

# Improved performance of linear ion trap mass spectrometer with added octopole and dodecapole fields

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## Overview

- The linear ion trap mass spectrometer with added octopole and dodecapole fields was evaluated.
- The simulation program was developed by LabVIEW.
- The electrode geometry was optimized. The experimental instrument was constructed and it was confirmed that the mass isolation performance was improved.

## Introduction

The geometry of commercial ion trap mass spectrometer has been intentionally distorted. The distortion generates additional higher order multipole components. The non-linear resonance caused by the multipole components results in rapid ejection of ions and mass resolution and mass accuracy was improved<sup>(1)</sup>. The non-linearity of the ion trap also increases the trap efficiency and improve sensitivity and dynamic range. But excess amount of multipole components degrade the mass isolation

performance. For example, with the sole presence of positive octopole field in addition to quadrupole field, the resonance curve has sharp edge on high frequency side but has gentle slope on low frequency side and that degrades the mass isolation resolution. We have reported that the mass isolation performance was improved by optimizing 3D ion trap geometry<sup>(2)</sup>. Here we report that the same improvement can be achieved for linear ion trap mass spectrometer.

## Methods

To evaluate the characteristics of ion trap, it is crucial to accurately calculate the electric field. This can be done by surface charge method (SCM). But SCM is time consuming because it requires to integrate all the surface charge density on discretized electrode elements. In this work,

multipole coefficients were primary calculated from surface charge<sup>(3)</sup> and secondary, electric field was calculated from multipole coefficients. This method enabled fast calculation of the electric field with high accuracy.

The electric potential of linear ion trap shown in Fig.1 can be expressed as

$$\Phi(\rho, \theta) = V \sum_{n=0}^{\infty} \left(\frac{\rho}{x_0}\right)^n A_n \cos(n\theta), \quad (1)$$

## Improved performance of linear ion trap mass spectrometer with added octopole and dodecapole fields

where  $V$  is RF trapping voltage.  $A_n$  is  $n$ -th order multipole coefficients.  $x_0$  is the normalizing constant which is half distance between X-electrodes. Equation (1) is differentiated to acquire the electric field  $E_x$  and  $E_y$ ;

$$-E_x = \frac{\partial \phi}{\partial x} = V \sum_0^{\infty} A_n \left(\frac{1}{x_0}\right)^n \left\{ n \rho^{n-2} x \cos(n\theta) + \frac{\partial}{\partial x} \cos(n\theta) \right\} \quad (2)$$

$$-E_y = \frac{\partial \phi}{\partial y} = V \sum_0^{\infty} A_n \left(\frac{1}{x_0}\right)^n \left\{ n \rho^{n-2} y \cos(n\theta) + \frac{\partial}{\partial y} \cos(n\theta) \right\} \quad (3)$$

To enhance the accuracy, multipole coefficients up to 100<sup>th</sup> order ( $A_{100}$ ) were calculated by following recursive definition of cosine function.

$$\cos((n+2)\theta) = 2 \cos \theta \cos((n+1)\theta) - \cos(n\theta) \quad (4)$$

A 2D ion trajectory calculation program using SCM was developed by LabVIEW. The electric field components of quadrupole ( $A_2$ ), octopole ( $A_4$ ), dodecapole ( $A_6$ ) and higher multipole up to 100<sup>th</sup> order was directly calculated from electrode surface charge<sup>(3)</sup>. The ion trajectory was

calculated by 4<sup>th</sup> order Runge - Kutta method using electric field derived from multipole component for the purpose of fast computation. The resonance curve was obtained by scanning the frequency of dipole voltage which is applied between X-electrodes.

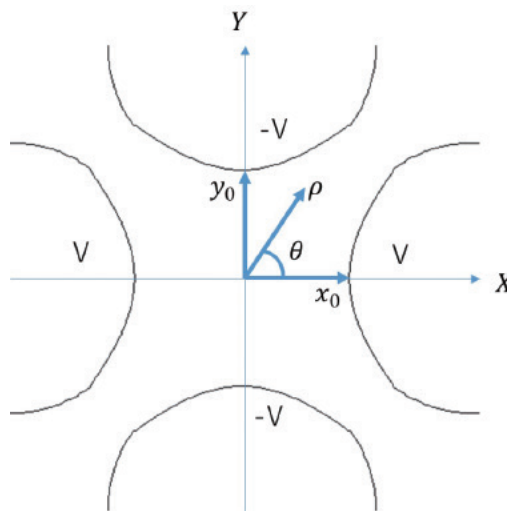


Fig.1. Coordinate system

## Improved performance of linear ion trap mass spectrometer with added octopole and dodecapole fields

3D simulation program using GPU (NVIDIA Quadro GP100) was also developed for more realistic simulation as shown in Fig.2. The surface integration was performed in parallel. Finally, the experimental instrument was constructed to confirm the validity of the simulation results.

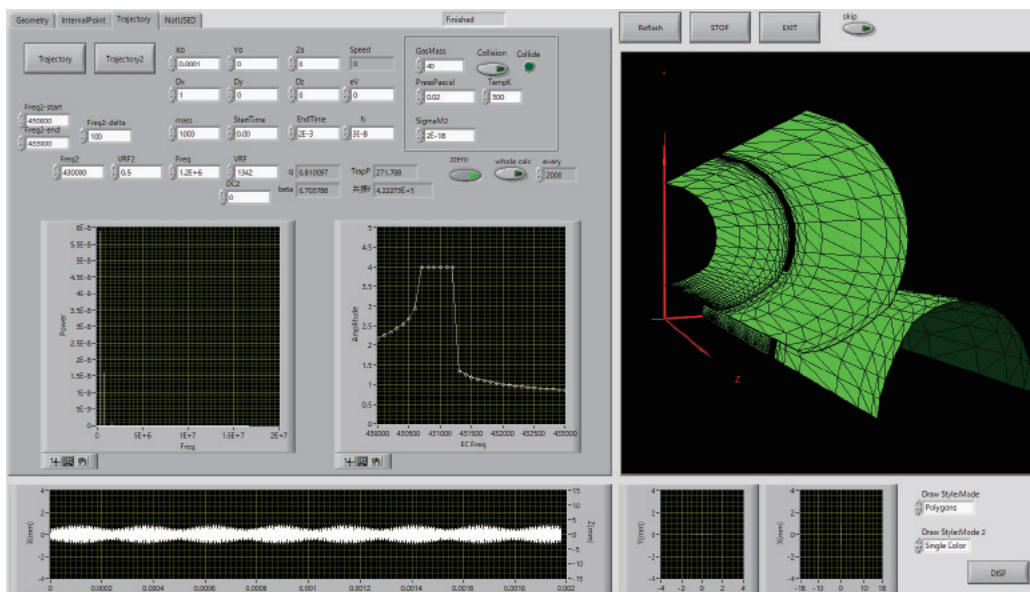


Fig.2. 3D trajectory simulation by LabVIEW

## Results

The inscribed radius of hyperbolic surface of original LIT electrodes in Fig.1 was  $x_0 = y_0 = 3.924\text{mm}$ . The geometry modification of LIT was done by shifting the pair of X-electrodes and Y-electrodes to inner direction as shown in Fig.3. In this study,  $dx$  was fixed to  $0.40\text{mm}$  and  $dy$  was varied as (A)  $0.60\text{mm}$ , (B)  $0.65\text{mm}$ , (C)  $0.7\text{mm}$ , (D)  $0.75\text{mm}$ , (E)  $0.80\text{mm}$ . The multipole components of  $A_2$ ,  $A_4$ ,  $A_6$  were calculated. Fig.4 shows the results of  $A_4/A_2$ ,  $A_6/A_2$ ,  $A_4/A_6$  for these models. It is shown that  $A_4/A_2$  is positive and  $A_6/A_2$  is negative. Model A is dodecapole( $A_6$ ) dominant and Model E is octopole( $A_4$ ) dominant. Model D has the same absolute value and opposite sign of octopole and dodecapole.

It is known that with presence of appropriate higher multipole field, the resonance curve has sharp edge which is caused by non-linear resonance<sup>(1)</sup>. The resonance curve was calculated for all models as shown in Fig.5. Model A shows the sharp edge on low frequency side by negative dodecapole. Model E shows the sharp edge on high frequency side by positive octopole. Model B, C, D shows sharp edge on both side because of balanced amount of octopole and dodecapole. The sharp resonance edge on both frequency side of resonance curve expected to improve the mass isolation performance.

# Improved performance of linear ion trap mass spectrometer with added octopole and dodecapole fields

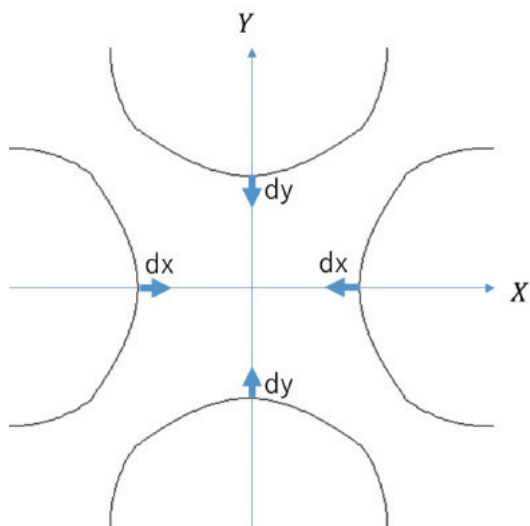


Fig.3. Geometry modification

$dx = 0.4\text{mm}$

MODEL	A	B	C	D	E
dy(mm)	0.60	0.65	0.70	0.75	0.80
A4/A2(%)	0.61	0.80	1.00	1.22	1.46
A6/A2(%)	-0.92	-1.01	-1.11	-1.22	-1.33
A4/A6	-0.66	-0.79	-0.90	-1.00	-1.10

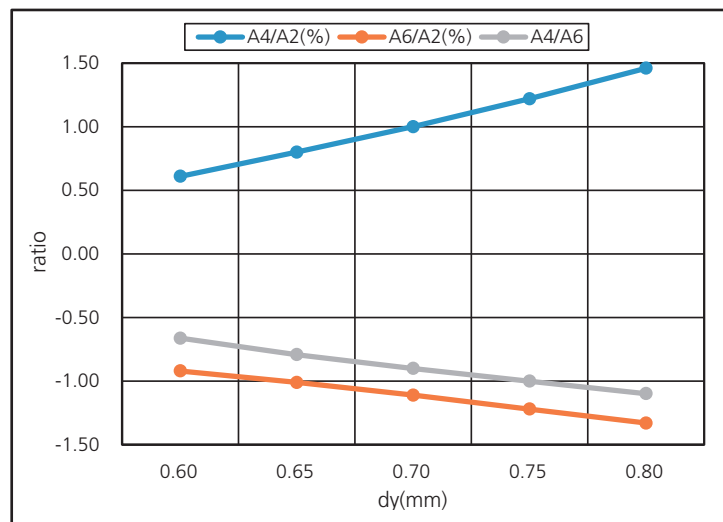
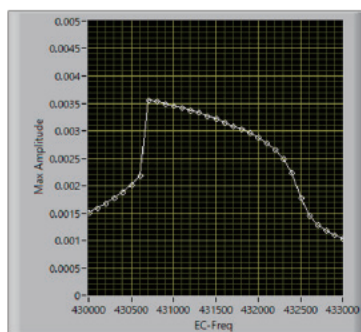
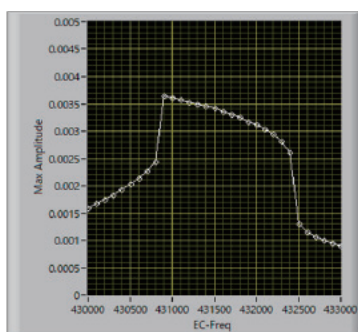


Fig.4. Multipole coefficients

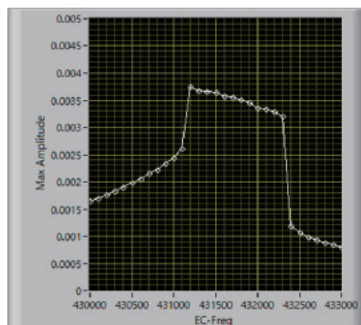
$dx=0.40\text{mm}$



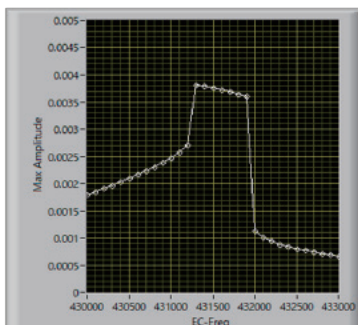
A:  $dy=0.60\text{mm}$



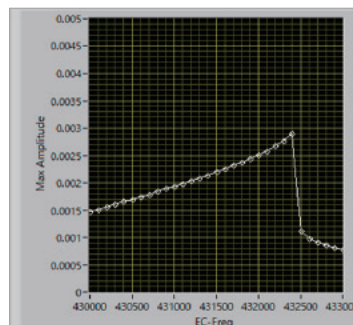
B:  $dy=0.65\text{mm}$



C:  $dy=0.70\text{mm}$



D:  $dy=0.75\text{mm}$



E:  $dy=0.80\text{mm}$

Fig.5. Resonance curve of models



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To confirm the validity of the simulation, experimental instrument was constructed based on LCMS-8050 (Shimadzu). A set of electrodes of model D was manufactured and installed where the collision cell was located. Argon cooling gas was introduced and the vacuum of LIT was maintained approximately 0.1 Pa. Isolation  $q$  value was 0.81 and CID  $q$  value was 0.25. Dipole excitation voltage between X-electrodes was

applied by an isolation transformer which was connected to one of the secondary wiring of resonance circuit. Polyethylene-glycol 1000 in 20:80 methanol/water solution was infused and the isolation profile of  $m/z$  921, 922, 923 were recorded by scanning the trap RF voltage amplitude while applying the isolation FNF waveform to X-electrodes. The result was shown in Fig. 6. Three peaks were more clearly resolved for modified LIT (model D) than original LIT.

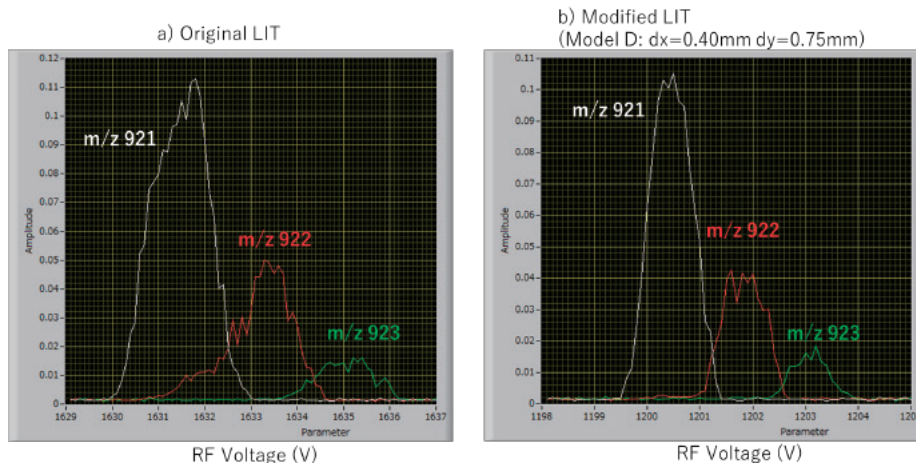


Fig.6. Mass isolation profile

The trap efficiency was evaluated by CID performance. Precursor ion  $m/z$  555 was fragmented to produce product ion  $m/z$  547. Fig.7 shows the profile of precursor and product signal intensity by CID excitation voltage. The

minimum excitation voltage to fragment precursor ion was 0.004V for original LIT and 0.012V for modified LIT. The voltage increased by a factor of three. Thus the trap efficiency was also improved.

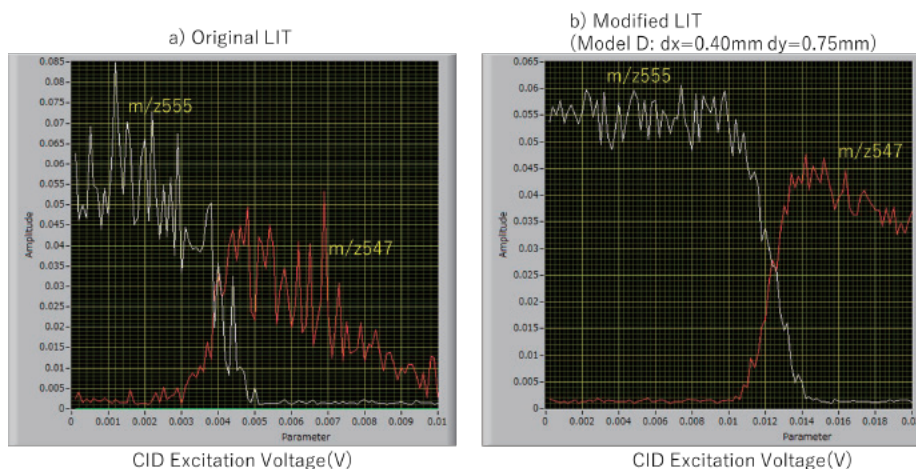


Fig.7. CID profile

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### Conclusions

The calculation program of multipole components and ion trajectory of linear ion trap was constructed and ion trap geometry was optimized to produce balanced amount of octopole and dodecapole component with opposite sign. The experimental results shows the improved mass isolation performance and trap efficiency.

### References

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- (3) A. Krishnaveni et al. , Int. J. Mass Spectrom. 275 (2008) 11-20

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