MRS Investigation

Internal Paper

Julian Bergmann, Samuel Ayet San Andres

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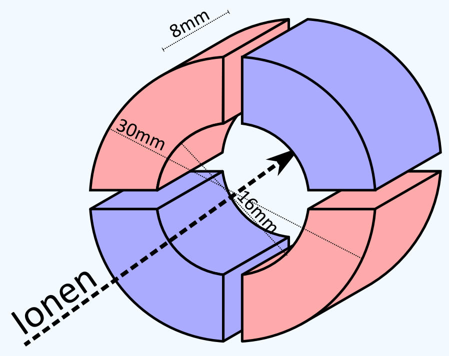


Figure 1: The 4 electrodes of the MRS.

1 Introduction

The *Mass Range Selector* (MRS) denotes four electrodes at the center of the analyzer of our *Multiple-Reflection Time-Of-Flight Mass-Spectrometers* (MR-TOF-MS) (Figure 1). A DC voltage applied to two opposing electrodes respectively is used to kick ions out of the analyzer. During injection these electrodes can also be used to steer the ion. By using the correct timings, the MRS can be used to only let a certein mass range through[1].

In this report, the cutting character of the MRS was investigated. Since the accuracy and needed amount of ion pass-throughs is highly depending on the field size, measurements of the MRS field size at early and late cutting was investigated. Another point of investigation is the influence of fringe fields and possible shifts in flight time by using the MRS.

2 Operation

The operation mode on cutting the detection mass range down by kicking out ions uses a short pulse on the MRS each time ions pass by. This mode allows very high cutting precision and free choice of upper and lower target mass range. Its downside is that it requires a high amount of CC for small mass ranges. For more information about the use of this mode, please see the internal document "Mass Range Selector Settings, Manual for the R Script MRS.R".

For the sake of clarity some terms needs to be defined. Every time a *cycle* is mentioned, it regards to the center mass that the MRS cutting is set to pass through. Each cycle during which the MRS is cutting is called a *cleaning cycle* (CC). Since ions pass the MRS twice in each CC, half-CCs are possible. *non cleaning cycles* (NCC) describes that the MRS stays deactivated for an amount of cycles before cutting (usually once). *Region of Loss* (RoL) is the mass region, the MRS is cutting away per CC. *Center of Loss* (CoL) is the center in time of this region. Those parameter play an important role in measuring the field size.

In a measurement the MRS is pulsing with a fixed duty cycle and frequency (translates to ON and OFF time) for a certain number of CC, before it switches off. This is regulated by a gate electronics (delay and on time). That way the MRS can be set up using those 4 parameters:

MRS_{on}: Time the MRS is kicking out ions within a CC

MRS_{off}: Time between cutting of the MRS
frequency $f = 1/(MRS_{on} + MRS_{off})$
duty cycle $d = MRS_{on}/(MRS_{on} + MRS_{off})$

$Gate_{on}$: Time the MRS is pulsing. Multiplied with the MRS-frequency results in the applied amount of CC

$Gate_{delay}$: Time after the MRS is activated

For measuring the field size, the RoL was determined. However it is not possible to produce a continuous ion spectrum to see at which mass exactly is cut. Thus the operation mode was slightly changed for the next part of the investigation:

An ion with known cycle-time was measured multiple times while the MRS_{off} was increased. That way the RoL was moved over the mass range. Once the region would reach the ion, fringe fields effects and then transmission loss can be observed. To check the cutting behavior at high turn numbers, an amount of NCCs can be done before cutting.

[1]Timo Dickel: *Design and commissioning of an ultra-high-resolution time-of-flight based isobar separator and mass spectrometer.*PhD thesis, Justus Liebig University Gießen (2010)

3 E-Field Size

3.1 ^{133}Cs

At first we used ^{133}Cs-ions with a MRS_{on} time of 500 ns. Figure 2 shows the transmission of ^{133}Cs while MRS_{off} was stepwise increased in 25 ns steps. MRS_{on} was set to 500 ns.

The RoL was now determined by checking at both flanks on which MRS_{off} value the transmission reached 50 % of its maximum. The difference of those equals the RoL. The CoL is the mean of those two points and describes the exact time when the ^{133}Cs-ion reaches the MRS center. To check for consistency, this test was done once with low NCC[2] and another time after 28 NCC[3].

NCC	CoL	RoL
0	10.97 µs	650 ns
0.5	28.78 µs	600 ns
1	46.61 µs	690 ns
∅	-	650 ± 40 ns
28	1009.19 µs	710 ns
28.5	1027.00 µs	670 ns
29	1044.85 µs	680 ns
29.5	1062.65 µs	770 ns
∅	-	700 ± 45 ns
$\varnothing_{\text{total}}$	-	680 ± 50 ns

Since the time an ion sees the MRS is depending on its kinetic energy and mass, the size in space should be calculated. At $E_{\text{kin}} = 1300\,\text{eV}$ and $m = 132.905\,\text{u}$ ^{133}Cs ions travel with $43.4\,\text{km}\,\text{s}^{-1}$. Since the MRS was pulsing for 500 ns, the remaining time can be used to determine the size in space by $x = v \cdot t$.

NCC	RoL-MRS_{on}	MRS-E-Size
0-1	150 ± 40 ns	6.5 ± 1.5 mm
28-29.5	200 ± 40 ns	8.7 ± 2.0 mm
∅	175 ± 50 ns	7.6 ± 2.0 mm

Since the MRS pulser require only 30 ns, there influence can be neglected as it is below the measured error margin. Using the evaluated CoL, the time for ^{133}Cs to reach the center of the analyzer can be estimated as 10.93 ± 0.04 µs.

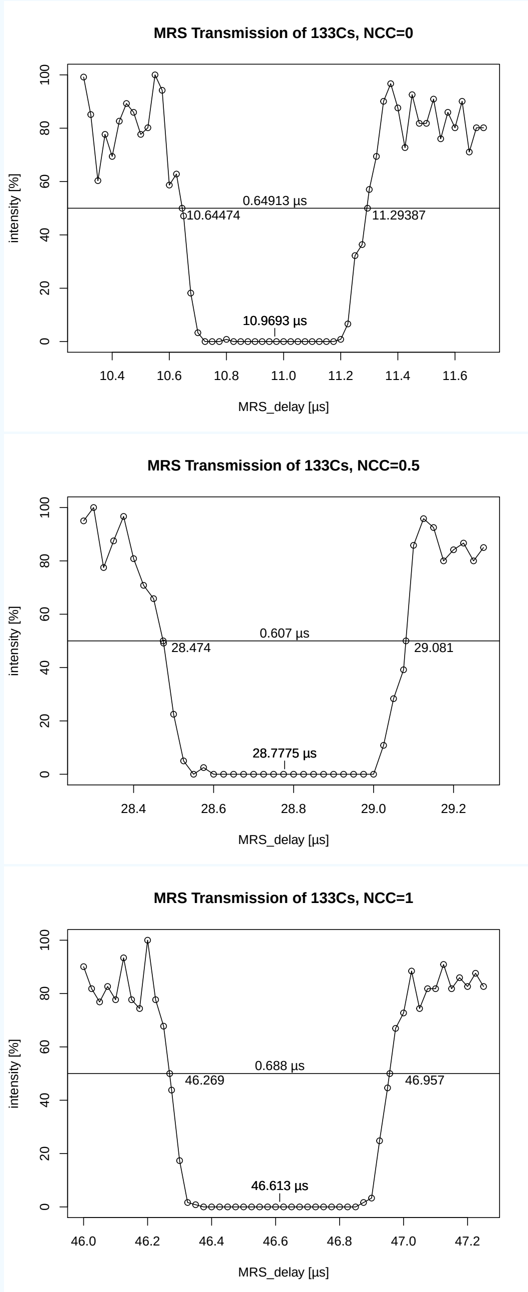


Figure 2: Transmission of ^{133}Cs during change of MRS_{off}.

3.2 ^{85,87}Rb

To check for a different behavior for separate masses, the measurement was redone ^{85}Rb and ^{87}Rb. MRS_{on} was now set to 150 ns [4]. The Plots can be found in the appendix 1.1 and 1.2.

[2] TOF_15072016_002_MRS_Timing_Test_MT
[3] TOF_15072016_003_MRS_Timing_Test_MT
[4] TOF_21072016_003_Rb_Cs_MRS_Timing_Test_MT

Element	NCC	RoL	CoL
^{85}Rb	0	250 ns	8.93 µs
^{85}Rb	0.5	170 ns	23.17 µs
^{85}Rb	1	220 ns	37.42 µs
^{85}Rb	1.5	310 ns	51.66 µs
^{85}Rb	2	300 ns	65.91 µs
^{85}Rb	2.5	200 ns	80.15 µs
^{85}Rb	3	240 ns	94.4 µs
^{85}Rb	∅	240 ± 50 ns	-
^{87}Rb	0	270 ns	9.03 µs
^{87}Rb	0.5	180 ns	23.43 µs
^{87}Rb	1	210 ns	37.86 µs
^{87}Rb	1.5	320 ns	52.27 µs
^{87}Rb	2	300 ns	66.69 µs
^{87}Rb	2.5	180 ns	81.09 µs
^{87}Rb	3	320 ns	95.52 µs
^{87}Rb	∅	260 ± 60 ns	-
∅	∅	250 ± 60 ns	-

Parameters:

name	value
E_{kin}	1300 eV
m(^{85}Rb)	84.912 u
v(^{85}Rb)	54.354 km s^{-1}
m(^{87}Rb)	86.909 u
v(^{87}Rb)	53.725 km s^{-1}

Now we can calculate the size in space of the electric field again. For that, we subtract the MRS_{on} time as we did with the ^{133}Cs measurement.

Isotope	RoL	MRS-E-Size
^{85}Rb	90 ± 50 ns	5.0 ± 2.8 mm
^{87}Rb	110 ± 60 ns	6.0 ± 3.4 mm
∅	100 ± 60 ns	5.0 ± 3.1 mm

3.3 CoL Shift

The CoL of ^{85,87}Rb can be used to check the delay time of our pulser.

During the investigations, a deviation of the expected CoF was noticed and a second measurement[5] of ^{133}Cs showed that there now is an additional delay of 180 ns.

[5] TOF_21072016_003_Rb_Cs_MRS_Timing_Test_MT

NCC	old CoL	new CoL	diff
0	10.97 µs	11.16 µs	190 ns
0.5	28.78 µs	28.96 µs	180 ns
1	46.61 µs	46.8 µs	180 ns
∅	-	-	180 ± 5 ns

This shift is likely caused by changes in the setup (e.g. cable lengths). Thus, to investigate the CoL–Shift we now use the new CoL values. With these we can calculate the CoL for Rb by scaling.

$$t_2 = \sqrt{\frac{m_2}{m_1}} \cdot t_2$$

$$t_{^{85}\text{Rb}} = \sqrt{\frac{84.912\,\text{u}}{132.905\,\text{u}}} \cdot 11.16\,\mu\text{s} = 8.920\,\mu\text{s}$$

$$t_{^{87}\text{Rb}} = \sqrt{\frac{86.909\,\text{u}}{132.905\,\text{u}}} \cdot 11.16\,\mu\text{s} = 9.025\,\mu\text{s}$$

Now we compare the calculated CoL with the measured CoL

Isotope	Calculated	Measured
^{85}Rb	8.920 µs	8.925 ± 0.003 µs
^{87}Rb	9.025 µs	9.026 ± 0.006 µs

Es the calculated and measured center of Loss are in good agreement, there is no delay time of our pulser.

3.4 Electric Fringe Fields

The MRS fringe fields can deflect ions that should have been transmitted. An overlaying effect is the pulser ramping time during which a weaker deflecting field is produced. The pulser ramping time was measured as 30 ns. To check the remaining effect of the fringe field, the MRS was again switched to cutting once, but now the flight time of ^{133}Cs was investigated[6].

In Figure 3 ^{133}Cs was measured at the CC at NCC 0-1. The time from where the fringe fields start affecting the ions until RoL is measured:

NCC	slope	max. position shift	slope width
0	left	-480 ns	240 ns
0	right	$+90$ ns	200 ns
0.5	left	-10 ns	170 ns
0.5	right	± 20 ns	230 ns
1	left	$+240$ ns	200 ns
1	right	-150 ns	250 ns
|∅|			220 ± 30 ns

[6] TOF_15072016_002_MRS_Timing_Test_MT

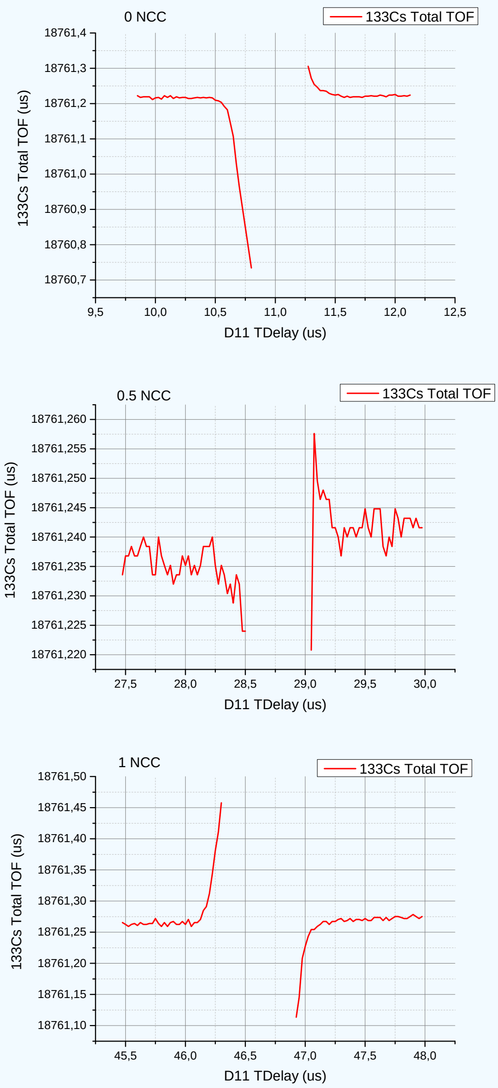


Figure 3: Peak Position of ^{133}Cs during change of MRS_{off} after 0, 0.5 and 1 NCC.

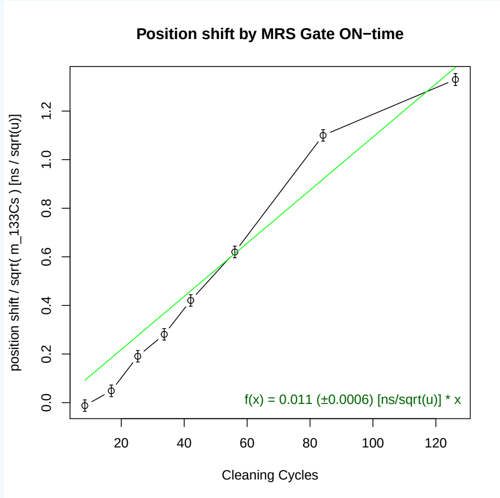


Figure 4: Position of peak shifted with rising working time of the MRS

The max. position shift shows how strongly the ions are affected. The slope width is the time span of the MRS gate delay at which the MRS was changing the peak flight time.

On average ions are affected two times about 220 ± 30 ns in its flight time per pass through the MRS ($\hat{=}9.0 \pm 1.3$ mm). The position shift direction is not following a clear pattern and its intensity is highly variable up to 480 ns.

What is

Concluding, the ramp time of the pulser (30 ns) can be neglected, but ions, that fly too close to the ion of interest and get into the fringe field might be shifted in flight time up to ± 0.5 µs in any direction.

4 Time of Flight Shift

Since the pulsing of the MRS generate a change in the supplied voltage, its influence on the time of flight on ^{133}Cs was measured[7].

4.1 Number of CC Influence

In this investigation (Figure 4) we were using a fixed $MRS_{on} = 1\,\mu s$ and $MRS_{off} = 16.83\,\mu s$.

The plot shows that the relationship is mostly linear with a shift about 4.0 ± 0.3 ns per ms $Gate_{on}$ time equalling $0.011 \pm 0.0006\,\text{ns}\,\sqrt{\text{u}}^{-1}$.

4.2 MRS Cutting Time Influence

To investigate the influence on the MRS_{on} time to the position shift, the time of flight of mass 100 u and 101 u was measured with MRS_{on} set to 5 µs and 10 µs each[8]. The MRS was set up to create a narrow mass range around those two masses. In all measurements the same target mass range for set up.

MRS_{on}	MRS_{off}	$Gate_{delay}$	CC
5 µs	10.5 µs	3.55 µs	33.5
10 µs	5.5 µs	6.0 µs	17.0

The change in flight time is displayed in Figure **??**.

mass	shift at 5 µs	shift at 10 µs
100 u	9.89 ns	6.6 ns
101 u	9.77 ns	5.26 ns

[7] TOF_10062016_021_Rb_Cs_MT.tof
[8] TOF_05072016_008_C3F8_MT_overnight

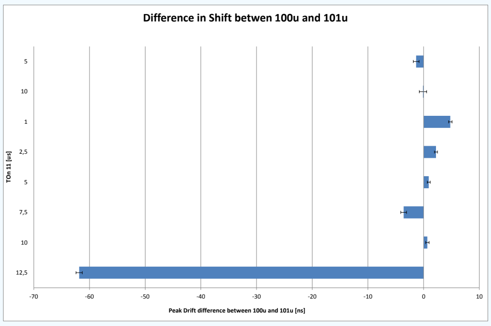


Figure 5: Difference in peak position shift with rising ON-time of the MRS

For 10 µs the change in flight time seem to differ between ions. This measurement was redone with a greater choice of MRS_{on} times[9]. Figure 5 shows the shift in time of flight for mass 100 u and 101 u at 1 µs to 12.5 µs. While the shifts are again in a smaller region (< 10 ns), compared with the previous measurement the shift at 10 µs switched its sign. When MRS_{on} was set to 12.5 µs there was also a large shift in time of flight for mass 101 u. This was likely due to exposure to the fringe field of the MRS.

MRS_{on}	MRS_{off}	$Gate_{delay}$	CC
1 µs	14.5 µs	1.55 µs	46
2.5 µs	13 µs	2.3 µs	41.5
5 µs	10.5 µs	3.55 µs	33.5
7.5 µs	8 µs	4.8 µs	25
10 µs	5.5 µs	6.05 µs	17
12.5 µs	3 µs	7.3 µs	9

In general there does not seem to be a direct correlation between any of those MRS settings and the direction or amount of shifts in time of flight measured. This implies that different opposing shifting effects might be influencing this measurement simultaneously.

5 Summary

In this report, the MRS electric field size and influence on the time of flight was investigated.

Through measurements with ^{133}Cs (^{85,87}Rb) the field was deduced to be 7.6 ± 2.0 mm (5.0 ± 3.1 mm).

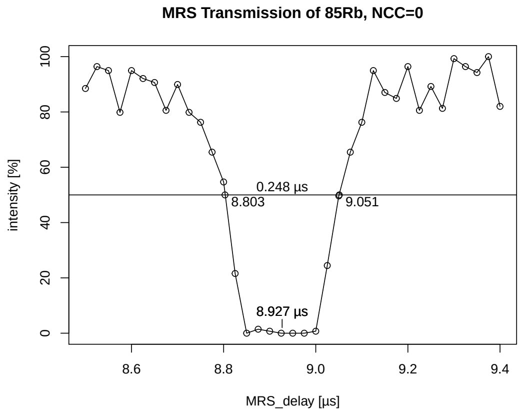
With ^{133}Cs the fringe field was deduced to span 9.0 ± 1.3 mm. Since this corresponds to a flight time of around 220 ± 32 ns it makes the effect of the pulser's ramp time of 30 ns negligible

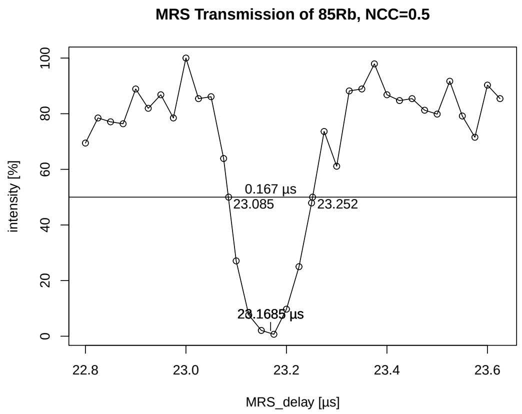
[9] TOF_13072016_001_C3F8_MRS-timing

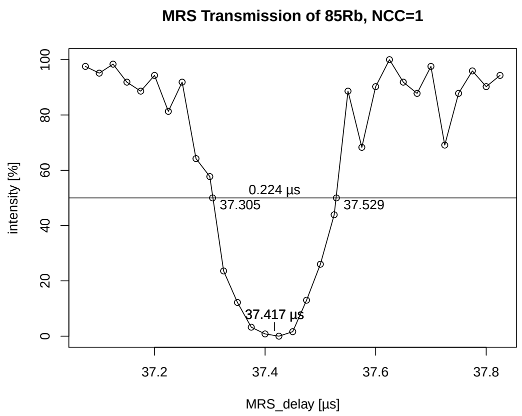
The time of flight increases 4 µs per ms the MRS is doing CCs. For ^{133}Cs this is 36 ± 5 ns per CC . The influence of cutting time per CC is in the order of 10 ns, but not fully understood yet. Increasing the gate delay will reduce the shift in time of flight in the order of 10 ns, but also shows unusual fluctuations.

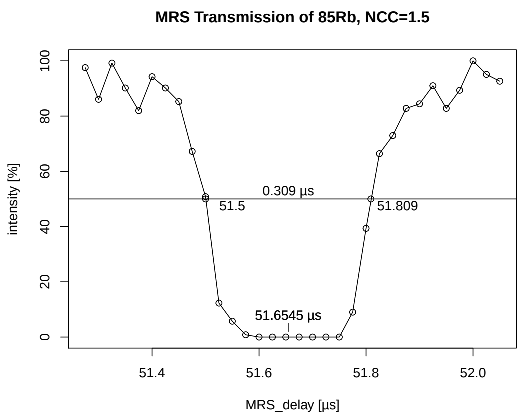
1 Appendix

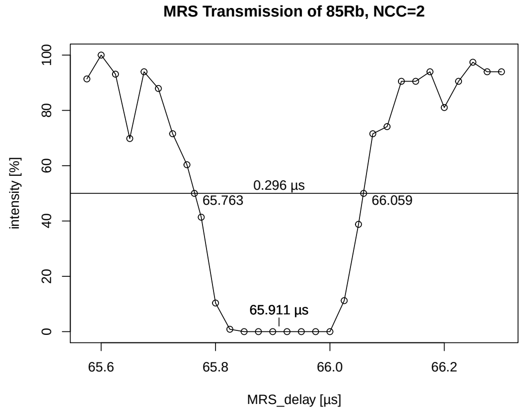
1.1 RoL of ^{85}Rb

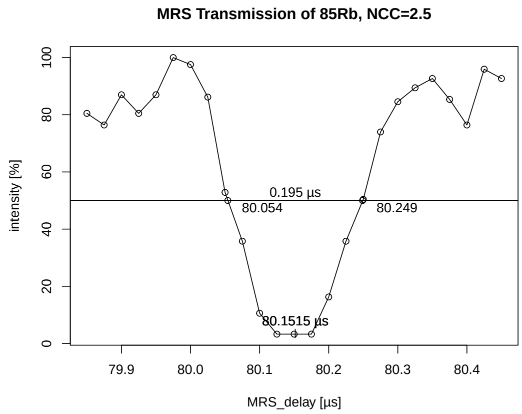


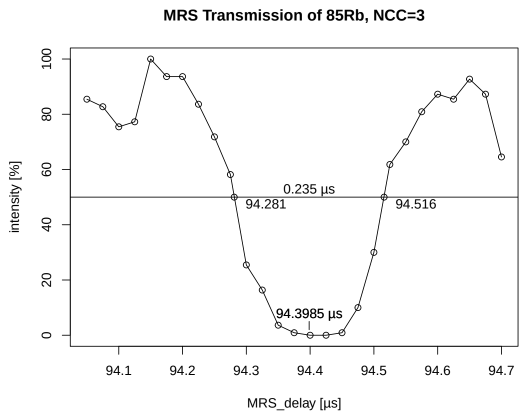












1.2 RoL of ^{87}Rb