Ion Optics for Multi-turn Time-of-flight Mass Spectrometers with Variable Mass Resolution

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The ion optics of multi-turn time-of-flight (TOF) mass spectrometry was investigated. Two feasible systems using toroidal sector plus quadrupole lenses and cylindrical sectors plus quadrupole doublets were found. The combination of a linear TOF with a figure-of-eight type multi-turn system is proposed. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Since time-of-flight mass spectrometry (TOF-MS) was introduced in the 1950s, it has continued to grow as a useful mass analyzer in various fields. The instrument became especially powerful and attractive after the introduction of laser ionization and very fast electronic data handling systems with computers. The introduction of matrix-assisted laser ionization extended the application area into the biochemical fields.[1] Its applications in space science and field work are also increasing year by year.

The merits of TOF-MS are well recognized: (i) ultimate mass range, (ii) very high sensitivity owing to no scanning and (iii) compact size and easy operation. The demerits are (i) low mass resolution and (ii) difficulty in hybrid operation such as with gas or liquid chromatography or MS. However several new ideas have partially solved these problems, e.g. mirror (reflector) systems and electric sector fields. Commercial TOF-MS systems have achieved a fairly high level and are used in many mass spectrometric fields. The mass resolution of TOF-MS is directly proportional to its total path length if its aberrations are reasonably compensated, i.e. double the size gives double the resolution.

The downsizing of MS instruments is an important factor for a useful mass spectrometer in certain fields such as *in situ* observations in space science and handy instruments for field work. In order to satisfy the two requirements of higher mass resolution and downsizing, multi-turn optics might be the only solution. Fourier transform ion cyclotron resonance MS and ion trap MS belong to such a category. In this work, we investigated the possibilities of multi-turn TOF-MS and found feasible ion optics for such a TOF-MS system and discuss the possibility of increasing the mass resolution without increasing the geometrical size.

We used the new trajectory calculation code[2] based on the original TRIO[3] and developed a new code, TRIO-DRAW,[4] which can draw colored ion trajectories under given initial conditions with an actual electrode flame. TRIO-DRAW can also draw image shapes at a detector plane and simulate theoretical mass resolution. These functions help considerably in understanding the directional focusing situation and isochronous focusing conditions. All calculations were executed up to the second-order approximation including the fringing field influences.

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FLIGHT TIME CALCULATION AND TRANSFER MATRICES

Flight time in electric fields can be calculated by paraxial approximation and the results can be expressed in the form of a transfer matrix. Here we do not repeat the explanation of how to calculate the flight time; the detailed processes have been given elsewhere.[5–7]

In addition to the lateral position of a particle, the flight time deviation t can also be described by a power series expansion of the small quantities, x_0, α_0, y_0, β_0, γ and δ as

$$t = t_0 + (t\,|\,x)x_0 + (t\,|\,\alpha)\alpha_0 + (t\,|\,\gamma)\gamma + (t\,|\,\delta)\delta + \cdots \quad (1)$$

where x_0, y_0, α_0 and β_0 are the initial position and angle deviation and γ and δ are the initial mass and energy deviation, respectively.

Since t is inversely proportional to the velocity v_0, a new quantity, the pathlength deviation l, defined by $l = v_0 t$, is introduced to eliminate v_0. l can be expressed by

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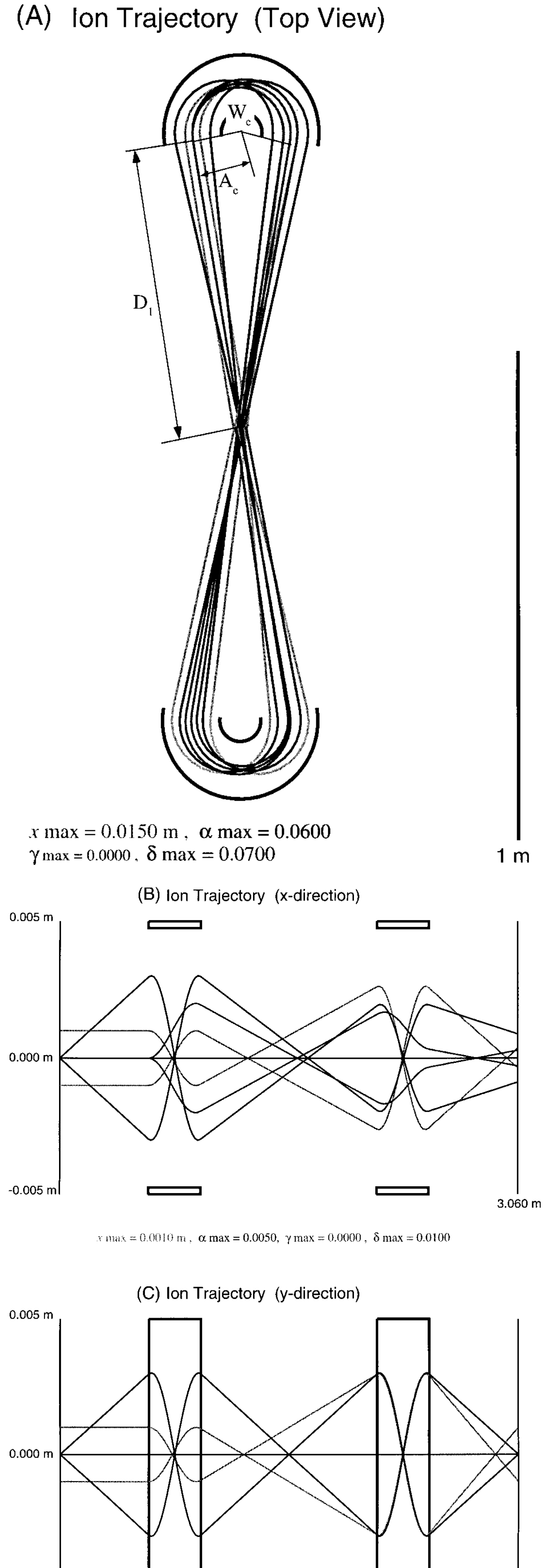

Figure 1. Ion trajectories of a figure-of-eight (Poschenrieder) type multi-turn TOF using spherical sectors without fringing field effect. (A) Top view; (B) x-direction; (C) y-direction.

a power series expansion as

$$\begin{aligned} l = {} & l_0 + (l\,|\,x)x_0 + (l\,|\,\alpha)\alpha_0 + (l\,|\,\gamma)\gamma + (l\,|\,\delta)\delta \\ & + (l\,|\,xx){x_0}^2 + (l\,|\,x\alpha)x_0\,\alpha_0 + (lx\,|\,\gamma)x_0\,\gamma \\ & + (l\,|\,x\delta)x_0\,\delta + (l\,|\,\alpha\alpha){\alpha_0}^2 + (l\,|\,\alpha\gamma)\alpha_0\,\gamma \\ & + (l\,|\,\alpha\delta)\alpha_0\,\delta + (l\,|\,\gamma\gamma)\gamma^2 + (l\,|\,\gamma\;\delta)\delta\gamma \\ & + (l\,|\,\delta\delta)\delta^2 + (l\,|\,yy){y_0}^2 + (l\,|\,y\beta)y_0\,\beta_0 \\ & + (l\,|\,\beta\beta){\beta_0}^2 \ldots \end{aligned} \tag{2}$$

The first-order transfer matrix reads

$$\begin{pmatrix} x \\ \alpha \\ y \\ \beta \\ \gamma \\ \delta \\ l \end{pmatrix} = \begin{pmatrix} (x\,|\,x) & (x\,|\,\alpha) & 0 & 0 & (x\,|\,\gamma) & (x\,|\,\delta) & 0 \\ (x\,|\,\alpha) & (\alpha\,|\,\alpha) & 0 & 0 & (\alpha\,|\,\gamma) & (\alpha\,|\,\delta) & 0 \\ 0 & 0 & (y\,|\,y) & (y\,|\,\beta) & 0 & 0 & 0 \\ 0 & 0 & (\beta\,|\,y) & (\beta\,|\,\beta) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ (l\,|\,x) & (l\,|\,\alpha) & 0 & 0 & (l\,|\,\gamma) & (l\,|\,\delta) & 1 \end{pmatrix} \begin{pmatrix} x_0 \\ \alpha_0 \\ y_0 \\ \beta_0 \\ \gamma \\ \delta \\ l_0 \end{pmatrix} \tag{3}$$

where the coefficients $(x\,|\,x)$, $(x\,|\,\alpha)$, etc., are the same transfer matrix elements as defined in the original TRIO.[3] Even in a complicated ion optical system, the total transfer matrix can be obtained simply by matrix multiplication.

The higher order transfer matrices can be defined in the similar way to that given in Ref. 8. The coefficients $(l\,|\,x)$, $(l\,|\,\alpha)$ and $(l\,|\,\delta)$ define the non-isochronicity with respect to the initial position, initial angle and initial energy deviation. The term $(l\,|\,\gamma)$ describes the mass dispersion which usually depends on the total path length of a system. The second-order coefficients $(l\,|\,xx)$, $(l\,|\,x\alpha)$, etc., and the third-order terms $(l\,|\,xxx)$, $(l\,|\,xx\alpha)$, etc., were calculated in Ref. 8 and their computer code is under preparation for publication.[2] It should be noted that the effects of the fringing fields are taken into account in our calculation. Their effects are very important and should not be neglected in the actual ion optical design.

In TRIO-DRAW, each trajectory possessing different initial conditions can be shown using different colors and this function helps different colors and this function helps considerably in understanding the characteristics of individual trajectories and the condition of focusing, although all figures in this paper are drawn only in black and white.

ISOCHRONOUS TIME FOCUSING

One of the most important problems in TOF-MS is to achieve the isochronous time focusing of ions having an initial energy spread, namely $(l\,|\,\delta) = 0$. Otherwise, the mass resolution cannot be increased. There are two major ways to solve these requirements, namely using (i) an ion mirror/reflector method[9] or (ii) electric sector fields. In this paper, we focus on the latter method. Isochronous time focusing using an electric sector was first introduced by Poschenrieder.[10] As an extension in this direction, Sakurai *et al.*[6] investigated the possibility of a

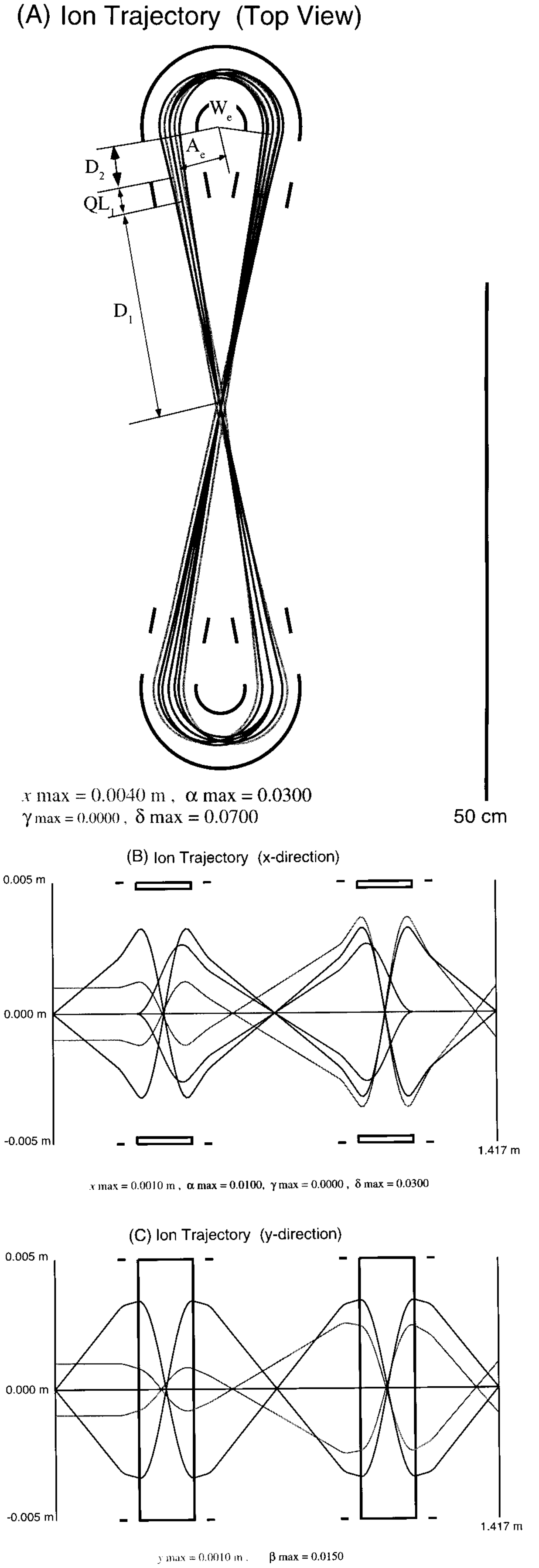

Figure 2. Ion trajectories of a figure-of-eight type multi-turn TOF using a toroidal sector and a quadrupole lens with fringing field effect. (A) Top view; (B) *x*-direction; (C) *y*-direction.

space and time focusing system. A four-sector system (clover-leaf type) which possesses sixfold focusing, $(x \mid \alpha) = (x \mid \delta) = (y \mid \beta) = 0$, $(l \mid x) = (l \mid \alpha) = (l \mid \delta) = 0$, was constructed and showed high mass resolution as predicted by calculation.[11] One feature of this system is its compact geometrical size even for a long effective flight length. Even after succeeding in improving the mass resolution by introducing elaborate optical elements, it is still limited by the total flight length and pulse width.

MULTI-TURN TOF SYSTEM

In order to achieve the highest mass resolution in a TOF mass spectrometer of fixed geometrical size, the use of multi-turn ion optics is required. There are two possibilities for such a geometry: oval type or figure-of-eight type. Wollnik and co-workers proposed a multi-turn isochronous oval TOF using an experimental storage ring (ESR), consisting of magnetic sectors and magnetic quadrupole lenses at GSI in Germany,[12] and also an energy-isochronous storage ring consisting of eight 45° electric sectors.[13] Our study requires a geometry that fulfils the requirements of both spatial energy focusing, $(x \mid \delta) = 0$, and temporal energy focusing, $(l \mid \delta) = 0$, simultaneously, which is not possible with an oval-type consisting of only two electric sectors. Our studies were therefore focused on figure-of-eight geometries only. The figure-of-eight TOF geomtry was originally proposed by Poschenrieder,[14] although we have made significant developments of the basic idea with the use of toroidal and cylindrical electric sectors and electrostatic quadrupole lenses.

The basic requirements for a figure-of-eight TOF are as follows. (i) With regard to spatial focusing, the image magnifications in both the x-direction and the y-direction should be unity. Angular (or direction) focusing in both directions should be satisfied, $(x \mid \alpha) = (y \mid \beta) = 0$. Energy focusing is automatically fulfilled, $(x \mid \delta) = 0$. (ii) With regard to the isochronous focusing condition, three first-order transfer matrix coefficients are required to be zero: $(l \mid x) = (l \mid \alpha) = (l \mid \delta) = 0$. It is not always possible simultaneously to set these elements to zero. The new configurations of the figure-of-eight systems may be divided into three groups, as follows.

Spherical sector ($c = 1$)

The simplest way to achieve a figure-of-eight type multi-turn system is to use 'spherical electric sectors' whose geometry was proposed by Poschenrieder.[14] Ion trajectories of ions having different initial conditions were calculated by TRIO and drawn by TRIO-DRAW and are shown in Fig. 1 and its ion optical characteristics are given in Table 1. The meaning of Fig. 1(A), (B) and (C) are as follows. Figure 1(A) shows a plan view of the ion trajectories through the theoretical system, as calculated by a transfer matrix method. From this figure it is

Table 1. All the parameters and final transfer matrix elements for the three systems discussed (spherical, toroidal and cylindrical)

Parameter[a]	Spherical type	Toroidal type	Cylindrical type	Parameter[a]	Spherical type	Toroidal type	Cylindrical type
Ae	0.05	0.05	0.05	(x|xx)	32.587	43.834	−0.1728
We	199.2	201.26	228.00	(x|xα)	0.000	−0.088	3.520
C	1.000	0.8559	0.000	(x|xδ)	−23.760	10.723	−0.6738
D_1	0.5912	0.2013	0.0741	(x|αα)	0.000	0.000	0.0008
D_2	—	0.040	0.010	(x|αδ)	−7.225	1.432	0.5648
D_3	—	—	0.010	(x|δδ)	1.188	−0.184	−0.1031
Qk_1	—	−12.1266	57.6807	(x|yy)	−31.505	−54.500	−0.7708
Qk_2	—	—	−60.3470	(x|yβ)	0.000	−0.050	4.6488
				(x|ββ)	0.000	0.000	0.0015
(x|x)	1.000	1.000	−1.000	(α|xx)	20.722	−335.02	−113.81
(x|α)	0.000	0.000	−0.0010	(α|xα)	−26.286	−89.023	−0.1328
(x|γ)	0.000	0.000	0.000	(α|xδ)	−54.441	71.086	−32.507
(x|δ)	0.000	0.000	0.000	(α|αα)	0.000	0.0438	−1.7603
(α|x)	6.577	14.960	0.0592	(α|αδ)	−23.76	10.702	0.6059
(a|a)	1.000	1.000	−1.000	(a|dd)	3.907	−1.381	−0.8883
(a|g)	0.000	0.000	0.000	(a|yy)	−152.17	−448.59	−491.39
(α|δ)	0.000	0.000	0.3635	(α|yβ)	−14.765	−6.035	−0.4162
(y|y)	1.000	1.000	−1.000	(α|ββ)	0.000	0.0269	−0.3052
(y|β)	0.000	0.000	0.0007	(L|xx)	111.81	−43.402	33.974
(β|y)	0.000	14.112	0.2223	(L|xα)	47.520	−13.222	1.2813
(β|β)	1.000	1.000	−1.000	(L|xδ)	−15.627	4.465	2.4420
(L|x)	0.000	0.000	−0.7275	(L|αα)	7.225	−0.8822	0.5926
(L|α)	0.000	0.000	−0.0004	(L|αδ)	−4.752	0.5967	−0.0084
(L|γ)	1.530	0.7083	0.4236	(L|δδ)	3.591	1.1336	0.1885
(L|δ)	−0.008	0.000	0.0000	(L|yy)	−74.523	−1.366	258.63
				(L|yβ)	−32.398	1.984	1.6943
				(L|ββ)	−4.926	0.1416	0.8116

[a] The following parameters were used, as shown in Figs 1, 2 and 3: *Ae* = radius of the electric sector; *We* = aperture angle of the electric sector; *c* = field constant of the electric sector; *Dx* = drift length *x*; *QKx* = field strength of electrostatic quadrupole X. The length of the electrostatic quadrupole lens in each case is 0.01 m. The total transfer matrix elements are represented as (x|x), (x|xx), etc.

possible to estimate the focusing properties of the system, including the beam waist and the size of the instrument. In the original output of the ion-optical program TRIO-DRAW, ion trajectories derived from different initial conditions are plotted in different colors, which provides a simple visual understanding of the system properties.

Figures 1(B) and (C) are linear representations of the beam trajectories for the instrument depicted in Fig. 1(A). In the horizontal plan view [Fig. 1(B), *x*-direction], the trajectories show the angle and energy focusing points of the instrument, which will govern the efficiency of the system with regard to the mass analysis. In the vertical plan view [Fig. 1(C), *y*-direction] the beam paths illustrate the efficiency of the system with regard to ion transmission (and hence instrument sensitivity), which is essential if a multi-turn system is to be developed.

The maximum magnitudes of x_0, y_0, α_0 and β_0 are chosen such as to show the characteritics of each deviation and are not equal to the actual values. They are given in the lower part of the figures. In the original system,[14] the fringing field influence was neglected and the problem of ion injection and ejection was not addressed. If fringing field effects are included, this geometry no longer provides directional focusing. It should be noted that geometrical parameters should be changed drastically if the fringing effects are taken into account properly. No feasible optical system was found for practical use.

Toroidal sector plus quadrupole lens system

We introduced two electric quadrupole lenses to a toroidal sector and searched for good geometrical parameters using the simplex optimization method.[15] One such system is shown in Fig. 2 and its ion optical characteristics are given in Table 1. The most of important aberration coefficients are small enough under acceptable initial conditions even for three turns. The spatial beam spread is also satisfactory although fairly large initial values are chosen so that the individual focusing characteristics can be well understood.

Cylindrical sector plus quadrupole system

Another way to achieve a similar goal is to employ a cylindrical sector and a quadrupole doublet. By using the simplex fitting routine, a feasible solution can be found. Ion trajectories are shown in Fig. 3 and ion optical parameters are given in Table 1. The merit of this geometry is that it is easier to construct and more compact than the system using a toroidal sector. The

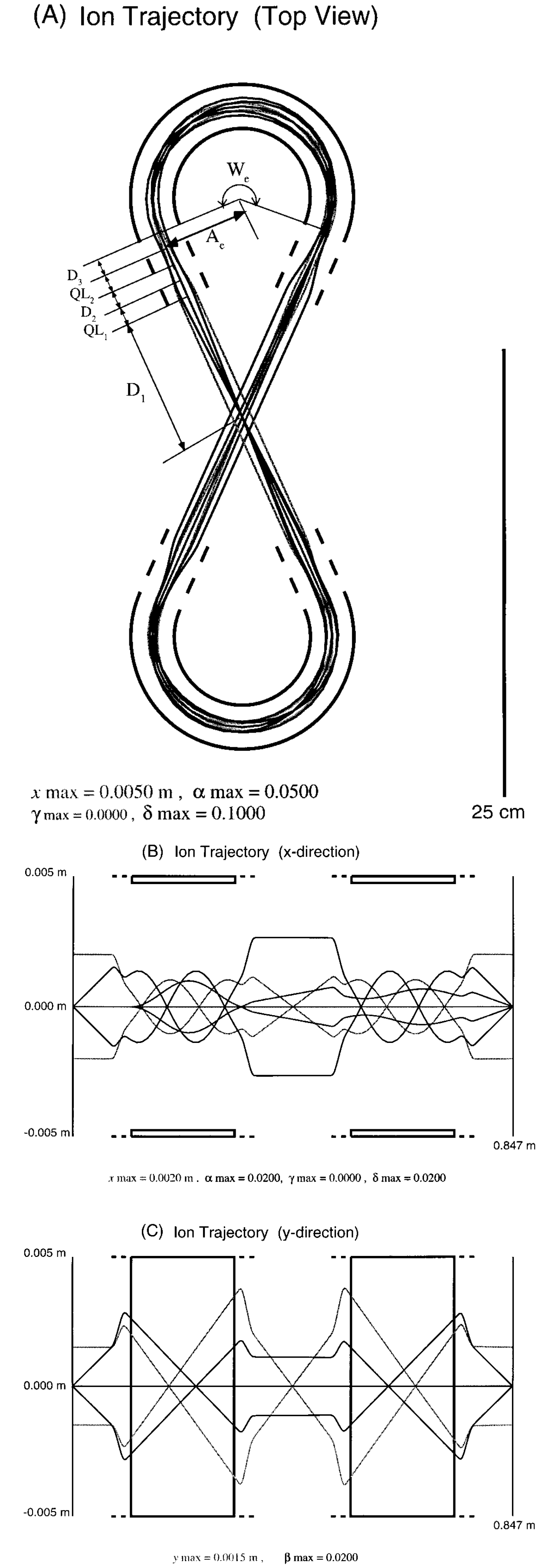

Figure 3. Ion trajectories of figure-of-eight type multi-turn TOF using a cylindrical sector and quadrupole doublet with fringing field effect. (A) Top view; (B) x-direction; (C) y-direction.

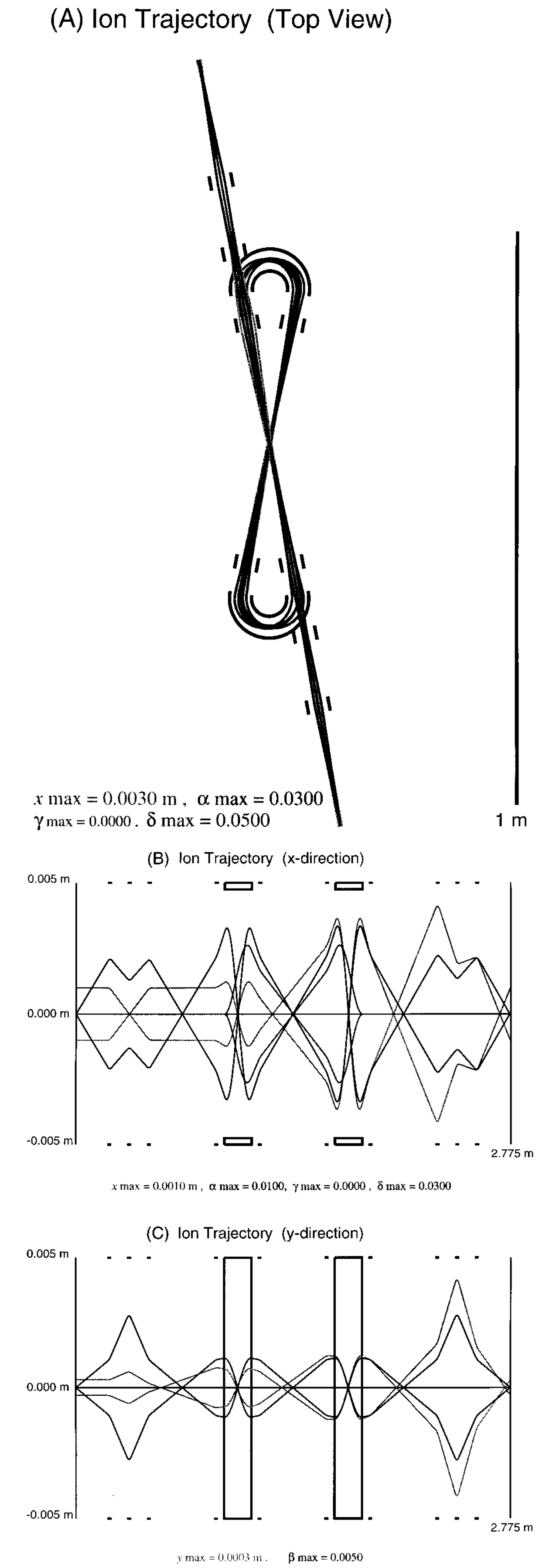

Figure 4. Ion trajectories of the combined system of linear TOF and two turn of figure-of-eight TOF. (A) Top view; (B) x-direction; (C) y-direction.

demerit is that the isochronous focussing is not satisfied, $(l\,|\,x) \neq 0$.

COMBINATION OF A LINEAR TOF WITH A MULTI-TURN SYSTEM

One of the most important points for a multi-turn system is how to inject ions into the mass spectrometer and how to eject them from it. We propose the combination of a linear TOF system consisting of quadrupole lenses and the above-discussed figure-of-eight type geometry. The basic concept of this arrangement is a small telescope attached on top of a large high-resolution telescope to obtain coarse information. A block diagram of this arrangement is shown in Fig. 4. The expected operation is as follows: (i) Operating the system as a linear TOF system by only using a quadrupole lens, one obtains a low-resolution mass spectrum. Higher resolution can be expected by employing an energy–time focusing ion source such as a Wiley-type two-stage extracting ion source.[16] (ii) The electric sector field should be switched on when an ion group of interest is passing the sector region. The field strength of the quadrupole lens should be adjusted properly. (iii) After passing the ions through the system for a suitable time, the electric sector field should be switched off and the ion groups of interest should be guided to a detector. The features of this combined system are (i) the mass resolution can be controlled by choosing the number of turns in the figure-of-eight system without increasing the geometrical size of the instrument, (ii) the number of points per peak can be increased even using the same sampling speed, and quantitative analysis will accordingly be more reliable, (iii) the linear operation mode guarantees TOF operation for low resolution, which is important, e.g., for a remotely operated miniature mass spectrometer sent to a comet or planet and (iv) computer and electronic technology are progressing rapidly so that today's difficulties should be overcome in the near future.

COMPARISON WITH OTHER SECTOR TOF-MS SYSTEMS

We compared the ion optical characteristics of several sector-type TOF-MS systems developed by our group from two viewpoints: (i) spatial focusing condition by drawing inidividual trajectories as colored rays and (ii) isochronous focusing by simulating theoretical mass resolution under given initial conditions. We selected four cases: (i) two-sector TOF given as system a-1 in Ref. 6, (ii) four-sector TOF as give in Ref. 11, (iii) toroidal sector plus quadrupole lens and (iv) cylindrical sector plus quadrupole doublet. For comparing their overall geometrical sizes, the radius of the electric sector was chosen to have the same value (5 cm). It is noted that the mass resolution, of course, depends on the total path length and the calculated mass resolutions simply should not be compared.

The isochronous focusing plane could be simulated by computer code and is shown in Fig. 5. This peak means that the position of individual ions having different initial conditions arrived at a certain time when the reference particle arrived at a certain reference point

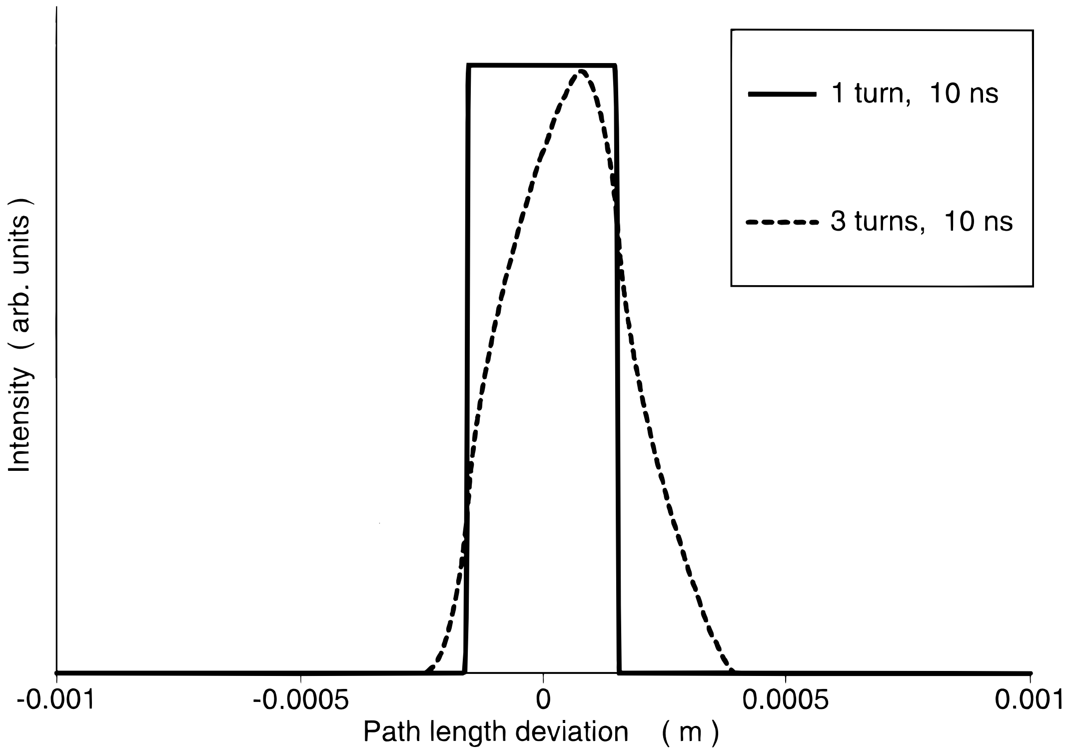

Figure 5. Isochronous focusing plane at the detector point. Flight length = 1.4167 m; flight time = 45.622 µs; velocity of reference particle = 3.105×10^4 m s^{-1} (e.g. $m/z = 200$, accelerating voltage = 1.068 kV); $x_0 = 0.0022$ m; $y_0 = 0.001$ m; $\alpha_0 = 0.001$; $\beta_0 = 0.001$; $\delta = 0.001$.

Table 2. Comparison of calculated mass resolution for four TOF-MS systems[a]

Parameter	Two-sector	Four-sector	Figure-of-eight type (toroidal)	Figure-of-eight type (cylindrical)
	Type			
Radius of electrode (m)	0.05	0.05	0.05	0.05
Total pathlength (m)	0.6973	1.7270	1.4166	0.8472
Mass resolution (H mode)	1161	2875	2282	1107
Mass resolution (L mode)	1161	2875	2282	190

[a] Initial conditions are for H mode ($x_0 = 0.0002$, $y_0 = 0.001$, $\alpha_0 = 0.001$, $\beta_0 = 0.001$, $\delta = 0.001$ and for L mode $x_0 = 0.001$, $y_0 = 0.005$, $\alpha_0 = 0.005$, $\beta_0 = 0.005$, $\delta = 0.005$. Pulse width = 10 ns. The velocity of reference particle is chosen to be 3.105×10^4 m s^{-1} (e.g. $m/z = 200$, accelerating voltage = 1.068 kV).

Table 3. Improvement of mass resolution after multi-turn operation

System[a]	Parameter[b]	Pulse width (ms) 5		10		20	
A	No. of turns	1	3	1	3	1	3
	H mode	4563	9482	2282	6807	1141	3426
	L mode	4471	2334	2282	1585	1141	1096
B	No. of turns	1	3	1	3	1	3
	H mode	1288	2415	1107	2010	682	1560
	L mode	198	576	190	556	179	528

[a] (A) New type of figure-of-eight system using toroidal sector plus quadrupole lens and (B) new type of figure-of-eight TOF system using cylindrical sector plus quadrupole doublet.
[b] Initial conditions are for H mode $x_0 = 0.0002$, $y_0 = 0.001$, $\alpha_0 = 0.001$, $\beta_0 = 0.001$, $\delta = 0.001$ and for L mode $x_0 = 0.001$, $y_0 = 0.005$, $\alpha_0 = 0.005$, $\beta_0 = 0.005$, $\delta = 0.005$.

such as the detector plane. From such a peak shape, the mass resolution (full width at half maximum definition) for the above four cases can be estimated and the results are given in Table 2. The improvement in mass resolution after multi-turn operation is given in Table 3. Here two types of initial conditions were selected: high-resolution mode ($x_0 = 0.0002$, $y_0 = 0.001$, $\alpha_0 = 0.001$, $\beta_0 = 0.001$, $\delta = 0.001$) and low-resolution mode ($x_0 = 0.001$, $y_0 = 0.005$, $\alpha_0 = 0.005$, $\beta_0 = 0.005$, $\delta = 0.005$). It is necessary to give the velocity or the flight time of the reference particle, which are given as a function of acceleration energy and mass. One example is given in the caption of Fig. 5.

It is important to check the ion optical characteristics by experiment and we are constructing such a multi-turn TOF-MS system.

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