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HANDLING THE NOTICEABLE NON-LINEARITY OF MASS CALIBRATION IN HIGH RESOLUTION TOF MS

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OVERVIEW

PURPOSE: Evaluation of the main factors that violate the mass calibration of ToF mass spectrometers at the ppb level

RESULTS: Formulas are derived and their predictions are verified using accurate SIMION simulations for deviations caused by:

1. **Non-ideal time of flight focusing**
2. **Non-uniform accelerating field**
3. **Initial difference of ion energies**

INTRODUCTION

The high resolution of modern ToF mass spectrometers rises high demands on accurate mass calibration[1]. We assume regular (we call it "linear") calibration for mass <=> time of flight being :

$$m = a(t - t_0)^2$$

(for simplicity, we omit the charge).

We know that the rise time of the pushing pulse by itself does not cause a calibration deviation[2].

However, the non-uniform accelerating field or the imperfection of the time-of-flight focusing, combined with the finite rise time of the accelerating field, leads to calibration deviations

Also, deviations are inevitable if ions of different masses have different average velocity in the direction of acceleration. This might be due to

- **the inclination of the ion beam in OA varies depending on the mass,**
- **delayed extraction of ions at some distance from the surface of the pulsed desorption**

There may be other causes of mass calibration non-linearity (not discussed here) such as the following:

1. **Presence of magnetic fields**
2. **Variation of the electric field with time during the ion flight (should be avoided).**
3. **Ions of some masses leave the Push-out gap or Accelerator while the acceleration field is not yet stabilized (should be avoided)**
4. **Peak shifts due to space charge and image-charge[3]**
5. **Fine structure of mass peaks and mass peaks overlapping**

MAIN MODEL

At some moment t_r after the appearance of the pushing field, it stabilizes at a certain value of E_0, and by this moment the ions are shifted in space by

$$\Delta x_r = \frac{q}{m}\int_0^{t_r}\int_0^{t_r} E(t)\,dt\,dt + V0 \cdot t_r$$

and accumulate an addition to the velocity

$$\Delta V_r = \frac{q}{m}\cdot\int_0^{t_r} E(t)\,dt$$

After t_r these ions behave in the same way as if they were pushed out by a rectangular pulse, if they have the same velocity at the same point. The difference will be only "in the history". The "rectangular pulse" ions will have to start later by Δt_{virt} and pass a distance shorter by Δx_{virt}

$$V_{virt} = V_r\ ;\quad a_0 t_{virt} = \int_0^{t_r} a(t)dt\ ;\quad \Delta t_{virt} = t_r - \frac{\int_0^{t_r} E(t)dt}{E_0}$$

Note: the time shift does not depend on either the mass or the initial velocity for any shape of the rising edge of the Pushing pulse!

The calibration deviation will only relate to the virtual initial position offset Δx_{virt} unless acceleration field is NOT spatially uniform

The main approach is to compare the behavior of the ions with the case of an ideal "rectangular" Pushout and to find out whether the time t_{virt} required for different ions to reach the "end-of-rise" velocity V_r depends on the mass. Then the mass calibration deviation will be approximately defined by the formulas $\Delta t_{virt}/t_{flight} = dm_{dev}/m$ and $\Delta t(\Delta x_{virt})/t_{flight} = dm_{dev}/m$

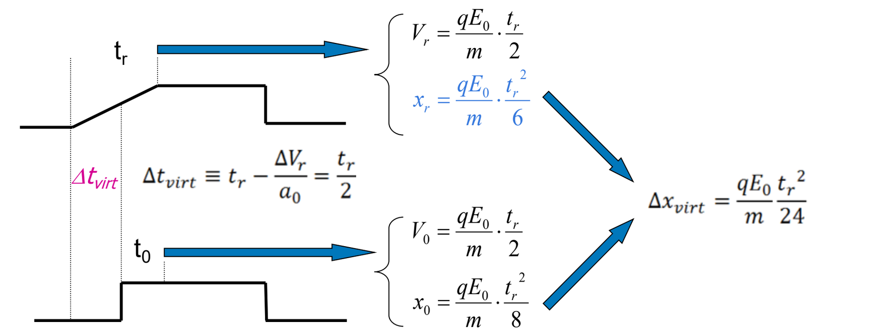


Figure 1. Equivalence of the linear rise of the Pushing pulse and the instantaneous appearance of the field[3]

1. NON-IDEAL TIME-OF-FLIGHT FOCUSING

Mass scale becomes non-linear when the time-of-flight changes with the energy K_e, accumulated by ions with different start position x_{start} . The average flight time will shift if there is a change in the flight time depending on the start position x with some coefficient $\kappa \neq 0$.

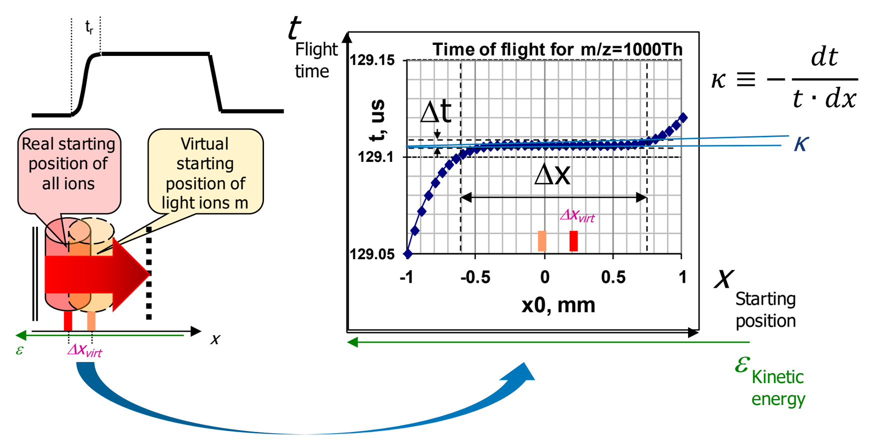


Fig.2 Shift of the flight time due to the virtual shift of the start position[3].

To estimate the mass calibration deviation, we consider a linear rise of the accelerating field during t_r leading to a virtual shift of the start position Δx_{virt}

As we assume the effective shift of the start position being

$$\Delta x_{virt} = E_0 \frac{q}{m}\frac{t_r^2}{24}$$

The deviation from the regular mass calibration can be estimated by the following formula:

$$\frac{dm}{m} \approx 2\frac{dt}{t} \approx 2\kappa\Delta x_{virt} \approx 2\kappa E_0 \frac{q}{m}\frac{t_r^2}{24}$$

2. NON-UNIFORM ACCELERATION FIELD (E_0 GRADIENT)

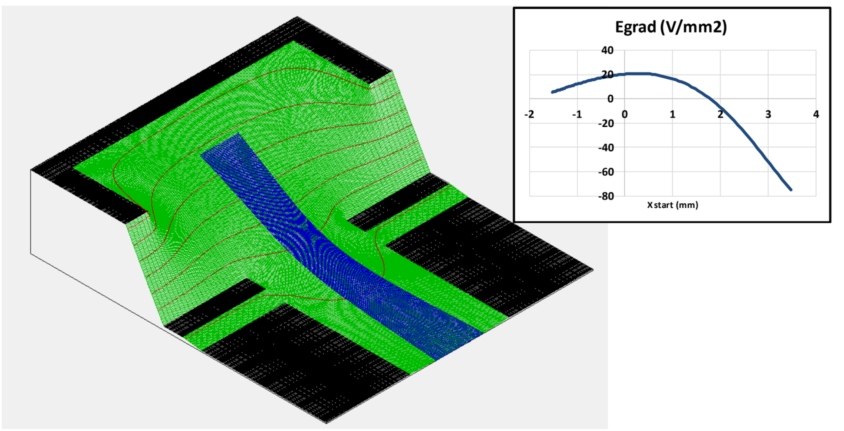


Fig.3. Example of the non-uniform acceleration field in a gridless OA.

Even if the virtual start position shift Δx_{virt} does not affect the flight time, the virtual start time now becomes mass-dependent, since different masses experience different E-field time-dependence due to their different positions in time.

For quasi-linear Pushing rise and constant field gradient *gard(E_0)* we have approximate expression for mass-deviation via virtual delay:

$$V_{virt} = V_r\ ;\ a_0 t_{virt} + grad(a0)a_0\frac{5t_{virt}^{\ 3}}{24} \approx a_0\frac{t_r}{2} + grad(a0)a_0\frac{t_r^{\ 3}}{30}$$

Note that the virtual acceleration starts from initially higher acceleration $a0_{virt}$ as the virtual start position is shifted by Δx_{virt}. The approximate solution is

$$\Delta t_{virt} \approx \frac{t_r}{2} + grad(a0)\cdot\frac{7}{960}t_r^{\ 3}$$

$$\frac{dm}{m} \approx 2\sqrt{2\left(\frac{q}{m}\right)^3 grad(E0)\frac{7}{960}t_r^{\ 3}}\cdot\frac{\sqrt{U_{eff}}}{L_{eff}}$$

3. CORRELATION OF THE INITIAL ENERGY WITH THE ION MASS

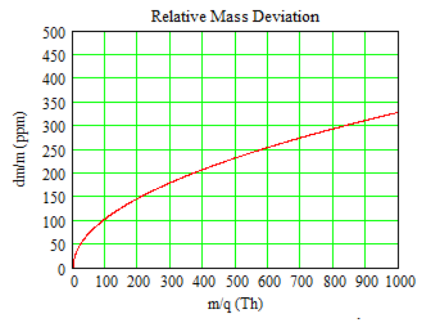
When the averaged energy of the initial motion in the direction of acceleration (x) for mass m differs by dK_{in} , there is a deviation of mass calibration determined by the delay required to compensate for the difference in initial energy. The delay can be estimated in the same way as the "turn-around time". The final mass deviation formula is:

$$\frac{dm}{m} = 2\frac{dt}{t} = 4\frac{\sqrt{dK_{in}K_{eff}}}{E_0 q\, L_{eff}}$$

Here K_{eff} – energy of accelerated ion, L_{eff} – effective flight path length, E_0 – acceleration field, $dK_{in}=mV_x^2/2$

Version for delayed extraction from a remote distance

A large deviation of mass calibration occurs with delayed extraction from remote position (axial accelerator at L_{start} from a pulsed ion source)



$$\frac{dm}{m} = 4\frac{\sqrt{K_{eff}}}{E_0 q\, L_{eff}}\sqrt{\frac{m}{2}}\frac{L_{start}}{t_{start}}$$

Fig. 4. Calculated mass deviation for ToF with axial extraction at 10mm delayed by 10 us

Version for Variation of the incoming angle α

If the angle α of ions coming orthogonal to the acceleration with energy K_y varies with mass, then there will be mass calibration deviation depending on the angle.

$$\frac{dm}{m} = 4d\alpha\frac{\sqrt{dK_y K_{eff}}}{E_0 q\, L_{eff}}$$

With our model parameters of ToF MS dm/m ≈11.5 ppm/degree

4. OVERSHOOT AT THE LEADING EDGE

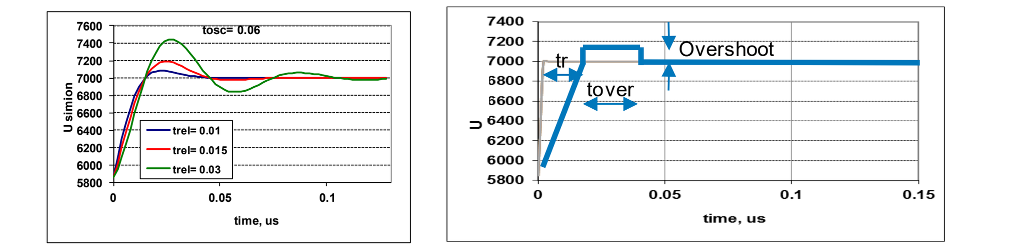


Fig. 5. Overshoot Push-pulse leading edge models used in SIMION and analytical simulations.

We suggest a simple approximation of non-monotonic rise of the Pushing pulse for a qualitative description of the main features.

The mass calibration deviation in this case can be estimated according to the following expression

$$\frac{dm}{m} \approx -2\alpha E_0\frac{q}{m}\frac{dE}{E_0}\left(t_r\cdot t_{over} + t_{over}^{\ 2} + \frac{dE}{E_0}t_{over}^{\ 2} - \frac{t_r^{\ 2}E_0}{12dE}\right)$$

Thus, the overshoot can partially compensate for the deviation caused by the rise time. For example, for $t_{over}=t_r$ the mass deviation will be minimal when overshoot amplitude dE is about 40% of the target pulse amplitude

THREE-POINT CALIBRATION

Deviations in cases 1, 4, 5, 6 have a similar pattern $m = a(t - t_0)^2 + dm$

We can use the coefficients obtained from the three-point calibration, by a method similar to that used in [4], assuming the deviation being small

$$dm = -2\frac{\sqrt{m_1 m_2 m_3}\left(t_1\left(\sqrt{m_3}-\sqrt{m_2}\right)+t_2\left(\sqrt{m_1}-\sqrt{m_3}\right)+t_3\left(\sqrt{m_2}-\sqrt{m_1}\right)\right)}{\left(\sqrt{m_1}-\sqrt{m_3}\right)\left(\sqrt{m_2}-\sqrt{m_1}\right)\left(\sqrt{m_3}-\sqrt{m_2}\right)}$$

$$a = \left[\frac{\left(\sqrt{m_1}-\sqrt{m_3}\right)\left(\sqrt{m_2}-\sqrt{m_1}\right)\left(\sqrt{m_3}-\sqrt{m_2}\right)}{t_1\sqrt{m_1}\left(\sqrt{m_3}-\sqrt{m_2}\right)+t_2\sqrt{m_2}\left(\sqrt{m_1}-\sqrt{m_3}\right)+t_3\sqrt{m_3}\left(\sqrt{m_2}-\sqrt{m_1}\right)}\right]^2$$

$$t_0 = \frac{t_1\sqrt{m_1}(m_2-m_3)+t_2\sqrt{m_2}(m_3-m_1)+t_3\sqrt{m_3}(m_1-m_2)}{\left(\sqrt{m_1}-\sqrt{m_3}\right)\left(\sqrt{m_2}-\sqrt{m_1}\right)\left(\sqrt{m_3}-\sqrt{m_2}\right)}$$

For other cases, 3-point calibration is derived in a similar way

COMPARISON OF ANALYTICAL ESTIMATES WITH THE RESULTS OF SIMION SIMULATIONS

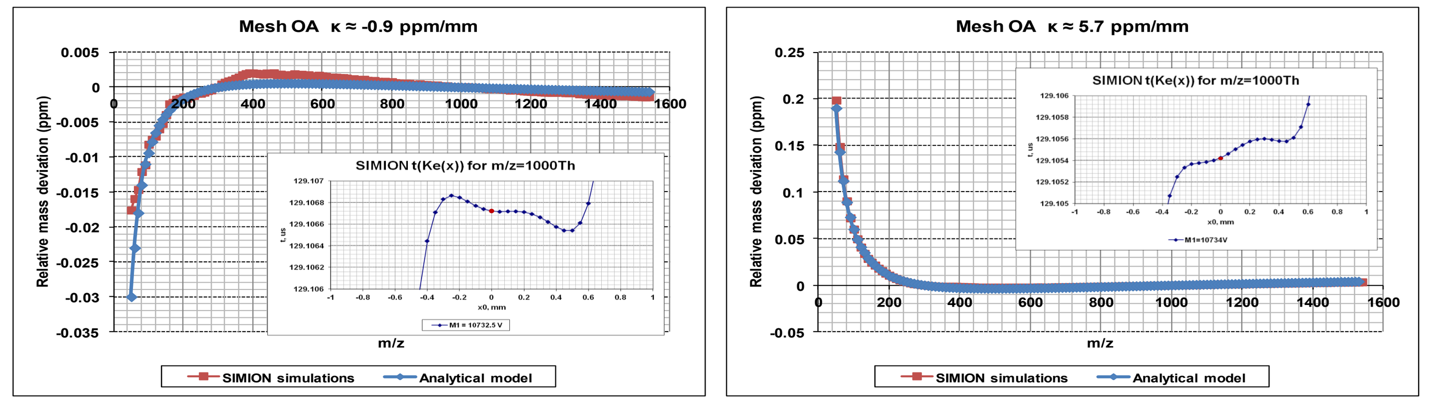


Fig.6 Non-ideal time focusing. SIMION used the ToF MS model with fine-mesh Accelerator

ToF Reflector was defocused to give slight slope of the *t(x)* curve as shown on the insets.
For simplicity, one start point (shown in red) and the local slope κ for this point were used for all masses.
Other parameters used in simulations: Push pulse linear rise time t_r=30 ns, Accelerating field E_0=500V/mm
Effective flight energy $U_{eff}\,q$ =6keV, effective flight length L_{eff}=4 m
Note: Tuning of ToF ms at resolving power R~100K implies a tolerance of κ~5ppm/mm

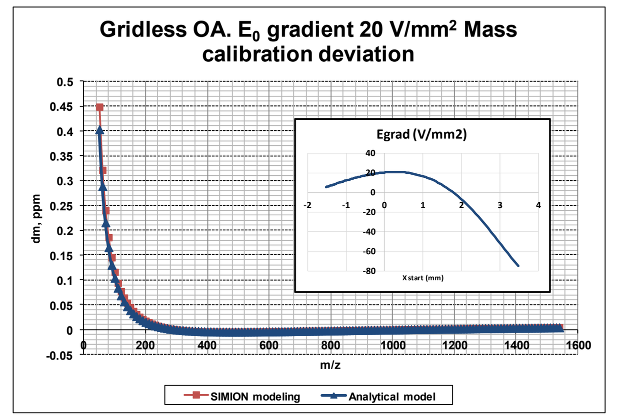


Fig.7 Mass calibration deviations for the case of a non-uniform field in the Accelerator. Comparison of the Simion simulations with the results calculated by the proposed formula.

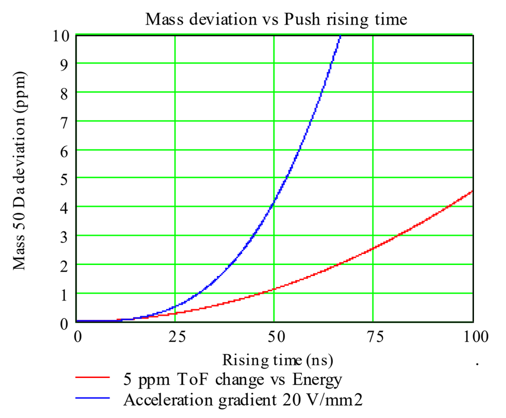


Fig 8. Calculated (according to the formulas) dmass calibration deviation dm/m vs rising time t_r.

The results are shown for m/z=50Th, E_0=500V/mm, $U_{eff}\,q$ =6keV, L_{eff}=4 m

To compare SIMION results with the analytical model, we used a 2-points recalibration with the same reference masses: m_1=300Da and m_2=1000Da.

5. RELATIVISTIC DEVIATION

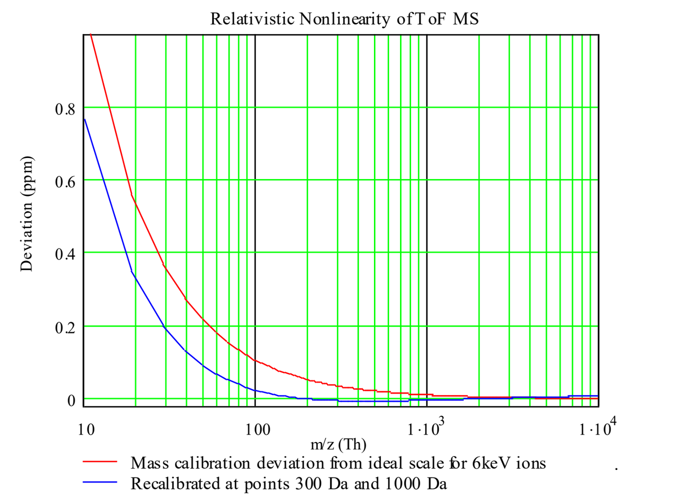


Fig 9. Mass calibration deviation due to relativistic effects for ToF with ion energies $U_{eff}\,q$ =6keV

$$\frac{dm_{rel}}{m} \approx \frac{3}{2}\frac{Uq}{mc^2}$$

6. MASS OF ELECTRON

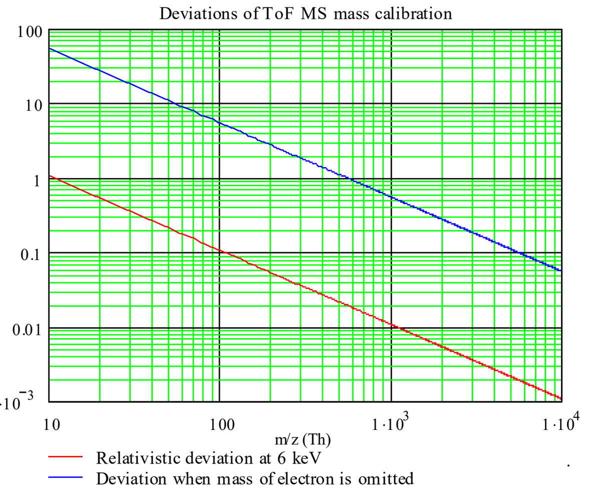


Fig 10. The use of neutral mass values for calibration (omitting electron mass) leads to a mass calibration nonlinearity approximately equal to the relativistic deviation at 340 keV

CONCLUSIONS

- **Most of the actual causes of mass calibration irregularities in of ToF mass spectrometers have been modeled and quantitatively tested using SIMION models.**
- **All deviations are most pronounced at the range of small masses, and most of them increase sharply with increasing time of the rise of the Pushing pulse**
- **The knowledge of the nature of deviations can be used to account for and minimize them**
- **Analytical expressions for deviation from classical calibration are provided for all considered cases.**
- **For practical needs the deviation value can be found from a 3-point calibration, when the nature of the deviation is known.**

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