Planar multi-reflecting time-of-flight mass analyzer with a jig-saw ion path

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Abstract

In the paper a multi-reflecting time-of-flight analyzer is described in which ions move along a jig-saw path between two parallel planar gridless ion mirrors. Since ion path contains no closed loops, the analyzer accepts ions in the full mass range. Stable ion confinement in the plane of jig-saw motion is provided by a periodic lens array located between the mirrors. Optimization of the mirrors leads to the 3rd-order time-of-flight focusing with respect to ion energy and 2nd-order time-of-flight focusing with respect to spatial spread in the direction normal to the plane of the jig-saw motion. Experimental tests demonstrated the mass resolving power up to 50,000 at one 20 m long pass through the analyzer while with closing ion path in loops the mass resolving power exceeding 100,000 was obtained. © 2008 Elsevier B.V. Open access under CC BY-NC-ND license.

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1. Introduction

Increasing the ion flight path length is a well-known resource of raising the mass resolving power of time-of-flight analyzers. If ions in the analyzer pass through N identical cells with \( T_0 \) being the flight time through one cell, the mass resolving of the analyzer is

\[
R_m = \frac{NT_0}{2(\Delta t' + N\Delta t_0)} = \frac{T_0}{2(\Delta t'/N + \Delta t_0)},
\]

where \( \Delta t' \) is the initial time width of the ion signal at the “primary time focus” behind the ion source and \( \Delta t_0 \) is the aberration widening of the time signal after each cell. Thus, increasing the flight path (that is the number of cells) allows to decrease the contribution of the initial time width of the ion signal usually referred to as the “turn-around time”. Taking into account that a typical value of the turn-around time produced by pulsed ion sources for ions of

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the mass 1,000 amu is about 3 ns, even in an “ideal” system without any time-of-flight aberrations reaching the mass resolving power of 100,000 in the analyzer with the pass kinetic energy of 4 KeV would require the total path length of almost 16 m. Achieving such a long ion path while keeping reasonable physical dimensions of a device is feasible by folding the ion path in a multi-reflecting time-of-flight (MR TOF) mass analyzer.

Most of so far existing MR TOF analyzers implement the scheme of organizing ion motion along a closed cycle either by multiple reflections in ion mirrors [1] or by periodic deflections in sector fields [2]. Such a scheme though allows to increase the flight length virtually infinitely, suffers from considerable shrinking the accepted mass range. Indeed, the analyzer can properly recognize only those ions which make the same number \( N \) of loops in the analyzer at the moment when they are sent to the detector. This condition leads to the following restriction of the ratio between the maximal and minimal ion mass:

\[
\frac{m_{\text{max}}}{m_{\text{min}}} = \left( \frac{N}{N-1} \right)^2. \tag{2}
\]

Many applications however require simultaneous analysis of a wide range of ion masses. Such analysis can be only performed in analyzers with a non-looped ion path which can be still long enough. Forming a non-closed 20 m long “8-type spiral” ion path in an analyzer based on sector fields was recently demonstrated in Ref. [3].

In this paper, we describe a MR TOF analyzer with a non-closed jig-saw ion path which allows accepting the full ion mass range. The idea of a jig-saw ion motion between two gridless ion mirrors substantially elongated in one “drift” direction was introduced in Ref. [4]. Ion paths in such analyzer are schematically shown in Fig. 1. This planar analyzer however can be only designed for a small number of reflections because ion bunches experience no focusing in the plane of the jig-saw motion and the angular divergence finally leads to overlapping of ion paths with different number of reflections. In our analyzer, we achieved a stable ion beam confinement along the extended path by introducing a periodic set of lenses in the drift space [5,6].

As is clear from Eq. (1), the mass resolving power of a MR TOF analyzer is limited by the ratio of \( T_0/(2 \Delta t_0) \), that is by time-of-flight aberrations per one ion cell which can be considered as one reflection. Therefore, a cell of a MR TOF must be designed with possibly low aberrations. For our analyzer we designed high-quality gridless four-electrode planar ion mirrors which allow achieving 3rd-order time focusing with respect to ion energy after each reflection. Care is also taken to keep the flight time independent in 2nd order of coordinate and angular ion spread in the direction perpendicular to the plane of jig-saw motion. Ion-optical design of the analyzer is discussed in Section 2.
High performance of the analyzer predicted by ion-optical calculations was confirmed experimentally using two prototypes of the analyzer, supplied with either orthogonal or linear trap pulsed ion source. At a single pass through the analyzer operated at 2 KeV ion energy the mass resolving power of 50000 was achieved at the ion path length of 20 m. To estimate the limit of the resolving power by analyzer aberrations as well as the quality of the ion beam confinement, we used closing the ion path into cycles by two deflectors located at the opposite ends of the lens array. In this way we achieved the mass resolving power exceeding 100000 at 400 m ion path length with still about 10% transmission for heavy ions (m > 1000 amu). Obtained experimental results are illustrated in Section 3.

2. Ion-optical design of the planar MR TOF analyzer

Ion motion in the proposed planar MR TOF analyzer is schematically shown in Fig. 2. The analyzer comprises two gridless ion mirrors substantially elongated in one (Z) direction. Ions which are injected into the analyzer through an entrance deflector, move under a small “drift” angle with respect to X direction being periodically reflected by ion mirrors and slowly drifting in the “drift” direction Z. In the middle between the mirrors, an array of 2D lenses is placed with focal length of each lens being equal to the ion path length from this lens to the next one. A parallel ion beam entering a lens is focused to the middle of the next lens and thus ions experience periodic re-focusing on their way through the analyzer. Such periodic focusing provides for a stable ion beam confinement along the ion path in the plane XZ of the jig-saw motion. As was shown in Ref. [7], ion beam focusing by a periodic electrostatic lens array possesses non-linear confinement property which allows to keep the beam confined at practically infinitely long path avoiding growth of spatial blurring. Besides, periodic focusing helps ions resist small external perturbing factors such as mechanical misalignments.

![Fig. 2. Ion motion in the proposed planar MR TOF analyzer with a periodic set of 2D lenses between the ion mirrors.](image)

After ions have passed the analyzer in the positive Z direction, they are deflected by the end deflector as shown in Fig. 2 and are sent back through the analyzer in the negative Z direction. This allows to double the ion path length without creating closed path loops.

Periodic ion beam focusing in the perpendicular XY plane is performed by two identical gridless planar ion mirrors. As shown in Fig. 3, each mirror comprises four tunable electrodes and a shielding electrode protecting the drift space from penetration of the mirror field. The electrodes are just pairs of parallel plates of equal width, except for one cap electrode (#1 in Fig. 3). Three of four tunable electrodes create a reflecting field while the electrode #4
creates an accelerating lens field, so that the electrostatic potential distribution which focuses the incoming ion beam, initially parallel in XY plane, to the point located in the middle plane between two mirrors (at X=0). If the y-coordinate in this middle plane after reflection is represented as an expansion

\[ y = (y | y) y_0 + (y | b) b_0 + (y | y \delta) y_0 \delta + (y | b \delta) b_0 \delta + \ldots , \]

(3)

where \( y_0 \) is the initial coordinate in the middle plane before reflection, \( b_0 = dy/dx \) at \( y = y_0 \) and \( \delta \) is the relative kinetic energy \( K \) deviation from the nominal kinetic energy value \( K_0 \): \( \delta = (K - K_0)/K_0 \), then the “parallel-to-point” focusing performed by the mirror is expressed as

\[ (y | y) = 0 . \]

(4)

Consider now time-of-flight properties of ion mirrors. The flight time \( T \) from the middle plane \( X = 0 \) through the mirror back to this middle plane can be in general represented as

\[
T - T_0 = (t | \delta) \delta + (t | \delta \delta) \delta + (t | y y) y_0^2 + (t | y b) y_0 b_0 + (t | b b) b_0^2 \]
\[
+ (t | z z) z_0^2 + (t | z a) z_0 a_0 + (t | a a) a_0^2 \]
\[
+ (t | \delta \delta \delta) \delta^3 + (t | y y \delta) y_0^2 \delta + (t | y b \delta) y_0 b_0 \delta + (t | b b \delta) b_0^2 \delta + (t | \delta \delta \delta \delta) \delta^4 + \ldots
\]

(5)

where \( T_0 \) is the flight time for ion moving with the nominal kinetic energy along the central trajectory. Some terms in Eq. (5) are absent due to the symmetry conditions. The terms containing the coordinate \( z \) and the corresponding angular parameter \( a \) (which is the tangent of inclination of ion trajectory in XZ-plane with respect to the mean direction of the jig-saw motion) appear in Eq. (5) due to presence of 2D lenses located between the mirrors.

By a proper choice of potential distribution at the axis of the ion mirror (see Fig. 4), that is by optimization of mirror electrode potentials and of the distance \( L \) from the mirror to the middle plane, it is possible to achieve 3\textsuperscript{rd}-order time-of-flight focusing with respect to ion energy. This means fulfilling the conditions

\[ (t | \delta) = (t | \delta \delta) = (t | \delta \delta \delta) = 0 \]

(6)

in Eq. (5). Four conditions of Eqs. (4) and (6) require tuning four parameters: three potentials at the mirror electrodes and the distance between the mirrors. One remaining free parameter (fourth mirror electrode potential) can be used to tune the condition of 2\textsuperscript{nd} order time-of-flight focusing with respect to the initial y-coordinate:

\[ (t | y y) = 0 . \]

(7)

Remarkably, two conditions of Eqs. (4) and (7) lead to additional focusing properties caused by the system symmetry. First, because of the mirror symmetry of the cell “drift-ion mirror-drift” from the middle plane back to this middle plane, Eqs. (4) and (7) lead to elimination of 2\textsuperscript{nd} order time-of-flight aberration with respect to the angular parameter \( b \):

\[ (t | b b) = 0 . \]

(8)
Moreover, the same two mentioned conditions lead to elimination after each two cells of the system (that is after two reflections) of the 2nd-order time-of-flight combined aberration

\[(t \perp yb) = 0. \tag{9}\]

The conditions of Eqs. (7) – (9) means full 2nd order time-of-flight focusing with respect to spatial parameters in the XY-plane.

Yet another useful property of the system follows from the symplectic relations between the aberration coefficients [8]. Due to these relations the conditions of Eqs. (4), (7) – (9) lead to elimination of 2nd-order chromatic aberrations in Eq. (3):

\[(y \perp y\delta) = (y \perp b\delta) = 0 \tag{10}\]

after each two reflections. Elimination of chromatic aberrations means independence of the position of the focal point defined by Eq. (4) on ion energy. Such independence improve stability of spatial confinement in XY-plane for ion beams with a large energy spread.

With proposed aberration correction scheme, most important time-of-flight aberrations which define the term \(\Delta t_0\) in Eq. (1) remain the following:

- 2nd-order aberrations with respect to the spatial ion spread in XZ-plane: \((t \perp zz)\) and \((t \perp aa)\) (the combined aberration \((t \perp za)\) vanishes after passing through each four lenses),
- 3rd-order chromatic aberrations \((t \perp yy\delta)\) and \((t \perp bb\delta)\) (the combined aberration \((t \perp yb\delta)\) vanishes after each two reflections),
- and 4th-order aberration with respect to ion energy \((t \perp \delta\delta\delta)\).

The first of the last mentioned three groups of aberrations occurs due to presence of 2D electrostatic lenses. These 2nd-order aberrations define the minimal possible width of 2D lenses and thus restrict the number of jig-saw steps for a fixed analyzer length in Z-direction and given value of the resolving power. The other two groups restrict the energy spread in the ion beam and the beam height in Y-direction. Ion-optical simulation shows that for a typical distance between the ion mirror caps of 600 mm and the 2D lens array step of 15 mm the aberration limit of the mass resolving power of the analyzer with the mirror window height in Y-direction 30 mm is about 150000 (FWHM) for the energy spread \(2\delta = 6\%\), the beam size 3 mm (Z) \(\times\) 6 mm (Y) and the beam angular divergence of 0.4 degree in Z-direction and 1 degree in Y-direction.
With the high quality of the time-of-flight focusing, the turn-around time formed by the pulsed ion source remains the main parameter restricting the mass resolving power in Eq. (1) in case of a moderate total path length. In order to achieve the value of the mass resolving power close to the aberration limit, it might be in certain cases to increase the flight path length by closing ion trajectories in loops at the expense of cutting the accepted mass range. In the proposed analyzer design, organizing closed loops can be performed by switching potentials at the entrance deflector. Optionally, after insertion of ions into the analyzer this deflector can be switched such that to return them back into the analyzer after passing the full jig-saw path (multipass mode as shown in Fig. 5). Alternatively, the entrance deflector can initially direct the incoming ion beam perpendicular to ion mirrors and then switched off such that ions always pass only through this deflector (shuttle mode as shown in Fig. 5). In the latter case the entrance deflector after switching off deflecting voltages acts as a 2D lens which keeps the ions confined in XZ-plane.

![Multipass mode and Shuttle mode](image)

Fig. 5. Two schemes of closing ion paths in loops in the planar MR TOF analyzer.

3. Experimental tests

Experimental testing of the planar MR TOF analyzer was performed using two prototypes of the analyzer. One of them (I) comprised ion mirrors with a large separation of 600 mm between the mirror caps and only five 2D lenses as shown in Fig. 6 (later the number of lenses was increased to 10 thus achieving the effective flight path length of 12 m at the 2D lens array step of 15 mm). In this analyzer, ion mirrors were manufactured from 1 mm thin metal window plates separated by 2 mm distances. The plates were electrically connected in groups of nine to create four electrodes. This analyzer was supplied with an ESI source with an orthogonal accelerator. The second prototype (II) used longer but narrower mirrors made of solid electrodes with only 220 mm separation between the caps. In this prototype, however, the number of 2D lenses was increased to 48 as shown in Fig. 7 to achieve a total effective ion flight path length of 20 m at the 2D lens array step of 12 mm. In the second analyzer an ion source was implemented with a pulsed ion ejection from a radiofrequency linear ion trap [9].

First transmission tests of the analyzer were performed with a test ion source which comprised a miniature Cs gun, a beam modulator and a focusing lens. The analyzer (prototype I) was tested in the wide range of ion kinetic energies from 10 eV up to 2000 eV using the multipass and shuttle modes of closing ion trajectories into loops. It appeared that even at low ion energies ions remained confined in the analyzer at very large path lengths. As shown in Fig. 8, at \(K = 100\) eV ion bunches retained 10 % intensity after 800 m path length, and at \(K = 2000\) eV the same result was observed after 6000 m path length. The most important factor of intensity losses was the residual gas pressure as illustrated by Fig. 8.
Experiments using the Cs gun pulsed ion source allowed to perform direct measurement of the dependence of the flight time on ion energy. This dependence is plotted in Fig. 9 for the nominal ion kinetic energy of 100 eV. Measurements confirm achieving the 3rd-order time-of-flight focusing with respect to ion energy in the analyzer. Optimal potentials at the mirror electrodes, corresponding to the demonstrated curve, differ by less than 1 % from theoretically calculated ones.

After the Cs gun source was replaced by the ESI ion source with an orthogonal accelerator, the mass resolving power of the prototype I was tested with molecular ions in different mass ranges (as test objects Aceton, Gramicidin and Insulin were used). For all these ions similar values of mass resolving power were obtained. At a single pass through the analyzer (12 m path length) the typical value of the achieved mass resolving power was about 25000–35000 at ion kinetic energy of 2000 eV and the energy spread within 5 – 6 %.
Fig. 8. Dependence of pulsed ion beam intensity on the path length inside the planar MR TOF analyzer for different values of ion kinetic energy and residual gas pressure in the analyzer.

Fig. 9. Calculated and experimentally measured dependence of the flight time of Cs ions through the analyzer (prototype I) on ion kinetic energy. Calculated curve corresponds to the 3rd-order focusing of the flight time with respect to ion energy.

To estimate the aberration limit of the analyzer, the shuttle-mode of its operation was used. In this mode the obtained limit of the mass resolving power was about 100000. As shown in Fig. 10, this limit was obtained at 2 ms flight time for Aceton ions. The corresponding peak shape is shown in Fig. 11. Note that the peak shape remained very good without prolonged tails.

Fig. 10. Dependence of the mass resolving power of the MR TOF analyzer (prototype I) on flight time measured by Aceton spectrum at ion kinetic energy of 2000 eV.
Similar results were obtained at the prototype II of the analyzer which operated with a pulsed ion source based on a linear ion trap. Tests of the source showed that it is able to form ion pulses of typical time width (FWHM) 6 ns for Gramicidin 2+ ions ($m/z = 570$) with the energy spread of 6% at ion kinetic energy 2000 eV. The ion beam diameter formed by the source was about 3 mm with a small angular divergence within 0.3 – 0.4 degree. In spite of smaller mirror window height, smaller lens array step and more frequent reflections from ion mirrors, the parameters demonstrated by this analyzer were not worse than the parameters of the prototype I. Namely, for a single ion pass through the analyzer in the full mass range mode (20 m ion path length) the value of the mass resolving power up to 50000 was achieved as illustrated in Fig. 12. In the multipass mode the highest mass resolving power of the analyzer slightly exceeded 100000 as shown in Fig. 13.

Fig. 11. Fragment of the Aceton spectrum demonstrating the aberration limit of the mass resolving power of 100000.

Fig. 12. Spectrum of Insulin recorded by the planar MR TOF analyzer (prototype II) at the full mass range operation mode (single pass through the analyzer, ion path length 20 m), demonstrating the mass resolving power of 50000.
Fig. 13. Spectrum of Gramicidin 2+ recorded by the prototype II in the multipass mode (20 full passes through the analyzer, ion path length 400 m), demonstrating the mass resolving power of 115000.

4. Conclusion

Ion-optical simulation and experimental tests of a planar MR TOF analyzer have shown high performance of its relatively simple gridless ion mirrors together with high transmission and stable operation of the analyzer. It can be concluded that the proposed principle of the device allows analyzing ions in the full mass range while achieving the values of the mass resolving power of 50000 – 100000.

References

[1] H. Wollnik and A. Casares, Int. J. Mass Spectrometry 227 (2003) 217.
[2] M. Toyoda, D. Okumura, M. Ishihara et al., J. Mass Spectrometry 38 (2003) 1125.
[3] T. Satoh, H. Tsuno, M. Iwanaga and Y. Kammei, J. Am. Soc. Mass Spectrom. 16 (2005) 1969.
[4] L.M. Nazarenko, L.M. Sekunova and E.M. Yakushev, SU Patent 1725289 A1 (1992).
[5] M.I. Yavor and A.N. Verentchikov, Nauchnoje Priborostroenie 14(2) (2004) 38.
[6] A.N. Verentchikov, M.I. Yavor, Yu.I. Hasin and M.A. Gavrik, Technical Physics 50(1) (2005) 73.
[7] A.N. Verentchikov and M.I. Yavor, Nauchnoje Priborostroenie 14(2), 46.
[8] H. Wollnik, Optics of Charged Particles, Acad. Press, Orlando, FL (1987).
[9] B.N. Kozlov, ASMS 2005 abstract (www.asms.org).