Feedback Software Stabilizer Report

Julian Bergmann, Samuel Ayet San Andres

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1 Description

The goal of the feedback software stabilizer (FSS) is to actively adapt voltages applied to electrodes to correct for shifts in time of flight for a specified calibrant, but without changing the peak shape.

This is done by measuring the shift in time of flight of the calibrant during a measurement and sending two electrodes an adapted voltage. The adapted voltage is calculated by multiplication with coefficients, which were calculated to minimize the aberrations (T|D)D kinetic energy, (T|XX)X^2 2. order position and (T|DD)D^2 2. order kin. E., while shifting the peak into position.

The Feature can be run in addition to any measurement in the background and has been implemented and tested in the MAc software on 10-2016.

2 Theory of Adapting Coefficients

M.Yavor authored an internal report "High quality axially symmetric mirror for shuttle-type MR TOF spectrometers" in 12-2010. There he investigated what effect voltage shifts of electrodes would have in an ions flight time and aberrations in kinetic energy and position.

The correlation of relative time of flight deviation for 0.1 % shift of electrode potential was presented like this:

Electrode	Rel. deviation
1	-2.8E-04
2	-1.6E-04
3	1.3E-05
4	-6.7E-05
5	
drift	2.6E-04

In this table electrode 3 and 4 (see figure 1) have the least influence on the flight time change, so with fixed voltage supply precision we can get the highest correction precision by using these electrodes. The abberations for each of these electrodes for 0.1 % shift of electrode potential are listed as

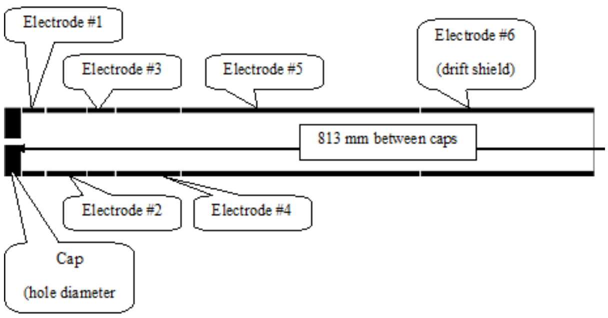

Figure 1: Numbering of analyzer electrodes in the model used for simulations.

Abbaration	Electrode 3	Electrode 4
(T|D)D	2.6E-05	5.1E-05
(T|XX)X^2	-3.0E-06	-4.5E-05
(T|DD)D^2	-5.1E-06	2.0E-06

Using the single aberrations, we construct a total aberration by adding them for each electrode:

$$((\mathrm{T}|\mathrm{D})\mathrm{D})_t = a \cdot ((\mathrm{T}|\mathrm{D})\mathrm{D})_3 + b \cdot ((\mathrm{T}|\mathrm{D})\mathrm{D})_4$$
$$((\mathrm{T}|\mathrm{XX})\mathrm{X}^2)_t = a \cdot ((\mathrm{T}|\mathrm{XX})\mathrm{X}^2)_3 + b \cdot ((\mathrm{T}|\mathrm{XX})\mathrm{X}^2)_4$$
$$((\mathrm{T}|\mathrm{DD})\mathrm{D}^2)_t = a \cdot ((\mathrm{T}|\mathrm{DD})\mathrm{D}^2)_3 + b \cdot ((\mathrm{T}|\mathrm{DD})\mathrm{D}^2)_4$$

With $((\mathrm{T}|\mathrm{D})\mathrm{D})_t$ as the total aberration and a and b parameters that need to be found later on. Now we need to minimize all total deviations, which we will sum up squared:

$$d \cdot ((\mathrm{T}|\mathrm{D})\mathrm{D})_t^2 + ((\mathrm{T}|\mathrm{XX})\mathrm{X}^2)_t^2 + ((\mathrm{T}|\mathrm{DD})\mathrm{D}^2)_t^2 \quad (1)$$

Equation (1) needs to be minimized for both electrodes. the parameter d is introduced to give the aberration of first order in kinetic energy a higher importance than the one of second order or the aberration of position.

In addition it is required to keep the set of a and b constant when calculating the shift in time of flight:

$$\Delta t_t = a \cdot \Delta t_3 + b \cdot \Delta t_4 \tag{2}$$

To consider both equations at once while minimizing the first, we divide equation (1) by equation (2) and get

$$\frac{d \cdot ((\mathrm{T}|\mathrm{D})\mathrm{D})_t^2 + ((\mathrm{T}|\mathrm{XX})\mathrm{X}^2)_t^2 + ((\mathrm{T}|\mathrm{DD})\mathrm{D}^2)_t^2}{\Delta t_t = a \cdot \Delta t_3 + b \cdot \Delta t_4}$$

Since this equation is not easy to minimize for 3 parameters, d and a are set constant and the equation is checked for minima in dependance of b. Afterwards the quotient

$$q_m = \frac{a}{b}$$

is calculated by using the fixed a from before and the b of the found minimum. This quotient can now be used in equation (2) to eliminate b and present a in dependance of Δt:

$$a = \frac{\Delta T}{(\Delta t_3 + \Delta t_4 / q_m)}$$

The fitting b for a ΔT can then be calculated using q_m.

This is done for different d to check at which aberation weight d the voltage weight quotient a/b is not changing much anymore. This would imply that the first order aberration in kinetic energy doesn't completely outweight the other aberrations but is the dominating factor. Figure 2 made us decide to use $d = 4$.

Under these conditions the optimal parameters for a and b are:

Parameter	Value	
a	22.8303	$\cdot\Delta t$
b	-10.4956368372	$\cdot\Delta t$

3 Example of Application

The following scenario shows how this theory is applied in pratice: A Signal of an Ion that takes

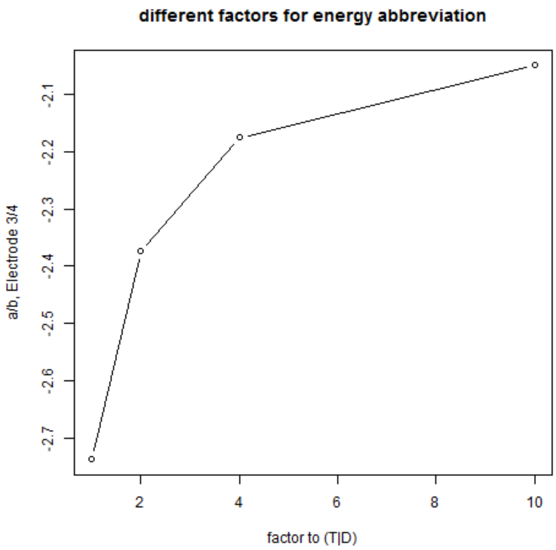

Figure 2: Quotient a/b ploted for differnt weights of the squared sum of the aberration in time at first order.

a total flight time of 18.939 05 ms appears 5 ns later than it should be. The relative deviation (2.64×10^{-5} %) is now multiplied by the calculated factors a and b and the voltages of electrode 3 and 4 is increased by the result in percentage:

$$\begin{aligned}
U_{3,\mathrm{start}} &= 300\,\mathrm{V} \quad , \quad U_{4,\mathrm{start}} = 1200\,\mathrm{V} \\
t_{\mathrm{start}} &= 18.939\,05\,\mathrm{ms} \\
\Delta t &= 5\,\mathrm{ns} \\
r &= \frac{-\Delta t}{t_{\mathrm{start}}} = -2.64 \times 10^{-7} \\
r_3 &= r \cdot a = -6.0273 \times 10^{-6} \\
r_4 &= r \cdot b = 2.7709 \times 10^{-6} \\
U_{3,\mathrm{corrected}} &= U_{3,\mathrm{start}} \cdot (1 + r_3) = 299.998\,\mathrm{V} \\
U_{4,\mathrm{corrected}} &= U_{4,\mathrm{start}} \cdot (1 + r_4) = 1200.003\,\mathrm{V}
\end{aligned}$$

As this example shows, high precision mass measurements require highly precice voltage control to the level of mV to avoid jumps in time of flight while running the stabilizer.

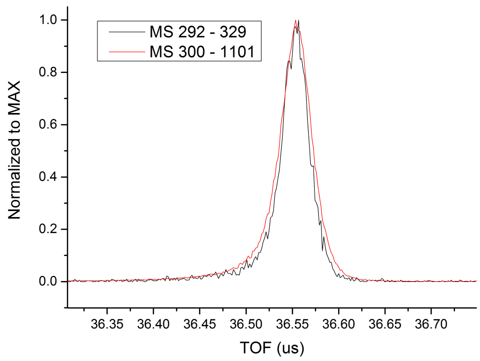

Figure 3: Comparison of peak shapes for different time ranges.

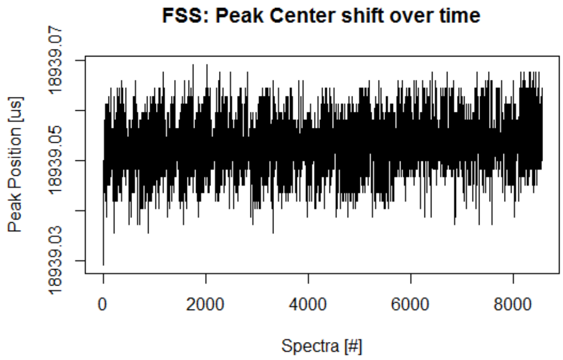

Figure 4: Peak center position over time of the long term measurement over night with FSS running.

4 Proof of Principle

In two high precision measurements the application of this theory was tested and verified. In the first measurement, the stabilizer was used overnight and the peak position and shape were investigated for stability. In the second measurement a third electrode in the analyzer was changed on purpose to change shape and position while the FSS was running. In that measurement, it was tested if the stabilizer could correct the third electrode's effect.

Overnight Measurement

Potassium was measured with 980 turns in a Multi-Reflection Time-of-Flight Mass-Spectrometer (MR-TOF-MS), having a flight time of ca. 18.939 ms. 8500 summed spectra of which each consists of 250 single spectra were taken over night with a 50 Hz rate equaling 11.806 h of measuring. Without further corrections the resulting peak has a FWHM of 24 ns, which corresponds to a resolving power of 400 000.

Figure 3 shows the effect of the stabilizer on the peak shape. In black you can see the peak shape for a small portion of the measurement, where the stabilizer's effect is only very slightly. In red you see a peak shape of data that was summed up from a longer time range, so the stabilizer shifted the electrode voltages more during the measurement. As you can see, the normalized plots almost overlap,

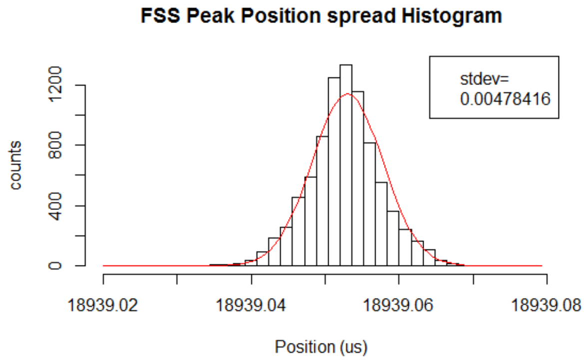

Figure 5: Peak center position distribution and fit for long term measurement with FSS running

which means that the peak shape is not changed by the stabilizer in long term measurements.

In Figure 4 the peak position over time (spectra number, 5 s each) is plotted with Figure 5 being the projection on time axis. As you can see in the projection, the standard deviation of the peak position is below 5 ns. With a Signal FWHM of 24 ns this means that the correction of signal position is working correctly and precise enough for long term measurements.

For comparison you can see a measurement overnight without feedback software stabilizer in Figure 6 for the peak position and Figure 7 for the projection on the time axis. As you can see we have a large drift, probably based on temperature shifts

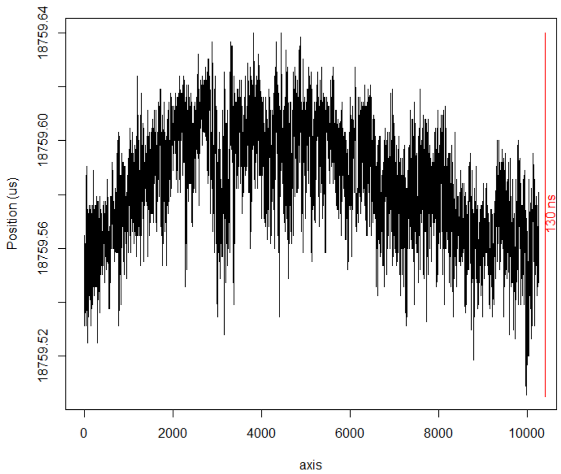

Figure 6: Peak center position over time of the long term measurement over night without FSS running

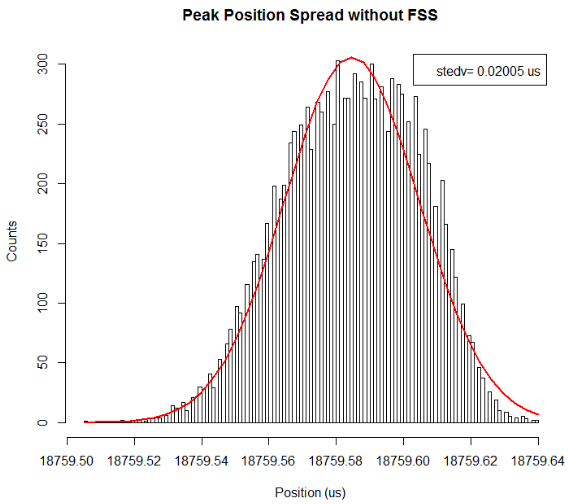

Figure 7: Peak center position distribution and fit for long term measurement without FSS running

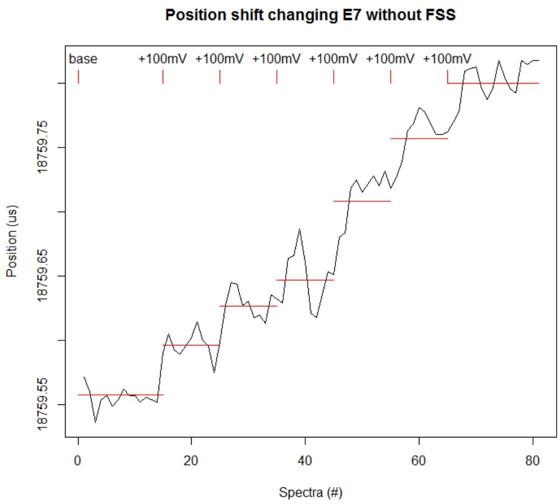

Figure 8: Peak center position when changing voltage at E7 without FSS active.

in day/night cycle, which cause a geometry change in the analyzer's electrodes.

In the end the measurement without stabilizer had a drift in position up to 130 ns with a standard deviation of 20 ns and a clearly changed peak shape. The stabilized peak had a drift in position of up to 40 ns with a standard deviation of 4.8 ns.

Adaption of E7

In another test measurement, electrode E7 (see Figure 1) was increased in 100 mV steps with and without stabilizer active. The resulting positions are shown without FSS active in Figure 8 and with FSS active in Figure 9. Red vertical marks are positions where the voltage at E7 was increased. Red horizontal marks are the mean position value for this voltage setting. As you can see, without the FSS the position increases drastically (about 250 ns), with FSS it stays within 50 ns, mean value even within 20 ns.

Another investigation was done about peak shapes. Figure 10 shows on the left side spectra without the FSS active and on the right side with FSS active. Each spectra is summed up of single spectra within a block (as shown in Figure 8 for inactive FSS and 9 with active FSS). A gaussian plot is plotted atop for comparison help. As it can be

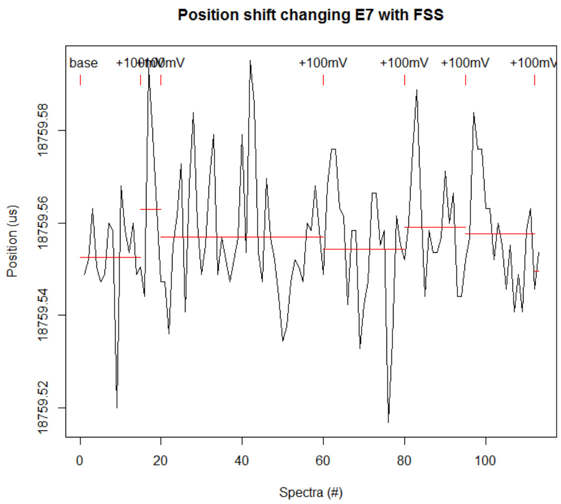

Figure 9: Peak center position when changing voltage at E7 with FSS active.

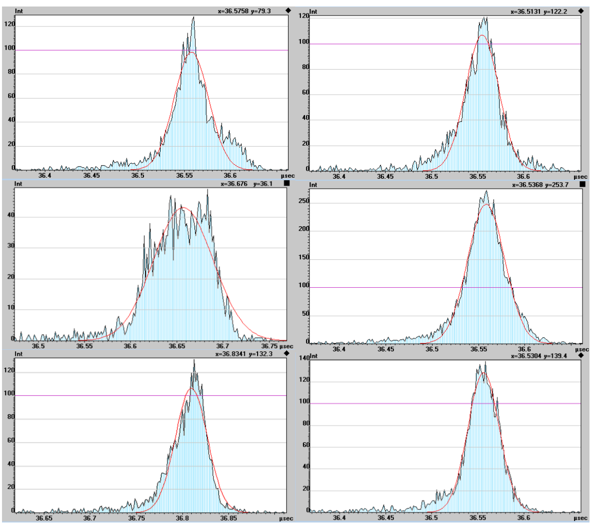

Figure 10: Comparison of peak shapes. Left without FSS (time range adapted), left with FSS (time range fixed).

clearly seen, the peak shape is changing drastically even for a position shift of 250 ns, but with FSS active, the peak shape is not changing at all.

Signal Shape Stabilization

To test the ability to prevent additional aberrations from changing the signal form, a time shift of 1 µs was performed. This shift was realized 3 times by adapting E3 and E4 respectively and by telling the stabilizer that the signal position has changed by −1 µs.

The result can be seen in Fig.11. As can be seen, shifting only with E3 or E4 by 1 µs will increase the peak width greatly, but also produce additional tail effects. Shifting over this large distance with the FSS doesn't seem to create any effect, neither in the general peak shape, nor in FWHM. As Fig.6 shows, we will expect a shift in the order of 100 ns, which FSS will be able to correct without adding aberrations, while having a single-electrode solution would clearly change the peak shape.

	Position	FWHM	Shape
Original	19.0 µs	11.85 ns	-
E3	20.1 µs	20.0 ns	Changed
E4	20.1 µs	14.6 ns	Changed
FSS	20.1 µs	10.3 ns	no change

Shifting Speed

In general, an analytical solution can be found easily how to adapt the voltages of two electrodes, so a certain shift in time of the signal is produced. Since the calculation in the theory chapter provided the relation between the voltage change, all that's left to do is reproducing the steps in chapter 3.

However, in reality the FSS needs multiple iterations to reach its destination point. In a measurement, where the FSS was told to shift the signal by 1 µs, it needed 43 steps (0.5 s per iteration).

Since no aberrations are added even for large shifts, the relation between both voltage changes must be correct. This leaves two possible sources of this behavior: statistical errors in determining the peak position and wrong relations between electrodes and time shifts. Since the statistical error should be in the order of a peak width, it is safe to exclude from further investigation of this problem as well.

This leaves a wrong relationship between electrode voltages and time shift. To investigate this, different corrected relationships have been

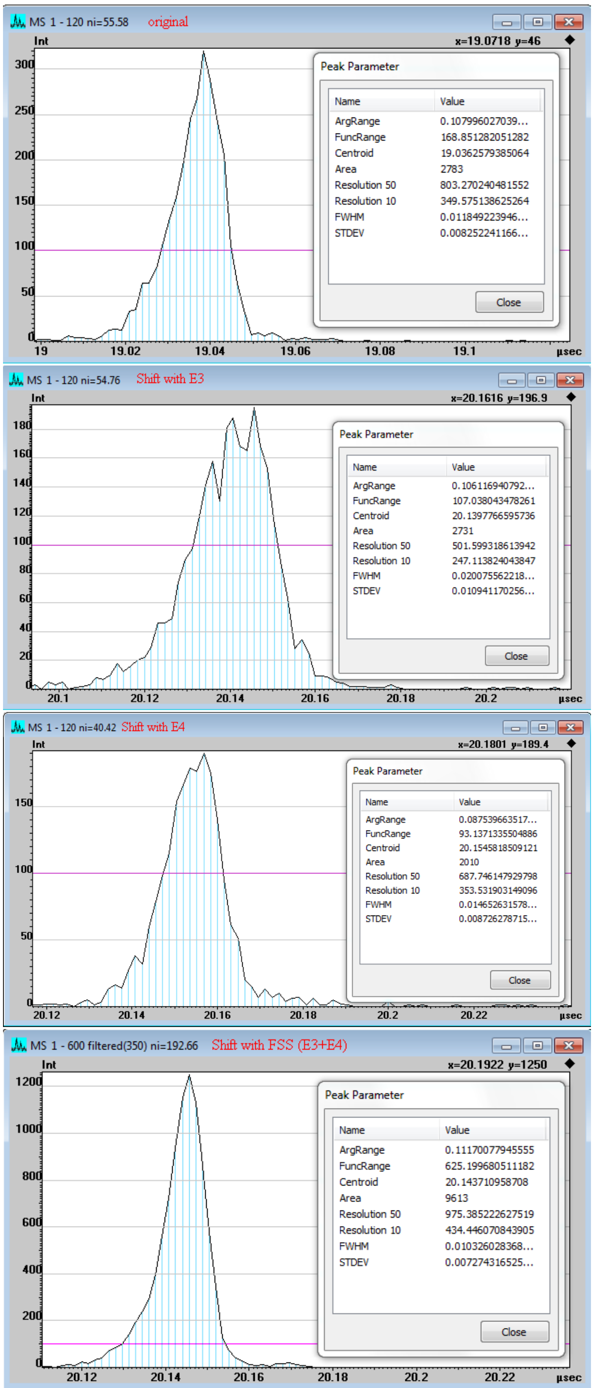

Figure 11: Comparison of peak shapes change when shifting the signal by 1 µs.From top to bottom: no shift, shift via E3, shift via E4,shift via FSS (E3 + E4)

determined. It was also calculated, how much the FSS has been corrected with the current parameters if the new relationships would be correct. Investigating the first 5 iterations of the 1 µs-measurement mensioned before shows that the FSS is only shifting between 7 % to 16 % of what it should have shifted in each iteration:

position	target	reached	fraction
19.037 µs	20.149 µs	19.120 µs	7.47 %
19.120 µs	20.149 µs	19.223 µs	10.01 %
19.223 µs	20.149 µs	19.357 µs	14.46 %
19.357 µs	20.149 µs	19.475 µs	14.81 %
19.475 µs	20.149 µs	19.585 µs	16.30 %

The shifts in this measurement only done by E3 or E4 (one electrode) are yielding a corrected relationship of shift in voltage and time:

$$t_{\text{start}} = 4.9465\,\text{ms}$$

$$t_{1,E3} = 19.0377\,\mu\text{s}\ , \qquad t_{2,E3} = 20.1405\,\mu\text{s}$$

$$u_{1,E3} = 333.9\,\text{V}\ , \qquad u_{2,E3} = 343.9\,\text{V}$$

$$\frac{\Delta t_{E3}}{t_{1,E3}} = 2.22 \times 10^{-4}\ , \qquad \frac{\Delta u}{u_1} = 2.995 \times 10^{-2}$$

$$\frac{\Delta t_{E3}}{t_{1,E3}} \Bigg/ \frac{1e3 \cdot \Delta u_{E3}}{u_{1,E3}} = 7.415 \times 10^{-6}$$

$$t_{1,E4} = 19.0377\,\mu\text{s}\ , \qquad t_{2,E4} = 20.1561\,\mu\text{s}$$

$$u_{1,E4} = -3373.5\,\text{V}\ , \qquad u_{2,E4} = -3350\,\text{V}$$

$$\frac{\Delta t_{E4}}{t_{1,E4}} = 2.25 \times 10^{-4}\ , \qquad \frac{\Delta u_{E4}}{u_{1,E4}} = -6.966 \times 10^{-3}$$

$$\frac{\Delta t_{E4}}{t_{1,E4}} \Bigg/ \frac{1e3 \cdot \Delta u_{E4}}{u_{1,E4}} = -3.233 \times 10^{-5}$$

So, assuming the shift in two electrodes, the following timeshift would be archieved:

Electrode	relative deviation	
	measured	simulated
E3	1.4830×10^{-5}	1.3×10^{-5}
E4	-6.466×10^{-5}	-6.7×10^{-5}

If these relationships were the case, using the current set of parameters to move a signal by 1 % in time would have moved it correctly:

$$\frac{\Delta t}{t} = 22.8303 \cdot 1.4830 \times 10^{-5} \cdot 10$$
$$+ (-10.4956) \cdot (-6.466 \times 10^{-5}) \cdot 10$$
$$= 1.0172\,\%$$

A different attempt was simulating ions in a similar setup and check their change in flight time when changing the electrodes. This yielded different relationships than the original simulation:

electroed	old	new
E3/7	1.3×10^{-5}	1.89×10^{-5}
E4/6	-6.7×10^{-5}	-4.11×10^{-5}

$$\frac{\Delta t}{t} = 22.8303 \cdot 1.89 \times 10^{-5} \cdot 10$$
$$+ (-10.4956) \cdot (-4.11 \times 10^{-5}) \cdot 10$$
$$= 0.861\,\%$$

In summary, the shift is correctly in theory (0.861 % is within margin of error), and applied correctly. However, when looking at the actual shift in voltage, then the shift is decreased to a fifth of the correct value. This can have multiple reasons. A miscalculation in the software code is a possible cause, but also additional influence in the actual experiment. The time needed to change the voltage applied can also be a cause. Since the program had no delay set, each spectrum would immediately result in a request to change the two voltages (every second).

5 Conclusion

The Feedback software stabilizer was used in multiple test measurements to demonstrate its advantages during a real measurement. As these measurements show, it can keep not only the time of flight constant (Figure 4 and Figure 9), but also the peak shape (Figure 10).

The current implementation requires a calibrant and an active TCP connection to the voltage controller software with a voltage precision of about 10 mV, but it is easy to use, creates a detailed log of its actions can be activated on all long term measurements in parallel.

Concluding the FSS seems to be the ideal tool to counter instabilities in electric fields, e.g. due to shifts in temperature, if the effect in time of flight caused is greater than 20 ns. For more precise corrections, MAc's *time resolved calibration* feature should be used in addition.