

Performance enhancement for a hybrid 1 T permanent magnet ESI-FTICR mass spectrometer using multiple frequency detection

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Introduction

Recently, we have developed first permanent magnet FTICR mass spectrometer with atmospheric pressure ionization sources including electrospray (ESI) and AP-MALDI. While this spectrometer has demonstrated rather high characteristics such as mass resolving power of 30,000 and mass measurement accuracy of 1 to 10 ppm for peptide ions in a mass range of m/z 200 to 1200 its performance is limited by the low magnetic field and relatively small size of an ICR cell utilized. To overcome these limitations, we modified detection scheme for this spectrometer making possible detection of ICR signals at the frequencies multiple to the cyclotron frequency of ion motion.

Methods

1 Tesla permanent magnet FTICR mass spectrometer with electrospray ionization source was used. The spectrometer has a hybrid design and includes radiofrequency linear ion trap (LIT) operated at the pressure of 10⁻⁴ Torr, five stage differential pumping vacuum system allowing to obtain ultra-high vacuum of 10⁻⁹ Torr in analyzer region, and 1-inch cylindrical FTICR cell. A compact permanent magnet assembly based on reversible magnetic field (RMF) approach generates homogeneous field of 0.97 Tesla in the central region and has a bore of 42 mm. Detection of FTICR signal was performed using data station that is based on the acquisition boards from National Instruments, Inc. (USA).

Experimental setup

Side-plates of the 1-inch FTICR trap are switched into double frequency detection mode using relay-based switch connected to the excitation plates (1 and 3).

Switch is made of reed relays (ECE, Taiwan):

- Low capacitance (< 10 pF)
- Low resistance of 150 mOhms
- High operation speed of 1 ms per switching

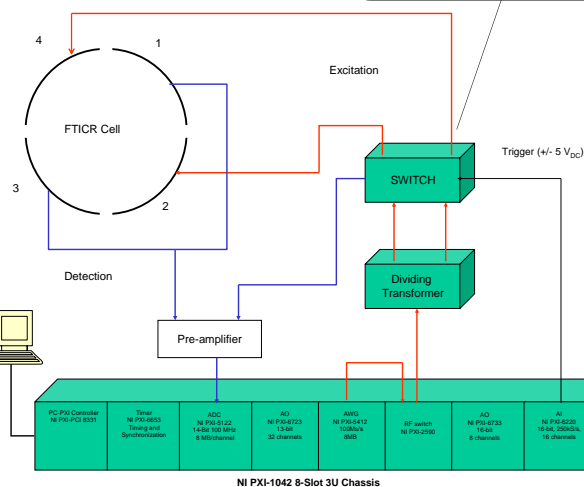
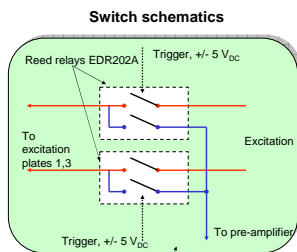


Figure 1.

Results and Discussion

Bradykinin, 2+

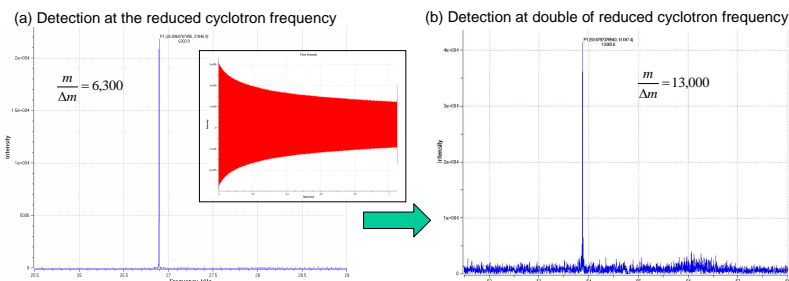
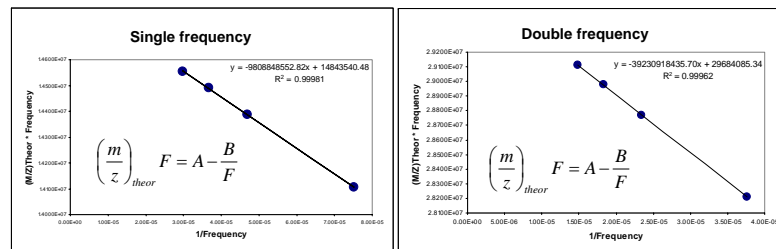


Figure 2.

Calibration equation (for coalesced peaks the instrument was calibrated using average mass values)

$$\frac{m}{z} = \frac{A}{F} - \frac{B}{F^2}$$

Calibration



A = 14843540.48; B = 9808848552.82;

A = 29684085.34; B = 39230918435.70

Peptide	(m/z) _{theor}	F _{measured} , Hz	(m/z) _{experimental}	Δ(m/z), Da
Brad ¹⁺	1061.23	13291.83	1061.22	-0.02
(Ang I) ²⁺	433.17	33396.03	433.11	-0.07
SubP ²⁺	674.83	21318.95	674.67	-0.16
brad ²⁺	531.12	27286.00	530.82	-0.30

Summary of results on mass measurement accuracy and resolving power

Parameter	Value for double frequency	Value for single frequency	Ratio of values for double and single frequencies
A	29684085.34	14843540.48	2.00
average resolving power*	8600.00	5800.00	1.48
average mass accuracy, Da	0.21	0.13	1.61

* Resolving power was measured for the fixed time period of 0.5 s and triangle apodization applied to the time-domains

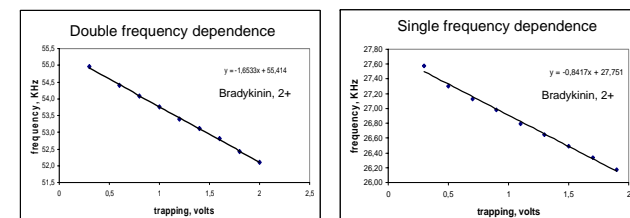
Magnetron shift in measured frequency

$$F = \omega_c - \omega_m = \omega_c - \frac{2\alpha V_{tr}}{Bd^2} \text{ reduced cyclotron frequency}$$

α FTICR cell geometry factor

d FTICR cell diameter

$$\omega_m = 720 \text{ Hz/V} \text{ theoretical magnetron frequency for FTICR cell used in this work}$$



Magnetron shift (double frequency): 1653 Hz/Volt Magnetron shift (single frequency): 841 Hz/Volt

$$\frac{\omega_m(2xF)}{\omega_m(F)} = 1.97$$

Space charge effect in magnetron frequency deviation from the theoretical value

$$\omega_m = (\omega_m)_0 + \frac{N_i q}{4\pi\epsilon_0 B R_m^3} \text{ change in magnetron frequency shift due to space charge effect by R.C. Dunbar et al. [3]}$$

$$N_i = \frac{\omega_m - (\omega_m)_0}{q} 4\pi\epsilon_0 R_m^3 \approx 10^4 \text{ estimated number of Bradykinin 2+ ions in FTICR cell (FTICR spectrum is shown in Figure 2(a)). } R_m \sim 2 \text{ mm}$$

Conclusions

- Detection of the FTICR signals at multiple of reduced cyclotron frequency using multi-electrode detection is equivalent to the corresponding increase in effective magnetic field and results in the increase in FTICR instrument's resolving power [4,5]
- Due to the space charge effects and the corresponding increase in the contribution of inhomogeneous factors into the line broadening (mainly, frequency drift during detection) for the signals at multiple frequency, the mass measurement accuracy may respectively deteriorate.
- Multiple-frequency detection technique may be useful in high-throughput applications of FTICR mass spectrometry, including high magnetic field instruments because it allows corresponding reduction in time-domain acquisition period without a loss of resolving power.

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