# ToFMS: Some Basic Concepts and Applications

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## 15.1 Introduction

A mass spectrometer is a device which identifies atoms and molecules from their mass-to-charge ratios (m/z's), where m is mass and z is integer number of charges. Time-of-flight Mass Spectrometer (ToFMS) is one such instrument and is based on the most fundamental underlying concept: Every ion has a unique flight time. One way of measurement of flight time is to move the ion in an electric field and record its flight time. In a real MS, the zero time starts with a laser pulse which creates ions between two electrodes (one having an aperture for ion motion) with applied voltages and ends when the ion flies a fixed distance and strikes the detector, a Microchannel Plate (MCP). Often a HV pulse applied to one of the electrodes acts as the start time. Moreover, the flight time is dependent on energy to which the ion is accelerated and the distance it travels as well as its m/z and is described in sectn. 15.2. Such time measurement is a pulsed event and hence a ToFMS is well suited for its use in conjuration with a pulsed laser which is commercially available. However, with tunable lasers one realizes Resonance Ionization Spectroscopy (RIS) and thus with conjunction of lasers and a mass spectrometer the method is called Resonance Ionization Mass Spectrometry (RIMS) — a very powerful technique to address many challenging applications, such as, spectroscopy of atoms and molecules, ultra-trace detection, nuclear forensic analysis, Laser Isotope Separation for atomic species [158], production of ultra-pure substances, studies of exotic nuclei, etc. In principle, the resonance ionization/photoionization (PI) relies on the tunable lasers at different resonant wavelengths whereby the atoms (molecules) are selectively excited stepwise, and finally ionized. The other associated important aspects of RIMS are the following:

- The requirement of laser power is reduced drastically, which not only simplifies the apparatus but also reduces the possible emissions from background ions;
- The selective PI enables ions of low- and very low-concentration components of the sample to be efficiently produced without the ionization of others.
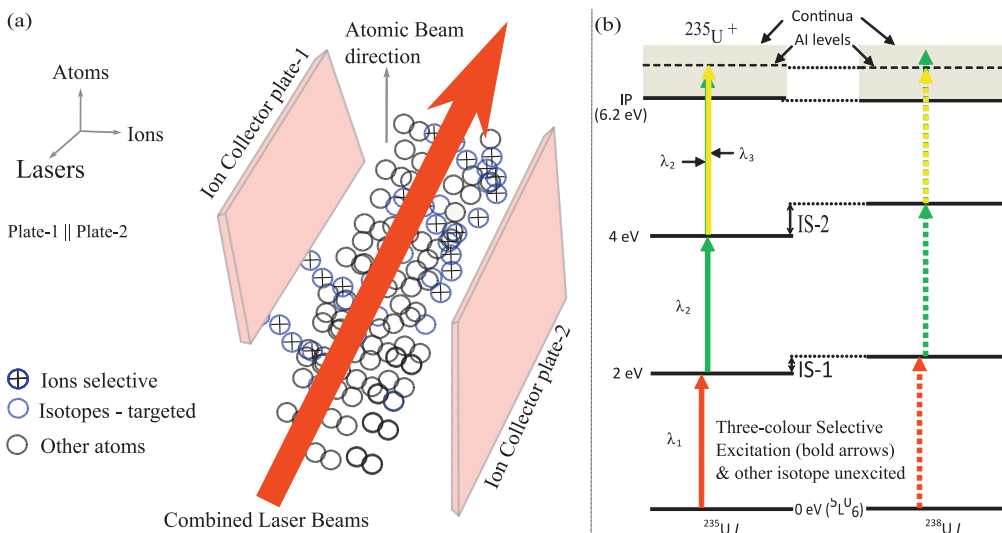
Figure 15.1: a) Typical Schematic of RIS & b) three-step selective PI of isotope of interest.

Conventionally, in RIMS setup mass spectrometers like, magnetic-sector, quadrupole and recently ToFMS are well adapted. Out of all these, the ToFMS in combination with pulsed lasers is one of the best suited from the following key points:

- Simplicity in design, mounting, handling and operation [159];
- Higher throughput, fairly high mass resolution, theoretical unlimited mass range and its independence on observed signal-to-noise ratio (SNR);
- Simultaneous measurement of all m/z's improves significantly the detection speed and sensitivity, which ensures that there is no loss in very precious information, and also
- It is made easier to identify the analytes as well as interpret the measurements.

With so many significant aspects and possibilities, a strong impetus is always there to indigenously design, develop, and customize the instruments. Seven distinct setups with various configurations were developed some of which are the following:

i) Linear,

ii) Reflectron and

iii) Compact reflectron.

Depending on the requirement, they can be used in applications of RIS (Fig. 15.1a) in atomic systems, which in simple terms, require a dense vapour of atoms, from which the isotope of interest is selectively ionized by lasers and the resulting ions are collected. Thus, knowledge of the basic physical parameters governing the interaction between the laser and the isotopes to be separated are very important and employing RIMS based spectroscopic studies of atoms most of these are precisely measured, e.g., radiative lifetimes, autoionization (AI) levels, excitation and AI cross-sections, low- and high-lying level Isotope shifts (ISs), etc. Then, from these parameters one can constitute various photoionization schemes (PISs) (Fig. 15.1b) and the highly isotope-selective and most efficient ones are used in RIS. To start with the description, the basic aspects of ToFMS and is discussed below.

## 15.2    Basic Concepts of ToFMS

The ToFMS operation principle is that a packet of ions of various m/z's are accelerated to the same final energy ($U_T$), which implies that the ions will have different velocities because of their differences in mass and thus will require different flight times to traverse a set distance. After acceleration and passage through the field-free region in drift tube, the ions strike an ion detector and result in a temporal output, representing the complete mass spectrum, which is an intensity vs. flight time plot. From the fact that the respective flight time is directly proportional to square root of m/z, one determines its constituent species. This way of operation of ToFMS is called as constant-energy mode [160]. The equations of motion are formulated as follows.

### 15.2.1    Mathematical descriptions

The ion motion in a system consisting of uniform electric fields can be deduced using the basic physics laws: Newton's second law of motion, i.e., Force ($\vec{F}$) = Mass (m)×Acceleration ($\vec{a}$) and energy conservation, i.e., for any conservative system the sum of potential and kinetic energies is constant. Also, in presence of electric field ($\vec{E}$), a charged particle of charge, q (= ze) experiences force, $\vec{F}$ (= q$\vec{E}$) and energy, U (= sqE, with E = $|\vec{E}|$) at position, $s$. Consider the schematic diagram (Fig. 15.2), where the positive ions are formed by PI of atoms using laser(s) at the interaction region that then travel towards right, as $V_1 > V_2$, and $E_d > E_s$. The interaction region has a small spatial spread $\Delta s$, centered about a mean
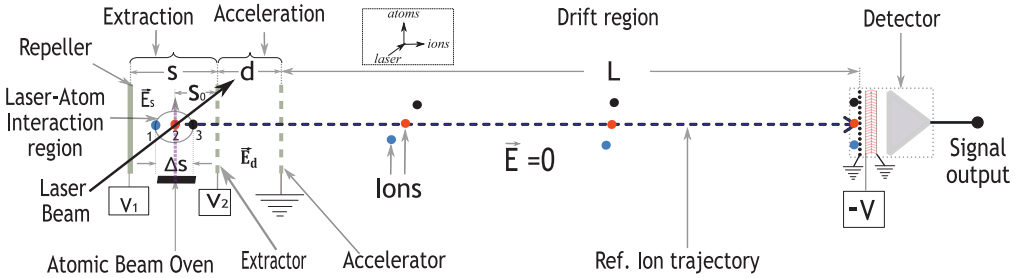


Figure 15.2: Schematic diagram of a ToFMS.

position $s_0$. Consider the three isomass ions labeled 1, 2 and 3, at positions $s_0 + \Delta s/2$, $s_0$, and $s_0 - \Delta s/2$ respectively. As such, the ion 1 travels the longest path while ion 3 travels the shortest path. Hence, the ToF of these ions will be different, with highest velocity change is for ion 1, and the consequent increase in velocity will enable it to catchup with the ions having shorter flight paths. As the ions move, the electric potential energy is converted to kinetic energy, and for all three ions, it can be written as: $\Delta U = \left(s_0 \pm \frac{\Delta s}{2}\right) zE_s$, where $\Delta U$ and $E_s$ are the change in energy and the extraction field respectively. It is possible that the isomass ions are at same time at a downstream distance. The point (plane) of 'catch-up' is called spatial-focusing, which corrects for initial spatial spread and is synchronous in time, as the isomass ions pass first-order, primary space-focus (SF).

**Derivation of the basic equations:**

1. For extraction region, $s$, From $F = ma$, (without using vector notations), one gets,
   $qE_s = ma_s => a_s = \frac{qE_s}{m}; \ s = \frac{1}{2}a_s t_s^2 => t_s = \sqrt{\frac{2s}{a_s}}$
   $=> t_s = \sqrt{\frac{2ms}{qE_s}};$

2. For acceleration region, d: $a_d = \frac{qE_d}{m}$, one can use the equation, $t_d = \frac{v-u}{a_d}$;

   where $u$ is the velocity in region s, $u = \sqrt{\frac{2qsE_s}{m}}$ $[\because \frac{1}{2}\text{m u}^2 = qsE_s]$ &

   $v$ is the velocity in region d, such that, $v = \sqrt{\frac{2U_T}{m}}$ $[\because \frac{1}{2}mv^2 = U_T]$

   $\Rightarrow t_d = \frac{\sqrt{2m}\left(\sqrt{U_T}-\sqrt{qsE_s}\right)}{qE_d}$.

3. However, for the drift region: $t_L = \frac{L}{v} = L\sqrt{\frac{m}{2U_T}}$.

## 15.2.2   Spatial focusing

In case of a simple system of one-stage extraction or acceleration, the space-focus point is $L_{SF} = 2s_o$, with d = 0, in Eq. (15.6). Moreover, this point is very close to the starting of the drift tube and hence temporal separation of different m/z's, which is achievable after passage through a long drift region, is difficult. However, a better option is considered, which employs, dual-stage ionization/ extraction region consisting of three electrodes. The resulting electric fields in three-regions are:

a) Ionization source/ extraction region s, $E_s = (V_1 - V_2)/s$;

b) Acceleration region d, $E_d = V_2/d$ and

c) Drift region L, E = 0 (Fig. 15.2).

Again, considering the case of isomass ions without any initial kinetic energy, an ion formed in the source region at a position s is accelerated by both the extraction and acceleration fields to acquire total energy $(U_T) : U_T = qsE_s + qdE_d$. The total ToF $(T_{TOT})$ is therefore comprised of three parts: source $(t_s)$, acceleration $(t_d)$, and drift $(t_L)$ as follows:

$$t_s = \frac{\sqrt{2m}}{qE_s}\sqrt{qsE_s} \tag{15.1}$$

$$t_d = \frac{\sqrt{2m}}{qE_d}\left(\sqrt{U_T} - \sqrt{qsE_s}\right) \tag{15.2}$$

$$t_L = L\sqrt{\frac{m}{2U_T}} \tag{15.3}$$

Therefore, adding each contribution, one realizes the benchmark Wiley-McLaren [160] ToF equation for spatial focusing:

$$T_{TOT}(U_0 = 0, s_0) = \sqrt{\frac{m}{2\,U_{TOT}}} \times \left(2\,s_0\,k_0^{\frac{1}{2}} + \frac{2\,d\,k_0^{\frac{1}{2}}}{k_0^{\frac{1}{2}} + 1} + L\right) \tag{15.4}$$

where $k_0 = \frac{s_0\,E_s + d\,E_d}{s_0\,E_s}$. Equation (15.4) depicts dependence of total ToF on the initial position where ions are formed. After calibrating the spectrometer once, the flight time of the isomass peaks in the recorded spectrum are measured and the corresponding mass can be identified by employing Eq. (15.5).

$$m(LTOF) = \frac{2\,U_{TOT}}{\left(2\,s_0\,k_0^{\frac{1}{2}} + \frac{2\,d\,k_0^{\frac{1}{2}}}{k_0^{\frac{1}{2}} + 1} + L\right)^2}T_{TOT}^2 \tag{15.5}$$

Differentiating Eq. (15.5) w.r.t. initial position $((dT(0, s_0))/ds = 0)$ yields space focus $L_{SF}$.

$$L_{SF} = 2s_0 k_0^{\frac{3}{2}} \times \left(1 - \frac{1}{k_0^{\frac{1}{2}} + k_0}\frac{d}{s_0}\right) \tag{15.6}$$

In a linear ToF geometry, the space focus is varied by manipulating the $E_d/E_s$ ratio, so that $L_{SF}$ coincides with the detector plane. This way, the initial spatial distribution is minimized, but there are other resolution-limiting factors as discussed in section 15.2.3. Figure 15.3 shows the variation of $L_{SF}$ w.r.t. the field ratio $E_d/E_s$. Further, the second derivative to determine if this ToF is maximum or minimum, results:

$$\left(\frac{d^2T}{ds^2}\right)_{(0,s_0)} = \frac{d}{s_0} - \frac{k_0-3}{k_0}\frac{L}{2s_0} \tag{15.7}$$

This is called the second focusing condition and $T(0,s_0)$ is maximum for $k_0 > 3$. The equations discussed above can be used for any specific instrument to determine ToF accurately with the given inputs of distances, voltages, and initial conditions. In general terms, such calculation accuracy is limited only by uncertainties in the precise values of the input parameters and also by the extent to which the simplified one-dimensional model represents the real three-dimensional instrument. However, there is three-dimensional simulation program like SIMION [161] to numerically simulate ion trajectory and generate the mass spectrum for the element (Fig. 15.4) in a mass spectrometer. Apart from these, some other aspects that need to be considered to further improve the resolution of a ToF machine and are discussed next.
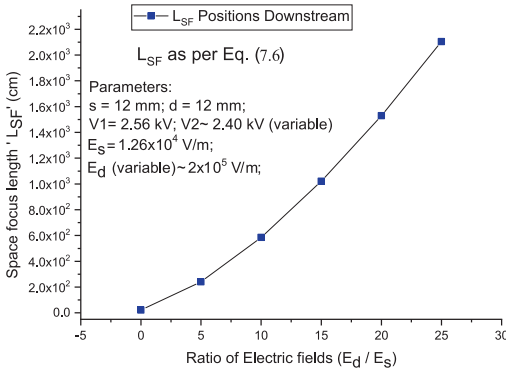


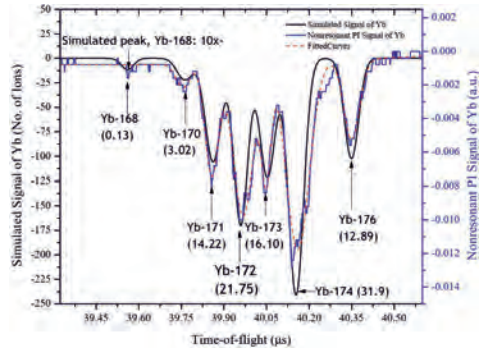Figure 15.3: Variation of $L_{SF}$ vs. $E_d/E_s$.

Figure 15.4: Typical simulated mass spectrum.

## 15.2.3    Mass resolution and improvements

The resolution in ToFMS is defined in terms of both mass and time by Eq. (15.8) below [162]:

$$R = \frac{m}{\Delta m} = \frac{T_{TOT}}{2\Delta t} \approx \frac{L}{2\Delta x} \tag{15.8}$$

where $\Delta m$ and $\Delta t$ represent the respective mass and temporal FWHM heights of the observed mass peak; L is the distance to be flown and $\Delta x$ is the ion packet thickness approaching the detector. Equation (15.8) also suggests, to increase resolution, one can lengthen the flight tube, as the resolution is proportional to both flight time and flight path. However, too longer flight tubes can also deteriorate the ToFMS performance, because of angular dispersion of the ion beam as well as loss of ions by scattering after collisions with gas molecules. Similarly, it is also possible to enhance ToF by lowering the acceleration voltage. But, by lowering this voltage the sensitivity is greatly reduced. Therefore, flight tube of about 1-2 m for high resolution and high acceleration voltages for high sensitivity are the optimal choice. The

mass resolving power is limited by other contributions to total ToF error as described below [162]:

$$\Delta t = \sqrt{\Delta t_p^2 + \Delta t_I^2 + \Delta t_g^2 + \Delta t_e^2 + \Delta t_d^2 + ... + \Delta t_v^2} \qquad (15.9)$$

Here, $\Delta t_p$ is due to an imperfect 'McLaren space focus' [160], which occurs downstream from the ion acceleration region, $\Delta t_I$ and $\Delta t_g$ are time errors in electrostatic lenses and grids, $\Delta t_e$ is due to unstable power supplies, $\Delta t_d$ is the signal width of the detection system and $\Delta t_v$ is due to initial thermal ion velocity or the 'turnaround time' as described by Price and Milnes [163]. This turn-around time is often the most important time error, $\Delta t_v = \frac{2mv_0}{zE}$, with $v_0$ as initial velocity, which is mass dependent. The most detrimental factor to resolution is the broad initial kinetic energies distribution (velocities) of isomass ions, which can be efficiently tackled by a reflectron [164] having apertured electrodes with gradually increasing fields. The faster the ion, it penetrates deeper into the repelling electric field of the reflectron, and in turn travels a larger distance. When the faster and slower ions come out of the reflectron, they catch each other thereby achieving energy focusing. In addition, there are advanced strategies like ion-mass gate, orthogonal acceleration ToF that can be implemented which depends on the requirement. However, as per present scope, applications in RIS are discussed below.
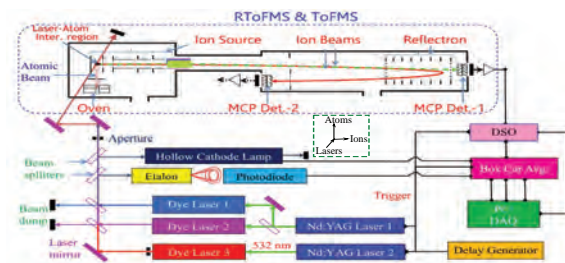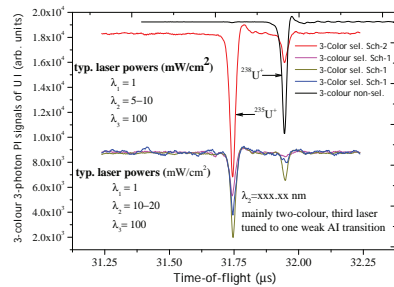


Figure 15.5: Typical three-colour RIMS setup.



Figure 15.6: Typical three-photon three-colour PI signals U I.

## 15.3   ToFMS Based RIMS and Applications

The applications enlist the various possibilities with atomic beam-based RIMS setups (Fig. 15.5, having three tunable dye lasers and its subcomponents, e.g., Spectroscopy of atoms: energy level positions and their J-values, parities, isotope shifts, radiative lifetimes, cross-sections, hyperfine structures and most of the fundamental parameters. From these investigations, it is possible to construct three-step three-colour PISs. These PISs are further studied for High Isotopic Selectivity to choose the best one and also to ensure the respective three-step laser wavelengths, powers and linewidths, stability, suitability of tunable (dye) lasers as well as other parameters for applications. A typical selectivity plot (Fig. 15.6) for different signals with various wavelength combinations is shown for an element having isotope of 0.72% (natural abundance) along with its major counterpart having 99.27%. In addition to this, before the actual process, validation of PIS, thereby monitoring of laser wavelengths and powers, can be done through RIMS. Also, in the process, after laser-atom interaction, the output laser beam (which is otherwise going to beam dump) maybe used to monitor the actual process selectivity which is truly online.

## 15.4   Summary

The important underlying design aspects of ToFMS are discussed. The related important one-dimensional equations of ion motion are presented and as a better approach the three-dimensional SIMION ion optics simulations can be performed which can be experimentally validated. This machine as part of a RIMS arrangement is used in spectroscopy and most significantly in isotope selective processes. Moreover, the existing compact instrument can be made further compact, and extended to miniature MS development for use in portable RIMS setups to realize in situ and on-field applications. Lastly, it is need of the hour to sync with the recent advances in ToFMS instrumentation, which is concentrating on new approaches that are directed to further modernize the present performance and unravel some of the yet-unrealized capabilities of the technique.

## Frequently Asked Questions

Q1. What are linear and reflectron ToFMSs and their advantages over other MSs?

Q2. What are spatial and energy focusing in a ToFMS?

Q3. What is resolution in a ToFMS and how to improve?

Q4. What is RIMS and why it is so important for isotope selective processes?

Q5. What is isotopic selectivity?

Q6. Derive the three basic ToF Eqs. (15.1)-(15.3).

Q7. What is numerical value of typical ion energy in ion source for ref. ion-2 (Fig. 15.2)?

Q8. What are numerical values of flight times in each region and total ToF for ref. ion-2?

Q9. Derive expression for mass resolution from ToF equation.