



# Wide-band mass measurements with a multi-reflection time-of-flight mass spectrograph



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## ABSTRACT

We characterize the mass bandwidth of the multi-reflection time-of-flight mass spectrograph, showing both the theoretical and effective mass bandwidth. We then demonstrate the use of a multi-reflection time-of-flight mass spectrograph to perform mass measurements in mass bands much wider than the mass bandwidth.

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## 1. Introduction

The multi-reflection time-of-flight mass spectrograph (MRTOF-MS), first proposed more than 20 years ago [1], uses a pair of electrostatic mirrors to compress a flight path of several hundred meters (or even many kilometers in some cases) within a reflection chamber of  $\approx 1$  m length. With properly designed ion traps to quickly prepare ions, the MRTOF-MS can achieve mass resolving powers of  $R_m > 10^5$  while operating at rates of 100 Hz or more [2–4].

In recent years, these devices have begun to prove useful for online measurement of nuclear masses [5,6]. The technique has been demonstrated to be able to accurately provide mass precision on the level of  $\delta m/m \sim 5 \times 10^{-7}$  or better. With its ability to achieve very high mass resolving powers while operating with very low intensities, the MRTOF-MS could become a useful instrument for analytical chemistry.

However, the multi reflection nature of the measurement has, thus far, made analysis of rich, wide-band mass spectra difficult or impossible. Starting with a detailed exploration of the mass bandwidth of the MRTOF-MS, we have developed a technique that allows simple analysis of even wide-band mass spectra using the MRTOF-MS. Employing such an analytic method, we believe the device could eventually provide wide-band measurements of nuclear masses much in the way of storage rings [7]. The device could similarly be useful in analytic chemistry, providing

wide-band analysis much like FT-ICR Penning traps, but with a much greater sensitivity.

## 2. MRTOF-MS technique

The MRTOF-MS begins with an ion trap to prepare ions as well-cooled pulses [3]. Ion pulses extracted from the trap are then transferred to the reflection chamber. The reflection chamber consists of a pair of electrostatic mirrors, a lens, and a field-free drift region. The outmost electrode of each mirror is switchable, allowing ions to enter and leave the reflection chamber. A multichannel plate (MCP) ion detector is mounted after the reflection chamber (Fig. 1).

The signal to extract ions from the trap also serves as the start signal for a time-to-digital converter (TDC). The potential on the outermost electrode of the injection-side mirror is reduced by  $\approx 1$  kV a few microseconds prior to issuing the signal to extract ions from the trap. Ions then enter the reflection chamber, travel to the ejection-side mirror turning-point and return toward the injection-side mirror. The potential on the outermost electrode of the injection-side mirror is returned to its nominal value before returning ions come close enough to sample the changing electric field. Ions will then reflect between the mirrors until the potential of the outermost electrode of the ejection-side mirror is reduced. Ions then will pass out of the reflection chamber and travel to the MCP, the signal from which serve as stop signals for the TDC. The time of flight, given by the time between start and stop signals, is recorded and the cycle is repeated until sufficient statistics have been accumulated.

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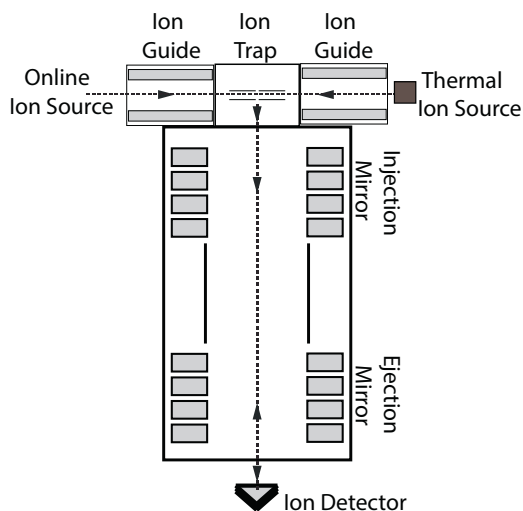


Fig. 1. Sketch of the MRTOF with ion source and preparation trap. Not to scale.

The time at which the ejection-side mirror is opened is chosen by using

$$t_{\text{eject}} = t_{\text{eject}}^{(0)} + nB \quad (1)$$

where  $B$  is the circulation time of the central species of interest and  $t_{\text{eject}}^{(0)}$  is chosen to ensure the ions are not too close to the ejection mirror at the time of ejection, as such would lead them to sample a changing electric field. For a chosen set of  $t_{\text{eject}}^{(0)}$  and  $B$ , one can produce a set of spectra for some range of  $n$  and produce a 2D color relief plot of counts against lap number  $n$  and ToF, a so-called “ $n$ -vs-ToF plot”, as shown in Fig. 2.

From such a figure, we can easily see that after not so many laps ions with mass differing by a couple percent start to make different numbers of laps. We can also see, at the edges of the plot, the deleterious effect of the switching ejection electrode on nearby ions. These effects will be discussed in detail in Section 3.

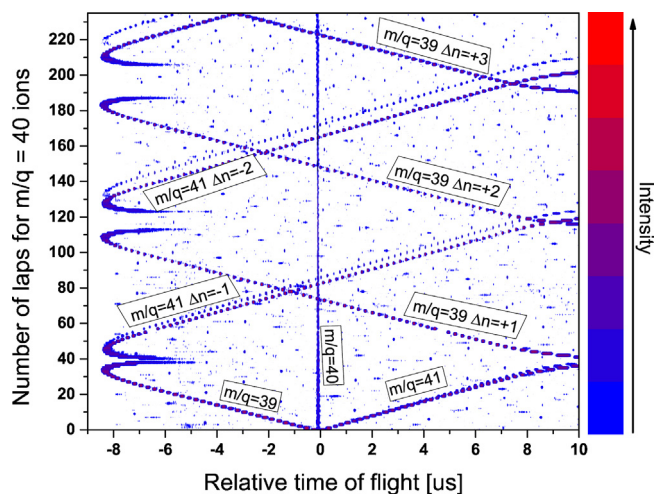


Fig. 2.  $n$ -vs-ToF plot centered on  $m/q = 40$  ions demonstrating ions of various masses making unequal numbers of laps. Each spectrum in the plot represents 10 min of accumulated spectra. It is worth noting that the molecular isobars with  $m/q = 41$  become separated by  $n = 50$  laps. The  $m/q = 39$  and 40 ions are  $^{39}\text{K}^+$  and  $\text{NaNH}_3^+$ , respectively, while the  $m/q = 41$  ions are  $^{41}\text{K}^+$  and  $\text{NaNH}_2\text{O}^+$ . The “noise” peaks in the  $n$ -vs-ToF plot are caused by ions with  $m/q$  very different from the central value.

The mass of an unknown species can be determined from a single species of reference ion that has traveled a flight path identical to the unknown ion species as

$$m = m_{\text{ref}} \left( \frac{t - t_0}{t_{\text{ref}} - t_0} \right)^2, \quad (2)$$

where  $t$  and  $t_{\text{ref}}$  are the times of flight of the unknown species and the reference, respectively, and  $t_0$  is the delay between TDC start signal and actual extraction of ions from the trap. This method has been verified to achieve relative mass precision of  $\delta m/m \leq 5 \times 10^{-7}$  [6] with only a few hundred ions. However, Eq. (2) requires that the reference and unknown species have both made the same number of laps in the reflection chamber. As can be seen from Fig. 2, due to a limited mass bandwidth it is often the case that peaks in a given spectrum are associated with ions that made  $n + \Delta n$  laps while the reference species made  $n$  laps. A means of accurately analyzing such peaks in a spectrum would be very useful.

### 3. Mass bandwidth

Ions moving in the MRTOF-MS can be described in terms of runners on a circular track, whose speeds are determined by their  $A/q$  ratio. After some number of laps, the faster (lighter) ones will overtake and “lap” the slower (heavier) ones. The fraction of  $m/q$  that is making the same number of laps is what we call the theoretical mass bandwidth of the MRTOF-MS.

Once all ions in a spectrum are no longer making identical numbers of laps in the MRTOF-MS, analysis can become difficult. The difficulty largely arises from ambiguities being introduced due to the differing lap numbers, resulting in the peaks no longer being ordered. For instance, consider analysis of natural Potassium. As long as the mass bandwidth of the MRTOF-MS is wider than 5%, the MRTOF-MS can be operated such that the peaks corresponding to  $^{39,40,41}\text{K}^+$  will be arranged with a monotonic relationship to mass. However, if the MRTOF-MS is operated with any smaller mass bandwidth, e.g. 4%, the device cannot be operated such that ordering of the peaks will be arranged with a monotonic relationship to mass. Specifically, the order of the peaks will be some permutation of  $\{39, 41, 40\}$  (see Fig. 2).

Because of this reordering, without sufficiently limiting the mass band sent into the MRTOF-MS, one cannot presume that the ions corresponding to peaks with a larger time-of-flight have a larger mass (or more precisely  $m/q$ ) than those corresponding to shorter times-of-flight. This prevents use of analysis by mass differences [8,9] as well as other straight forward analysis techniques used to identify unknown peaks.

At the same time, it is generally ill-advised to overly limit the mass bandwidth prior to the MRTOF-MS. Doing so reduces the sensitivity and increases the amount of analyte required. Thus, a discussion of the mass bandwidth is a useful endeavor.

#### 3.1. Theory

The time required to travel from the trap to the detector and make  $n$  laps in the MRTOF in the interim can be written as

$$t^{(n)} = t^{(0)} + bn\sqrt{m} = (a + bn)\sqrt{m} = (\zeta + n)b\sqrt{m} \quad (3)$$

where  $t^{(0)}$  is the time required to travel from trap to detector without any reflections,  $m$  is the ion mass (or mass-to-charge ratio),  $b$  is a constant given by  $\oint ((dl)/(\sqrt{2K}))$ , corresponding to the circulation time of a unit mass and  $a$  is a constant similar to  $b$  and given by  $\int_{\text{trap}}^{\text{detector}} ((dl)/(\sqrt{2K}))$  for ions that make no reflections, and the ratio  $\zeta = a/b$  is almost constant for any particular given voltage configuration of the MRTOF-MS.  $K$  is the kinetic energy of the ion, determined by the electric fields of the reflection chamber,

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