TOF-Disentanglement Concept

Internal Paper

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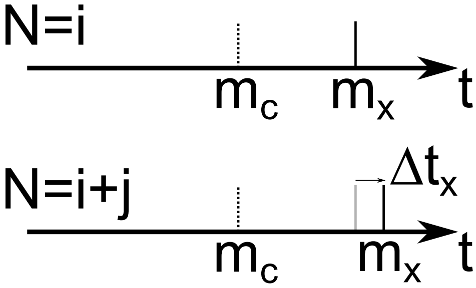

Figure 1: scheme of a tof-spectrum. m_c is a calibrant that is known in mass and flight time. In this approach, a virtual calibrant is used by using the scaling mass of the analyser. m_x is an unkown mass. The second measurement is done with m_c taking j more turns than in the first. The difference in position of m_x is called Δt_x.

Introduction

Identifying mass lines in a MR-TOF-MS spectrum can be troublesome as ions can do a different amount of reflections (turns). In a tof-spectrum their position will be folded onto other ion's positions obfuscating the actual flight time and thus making the identificaton difficult.

Goal of this Disentanglement approach is to use two measurements with deviating turn numbers of a calibrant to identify ions with unknown masses and turn numbers.

Idea

Typically in our MR-TOF-MS measurements a mass m_c is chosen to be centered time-wise in the analyser when the reflector opens. Increasing the delay until the reflector opens by a multiple i of the time this centered mass needs for one turn $t_{c,turn}$ will create a spectrum with increased resolving power (*spectrum with i turns*). In this spectrum, ions with different masses from m_c will drift away from m_c's position depending on their mass.

Calculations

If we compare two measurements with different turn numbers i and $i+j$ of m_c (fig.1), we get a deviation in time Δt_x for m_x. The deviation in time of m_c is

$$\Delta t_{c,total} = j \cdot t_{c,turn}$$

and for m_x it is

$$\Delta t_{x,total} = j \cdot t_{c,turn} + \Delta t_x \quad .$$

Furthermore we assume that the increase in flight path of both ions is the same:

$$\Delta x_{total} = j \cdot x_{turn}$$

With x_{turn} the flight path of a single turn.

Now we can calculate the velocity of both ions by dividing:

$$v_c = \frac{\Delta x_{total}}{\Delta t_{c,total}} = \frac{\Delta x_{turn} \cdot j}{t_{c,turn} \cdot j}$$

$$v_x = \frac{\Delta x_{total}}{\Delta t_{x,total}} = \frac{\Delta x_{turn} \cdot j}{t_{c,turn} \cdot j + \Delta t_x}$$

Since all ions were accelerated with the same kinetic Energy, the following relationship can be found for any mass inside a measurement:

$$eU = \frac{1}{2} m_l v_l^2$$

This means that m_c and m_x have the following relationship:

$$\frac{eU}{eU} = \frac{\frac{1}{2} m_c v_c^2}{\frac{1}{2} m_x v_x^2} \quad \Rightarrow \quad m_x = m_c \cdot \frac{v_c^2}{v_x^2}$$

Inserting v_c and v_x the following equation can be found:

$$m_x = m_c \cdot \left(\frac{t_{c,turn} \cdot j + \Delta t_x}{t_{c,turn} \cdot j} \right)^2$$

Application

Investigating two measurements[1] of Rn with $m_c = {}^{211}$Pb yields the following parameters:

$$i = 0, \qquad j = 8$$
$$m_c = 210.9882\,\mathrm{u}, \qquad t_{c,turn} = 45.556\,\mathrm{\mu s}$$

Three different masses were identified prior to this approach and now compared with the result of the previously described method:

Δt_x[µs]	$m_{x,calc}$[u]	element	$m_{x,lit}$[u]	$\frac{\Delta m}{m_{lit}}$[%]
6.838 98	218.9810	^{219}Rn	219.0089	0.0127
−0.022 97	210.9616	^{211}Rn	210.9901	0.0135
−3.503 12	206.9517	^{207}Rn	206.9902	0.0186

[1] *TOF_28082015_Rn_8MT.tof*, *TOF_28082015_Rn_NT_3.2kV.tof*

Limitation and Generalization

In this approach we used the scaling mass from the reflector ejection as m_c. This has the benefit that the mass doesn't need to be present, but it requires the same scaling mass being used in both timing schemes (in our case tdelay10 and tdelay9). If a measured calibrant m_a is used instead in both measurements, the equation for $\Delta t_{a,total}$ will change:

$$\Delta t_{a,total} = \Delta t_{turn,j,i} + \Delta t_a$$

With Δt_a analog to Δt_x. $\Delta t_{turn,j,i}$ is now being calculated by:

$$\Delta t_{turn,i,j} = \mathrm{t}_{\mathrm{del},10}(i+j) + \mathrm{t}_{\mathrm{del},9}(i+j) - \mathrm{t}_{\mathrm{del},10}(i) - \mathrm{t}_{\mathrm{del},9}(i)$$

This will result in the final equation being like

$$m_x = m_c \cdot \left(\frac{\Delta t_{turn,i,j} + \Delta t_x}{\Delta t_{turn,i,j} + \Delta t_a} \right)^2$$

Another limitation of this approach so far is the assumption that the difference in turn number of both measurements for m_c and m_x is j. However, since a different mass m_x can leave the spectrum on one side and reenter it from the other, j can be different for m_c and m_x. In case of a high j or a highly different i for m_c and m_x this gets more probable.

To counter this limitation, an iterative approach can be used: Mass candidates are evaluated by deviating Δt_x by multiples of $t_{c,turn}$. The equation for a deviating turn number k of the unkown mass is:

$$m_x = m_c \cdot \left(\frac{t_{c,turn} \cdot j + \Delta t_x + k \cdot t_{c,turn}}{t_{c,turn} \cdot j} \right)^2$$

or combining both generalizations:

$$m_x = m_c \cdot \left(\frac{\Delta t_{turn,i,j} + \Delta t_x + \frac{k}{j} \cdot \Delta t_{turn,i,j}}{\Delta t_{turn,i,j} + \Delta t_a} \right)^2$$

In our previous example of ^{219}Rn deviating k by ± 1 will lead to possible masses of 276.01 u and 168.540 u, which is clearly outside of the mass window and thus can be excluded.

However, for higher turn numbers and smaller distances to m_c the probable mass area is more likely not exceeded. In those cases the mass defect can be a good indication for a successfull identification. Other options include to take a third measurement and intersect the set of mass candidates, to use a mass filter to cut off masses or to do a library search for the possible candidates.