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TOF systems with two-directional isochronous motion

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ABSTRACT

A new approach for design of time-of-flight system is proposed. Unlike in conventional systems, where motion is isochronous in only one (flight) direction, new system has property of isochronous motion in orthogonal (drift) direction as well. Approach is applied for design of multi-reflecting time-of-flight system based on planar mirrors with zig-zag like trajectory. New system allows increasing flight path of the beam by order of magnitude compared to conventional systems, while keeping size of the ion mirror reasonably small. A new multi-reflecting time-of-flight system of size $500 \times 500 \times 20$ mm^3, with a flight path 20 m is designed. Simulations of ion motion in a new system show feasibility of resolving power over 50,000.

1. Introduction

Time-of-flight mass spectrometers (TOF-MS) utilise differences in flight velocity for spatial separation of charged particles on the basis of the mass-to-charge ratio (m/z) and consequent mass analysis [1]. Typical TOF system consists of pulsed ion source, some ion optical system and detector. Ion source produces pulses of ions of different m/z with substantially similar energy within some relatively small energy range. It is essential that ions of different m/z start from the source at the same time, which serves as a reference point for measurement of flight time. Latter is measured by ion arrival time at the detector, where point-charge detectors such as MCP or ETP are used. Purpose of ion optical system is to compensate for differences in flight time for ions of the same mass-to-charge ratio, but different flight energy. This can be achieved with the use of ion-mirrors. After leaving the source ion packets expand along the flight axis due to differences in initial flight energy. Arriving at the ion mirror, ions of higher energy penetrate into the mirror deeper than ions of lower energy and thus travel longer path. As a result ions of different energy arrive at the detector simultaneously. One can imagine this as a shooter, who simultaneously shoots many bullets of the same size but different initial velocity and all bullets arrive at the target at the same time. This trick is done by ion mirror and referred in literature as a space-energy focusing [2].

Typical size of TOF system is 1 m and usual flight energy is in the range below 10 keV, thus flight times of ions range from tens to hundreds micro-seconds (μs) depending on their m/z values. As a result TOF-MS can perform single mass analysis of a wide mass range within several hundred micro-seconds. No other mass-analyser is capable of such fast analysis, not even close. Another advantage of TOF-MS is the use of point-charge detectors which are potentially capable of detecting single particles. Leaders of mass spectrometry to date are Fourier's transform ion cyclotron (FTICR) [3] and Orbitrap [4] mass analysers. Both use image charge detection of ion vibration in a trap with recording of long time-domain signal and consequent Fourier's transform analysis in order to derive characteristic frequencies of ions and recover mass spectrum. Resolution of such analysers is directly proportional to the length of time-domain signal and for resolving powers of 100,000 is in the range of milli-seconds. Image charge detection method also has a threshold of detection of about 100 charges [5]. Thus both FTICR and Orbitrap mass analysers are inferior to TOF-MS in terms of analysis speed and detection threshold. Provided that resolving power of TOF is increased to the same level as in FTICR (1 million), they will become ideal instrument for mass analysis.

This paper discusses factors which affect the resolving power of TOF mass analysers and in particular physical limitation by so-called turn-around-time. Different approaches to overcome this physical limitation are described and compared. Among them mass analysers with unlimited mass range are preferable. Such mass analysers are based on planar mirrors, where ions follow zig-zag like trajectory with many reflections and slow drift along mirrors. Ensuring beam stability in drift direction in such systems is a problem. This problem can be efficiently solved using new approach for design of TOF systems: requirement of isochronous motion in two directions, direction of flight and drift direction simultaneously.

Equations of ion motions and general properties of new systems are considered. Further discussion is restricted for systems with substantially different energies in flight and drift directions. A new multi-reflecting time-of-flight system based on requirement of isochronous motion in two directions simultaneously is designed.

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While keeping size of system reasonably small ($500\times500\times20$ mm) flight path is increased by order of magnitude (20 m) compared to conventional TOF systems. Performance of new system is further investigated by means of simulations. Ion tracing shows feasibility of resolving power over 50,000.

2. Resolving power of TOF-MS

Mass resolving power of TOF analyser is given by equation

$$R=\frac{M}{\Delta M}=0.5\frac{T}{\Delta T} \tag{1}$$

where M is a nominal mass of ion and ΔM is width of mass peak. Due to relation between ion mass and velocity V at nominal flight energy K_0: $V=\sqrt{2K_0/M}$, for a fixed flight path L of the TOF, the resolving power is directly translates into actually measurable parameters: total flight time $T=L/V$ and time duration of ion pulses on the detector ΔT (see Eq. 1). Main contributions to the pulse width ΔT are: response time of the detector—$\delta t_{Detector}$, time spread due aberrations of ion optical system $\delta t_{Aberration}$ and so-called turn-around-time δt_{turn}. Assuming that those factors are statistically independent, the pulse width is defined by the following equation

$$\Delta T=\sqrt{(\delta t_{Detector})^2+(\delta t_{Aberrations})^2+(\delta t_{turn})^2}. \tag{2}$$

Modern detectors are very fast and response time of about 100 ps is feasible. Regarding aberrations, there are no limits for human ingenuity in developing designs of ion optics that as small aberrations as required. For some time researchers believed that by addressing those two factors the resolving power of TOF may be increased as much as possible. Further investigations and experimental evidence revealed that turn-around-time imposes physical limit on increasing the resolving power of TOF systems.

Physics behind turn-around-time can be understood on the basis of very simple considerations. Pulsed sources in TOF utilise ejection of ions from pulsar by fast rising high voltage pulses. Fig. 1 shows schematic of such pulsar with grounded electrode and grid at voltage—U_0. Ions inside pulsar always have some random spread of initial velocities due to temperature. Fig. 1 shows two ions of the same mass m and charge e denoted as "1" and "2". They have similar initial velocities V_0, but ion "1" has velocity V_0 along flight direction (x), while ion "2" has initial velocity in opposite direction. Upon application of ejection voltage—U_0 both ions experience acceleration from uniform electrical field:

$$a=\frac{eE}{m}=e\frac{U_0}{dm}. \tag{3}$$

Ion "1" immediately starts to acquire velocity in positive x direction, while ion "2" needs some time to reverse velocity in positive direction. This time is given by

$$t_{turn}=\frac{2V_0}{a}=\frac{2mV_0}{eE}. \tag{4}$$

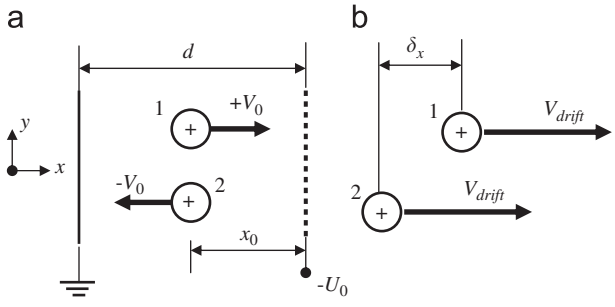

Fig. 1. Turn-around-time in TOF-MS.

After undergoing acceleration through the grid both ions have the same flight velocity V_{flight}, which is derived from conservation laws:

$$V_{flight}=\sqrt{V_0^2+\frac{2eEx_0}{m}}=\sqrt{V_0^2+\frac{2eUx_0}{md}}. \tag{5}$$

Fig. 1b shows, after leaving pulsar, the two ions travel with the same velocity V_{flight}, but at some distance from each other δx. The distance appears due to turning time of the second ion and equals

$$\delta x=V_{flight}t_{turn}. \tag{6}$$

These two ions are identical in terms of mass, charge and drift velocity. Therefore there is no means to distinguish these ions by means of any electrostatic ion optics. They will arrive at the detector having the same distance δx between each other, which immediately transforms into arrival time difference t_{turn}. This time difference contributes to the total width of ion pulses from corresponding ions.

In case when velocities of ions satisfy the Maxwell distribution, X component of ion velocity has normal distribution with standard deviation $\sigma=\sqrt{kT/m}$, where k is the Boltzmann constant and T is temperature. It is known from statistics that 68.2% of particles with normal distribution appear within the range $[-\sigma,+\sigma]$ near average. Consequently half width of ion peak due to turn–around–time can be estimated with good accuracy by following equation:

$$\delta t_{turn}=\frac{2m\sigma}{eE}=\frac{2dm}{eU_0}\sqrt{\frac{kT}{m}}. \tag{7}$$

Let's assume that ions start from the middle of pulsar: $x_0=0.5d$. The flight energy is $0.5eU_0$ and therefore flight velocity $V_{flight}=\sqrt{eU_0/m}$. Flight time for the total path L equals $T=L/V_{drift}$. Finally using Eq. (7), we obtain equation for maximum resolving power of TOF as follows:

$$R\le0.5\frac{T}{\delta t_{turn}}=\frac{L}{4d}\sqrt{\frac{eU_0}{kT}}. \tag{8}$$

For typical TOF parameters: $L=2$ m, $d=10$ mm, $U_0=10$ keV and temperature 300 K, from Eq. (8) we obtain maximum resolving power $R\le31{,}000$. Even such resolving power is rarely reached in commercial instruments due to misalignments, voltage instabilities, scattering of ions on residual gas and even roughness of the detector surface.

Here turn-around-time is explained using simple model of two particles. It can be shown that this limitation arises from conservation of phase space area according to the Liouville theorem. It imposes upper level on resolving power of conventional TOF mass spectrometers.

3. Ways to improve resolution. Multi-reflecting and multi-turn systems

Idea of increasing flight time for improving resolving power is very simple; it follows directly from Eq. (1). A number of optical schemes for this have been proposed. Pioneer in this field is Prof. Wollnik, who suggested and realised [6] a multi-reflecting system based on two axially symmetric mirrors. Ions are injected from one side and experience multiple reflections between mirrors before being ejected into the detector. Quite different implementation of similar idea is a system of Toyoda et al. [7], where ions travel 8-shaped trajectory many times in a system of sectors and quadrupoles. Although very high resolving power can be achieved, such systems allow measurements of only narrow mass range at a time. While heavy ions are making N turns along looped trajectory, ions of smaller mass catch up and overlap. Without overlapping the mass range of such devices is