass resolving power and sensitivity of the compensated trap with the theoretical predictions.

Compensation

- As the electric trapping fields in the analyzer electrically trap the ions, an increase in frequency of the ions confined to the trap is neither possible nor desirable. To compensate for this increase, an additional electric field of opposite sign and equal magnitude to the trapping field is needed.

Evaluation of Performance

- Evaluate the performance of the compensated trap at different nominal trapping voltages.
- Apply cell compensation to improve accurate mass measurement.

Tuning

- Narrowband detection parameters of a 1024 K or 2048 K point transient with an ADC rate of 10 kHz.
- Tuning a high-performance trap is surprisingly difficult, especially when performance is close to optimal.

Materials

- 99% Varyshap, insulin oxidized B-chain, TRF2, and cytochrome C were mixed with 2,5-diphenyloxazole and at ratios of 1:1-10000 (1:10000) prior to spiking.

Data Treatment

- Raw data were imported into a Fortran program for calculation of the complex FFT, the subsequent calculation of the frequency centroid and resolving power was performed in a Matlab (MathSoft, Cambridge, MA) worksheet.

Instrumentation

- FTMS utilizing the Pseudo-V MALDI FTMS [Lake Forest, CA], equipped with an external hexapole for compensation of off-mass ions produced by multiple laser pulses, and operated according to experimental sequence displayed in Figs. 1A, B, and C.

Theoretical Calculation

- Resolving power and sensitivity achievable with a new compensated trap for FTMS as a function of m/z and develop a protocol for tuning this trap.

References

[1] Zhang, Li-Kang; Rempel, Don; Pramanik, Birendra N.; Gross, Michael L. Accurate mass measurements by Fourier transform mass spectrometry, Mass Spectrometry Reviews, 2006, 24(2), 286-309