Electron Impact Source and MRS Dual Species Isolation for the TITAN MR-ToF-MS

TRIUMF

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1 Introduction

This paper will discuss a complete characterization of the Mass Range Selector (MRS). More specifically, the characterization will focus on topics such as efficiency, effectiveness, and systematic uncertainty. This paper will also discuss the installation of the new Electron Impact Source along with the development and commissioning of MRS dual species isolation. The final section contains a complete analysis on the MRS dual species isolation simulation software development and optimization. The overall goals for the characterization and upgrades were to improve species separation tools, improve mass measurement, and determine effective MRS settings for various experimental modes. These goals will be achieved through the characterization of the MRS and the adjustments made to the overall MR-ToF-MS system.

2 MRS Characterization

2.1 Overview

This section will discuss the procedures and results for MRS efficiency and systematics. The goal of this investigation are as follows:

- Determine the effectiveness of the MRS as an isobar separator
- Optimize MRS settings to improve species separation while minimizing systematic uncertainty
- Develop a deeper understanding of MRS operation and its potential aberrations
- Determine two optimal MRS settings/ranges, one for re-trapping and one for mass measurement

2.2 Procedure

The overall investigation was be divided into four distinct analyses:

1. MRS Window Analysis: An investigation into the effect of the MRS settings on the mass window size
2. Multiple Peak Detection Phenomenon: An investigation into the detection of multiple mass windows due to the use of an MRS start
3. MRS Centroid Investigation: An initial investigation of MRS settings and systematic uncertainty to determine the plausibility of further investigation into the systematics
4. MRS ON-OFF Systematics: A thorough investigation into the MRS systematics using peak shifts when MRS switches between ON and OFF

The results from the following investigations were used to determine two optimal MRS settings/ranges - one for re-trapping and one for mass measurement.

2.3 MRS Window Analysis

The objective of this investigation was to determine the sizes of the MRS windows for various settings. A separate analysis on the current drawn by the MRS was performed to help characterize the efficiency of the MRS settings. Additionally, the effect of each MRS setting was characterized for a more descriptive analysis. The following MRS settings and their effects are described in this section: MRS Proportion, MRS Voltage, MRS Cycles, MRS Start.

MRS Start and Proportion

Width(MRS Proportion, MRS Start Turn) : Mass 85, 130 V, 30 MRS Cycles								
		MRS Start Turn						
		0	50	70	100	200	500	800
MRS Proportion	10	0.3	0.129	0.10422	0.0798	0.0411	0.0253	0.0065
	20	0.46	0.22	0.2	0.12	0.06	0.027	0.017
	30	0.79	0.4	0.33	0.236	0.1265	0.052	0.027
	40	1.08	0.445	0.351	0.26	0.175	0.069	0.037
	50	1.3	0.5	0.41	0.33	0.17	0.071	0.044
	60	1.71	0.64	0.51	0.37	0.21	0.17	0.059

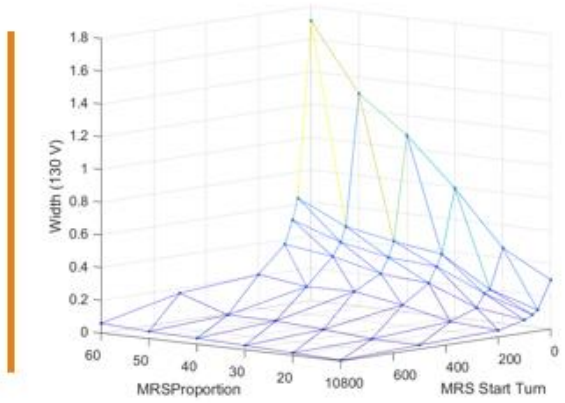


Figure 1: MRS Start and Proportions effect on the MRS window size (control settings: 130 V MRS, Mass 85, 30 MRS Cycles)

As the proportion decreases, the size of the window decreases (figure 1). This is as expected since more MRS on time will result in more blocking/deflection of unwanted species; this results in increased selectivity (smaller mass windows). This relationship appears to be linear. Interestingly, the slope of the relationship appears to increase as the MRS Start decreases. This could be due to the MRS start having a stronger effect compared to the proportion – when MRS start is implemented, the mass windows are much smaller.

Alternatively, increasing the MRS start turn decreases the mass window size. This is because the species are much more separated at higher turns. When the MRS is turned on at higher turn numbers, the unwanted nearby species are effectively cleaned. Thus, as MRS start is increased, the mass window is decreases at a rate like an exponential decrease. Once the start reaches about 200, the gain in cleaning effectiveness is much lower. On another note, the proportion of 10 and MRS start turn of 800 provides the smallest MRS window achieved - 0.0065 mass units.

MRS Cycles and Proportion

Width(MRS Proportion, MRSCycles) : Mass 85, 130 V								
		MRS Proportion						
		10	30	35	40	45	50	90
MRSCycles (turns)	20	0.41	1.24	1.33	1.55	1.86	2.05	3.63
	25	0.3	0.94	1.15	1.39	1.45	1.68	2.91
	30	0.3	0.79	0.87	1.08	1.24	1.3	2.38
	35	0.3	0.62	0.79	0.93	1.01	1.3	2.18
	40	0.2	0.62	0.77	0.85	0.97	0.92	1.86
	45	0.2	0.53	0.71	0.77	0.82	0.92	1.56
	50	0.1	0.53	0.71	0.62	0.69	0.92	1.45
	55	0.1	0.53	0.42	0.62	0.68	0.74	1.34
	60	0.1	0.53	0.42	0.46	0.67	0.56	1.24
	65	0.1	0.53	0.42	0.46	0.67	0.56	1.24
	70	0.1	0.53	0.42	0.46	0.42	0.56	1.03

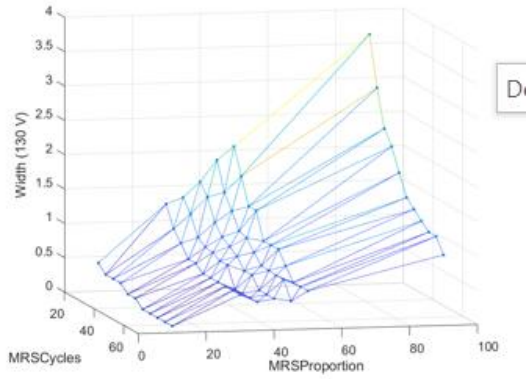


Figure 2: MRS Cycles and Proportions effect on the MRS window size (control settings: 130 V MRS, Mass 85, 0 MRS Start)

Proportions' effect on the window size appears to be a linear relationship, like the one demonstrated in the MRS Start and Proportion section. Figure 2 shows the slope of the MRS proportion curves increasing as the MRS Cycles decrease. On the other hand, MRS cycles seem to decrease the window size as it increases. This is because more MRS cycles leads to more deflection of unwanted species, leading to better cleaning and smaller mass windows. The MRS cycles' curves appear to be very similar to an exponential decrease; however, the curves appear to have lower slopes than the MRS start curves in the MRS Start and Proportion section.

MRS Cycles and Voltage

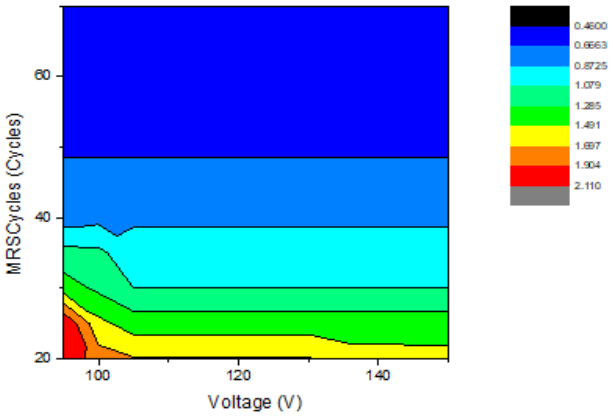


Figure 3: MRS Cycles and Voltage's effect on MRS Window Size (Mass 85 Rb)

Figure 3 shows that MRS Voltage has almost no effect on the MRS window size, whereas MRS Cycles continues to have a similar effect as discussed in the MRS Cycles and Proportion Section. Interestingly, the MRS Voltage seems to have an effect from 95 to 105 volts as the associated window sizes decrease as the voltage increases. However, this effect is not seen with Mass 39

Potassium and Mass 133 Cesium. The effect at 95 to 105 volts is likely a special case as the voltage of the MRS electrodes is expected to have no significant effect on the mass window sizes until much lower voltages are used. It is recommended to use an MRS voltage around 130 V to avoid the possibility that voltage affects the mass window and to also minimize the current drawn (MRS Voltage, Cycles, and Current Section).

MRS Cycles, Voltage, and Current

Current(Voltage, MRSCycles) (mircoAmperes)										
		Voltage								
		95	100	105	110	115	120	130	140	150
MRSCycles (turns)	20	63.19	66.265	70.555	72.91	77.135	79.58	87.295	92.795	101.255
	25	78.89	83.43	85.18	89.89	92.51	100.81	104.735	113.85	119.6
	30	90.28	97.055	98.845	104.34	108.72	113.11	122.405	132.45	144.25
	35	117.115	109.95	113.9	115.38	124.49	135.15	140.7	151.9	162.55
	40	129.5	122.05	128.85	134.05	140	146.3	158.1	170.65	188.9
	45	134.1	136.5	142.45	149.95	155.4	162.55	175.65	191.65	202.7
	50	141.1	148.6	162.9	164.2	173	185.1	192.75	211.15	226.45
	55	157.15	165.5	169.5	185.55	191.6	195.75	209.7	224.55	243.9
	60	166.45	171.05	187.7	187.6	199.95	210.15	227.95	243.85	263.55
	65	183.45	186.3	196	205.5	215.45	224.8	246.1	260.85	279.75
	70	191.65	203.5	210.95	221.6	231.35	238.4	260.25	278.6	300.6

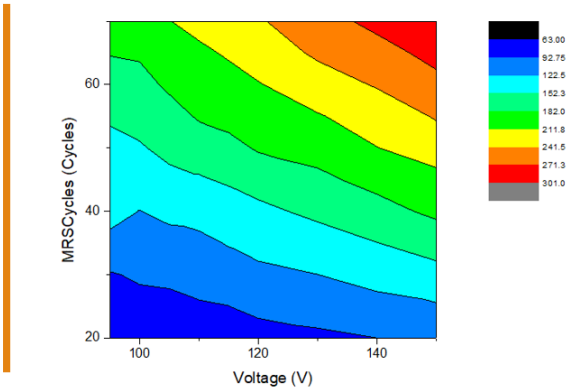


Figure 4: MRS Cycles and Voltage's effect on Current Drawn

The current drawn by the MRS electrode will act as the main factor in determining the efficiency of certain MRS settings. Figure 4 shows that there appears to be a strong increase in the current drawn when the MRS Cycles increase. Alternatively, an increase in voltage appears to have a small increase current drawn. Once higher amounts of MRS Cycles are used, the increase in voltage appears to strongly increase the current drawn. Figure 4 shows that the slope in the x (voltage) direction appears to increase as MRS Cycles increase. Thus, it is likely that there is an effect due to the interaction between MRS cycles and voltage. Most importantly, a voltage setting of 120V to 135 V appears to be the most effective setting. This is due to lower voltages near 100 V influencing the windows of mass 85 Rb. At the same time, voltages greater than 135 V seem to greatly amplify the effects of increasing MRS cycles on the current drawn.

Results

The overall analysis of the MRS efficiency and effectiveness has provided insight into optimal settings for electrode voltages, proportions, MRS cycles, and MRS start turns. The optimal ranges for further investigation are as follows:

Voltage: 120 – 135 V; a voltage of 130 V will be set as the default setting

Proportions: 10 – 60; a proportion of 10 will be set as the minimum since the absolute minimum is 7. The default setting for proportion is 40.

MRS Cycles: 0 – 850; the effect of MRS cycles and overall cleaning is still uncertain.

MRS start: 0 – 820; the MRS start is controlled by the number of MRS cycles.

Through further data acquisition and analysis of systematic uncertainty, a much more thorough understanding on MRS cycles, MRS start, and proportion will be developed and used to generate two optimal settings/ranges for re-trapping and mass measurement.

2.4 Multiple Peak Detection Phenomenon

This investigation was prompted by multiple mass windows appearing in MRS center scans when nonzero start turns were being used.

Procedure

For each setting of the MRS Cycles and duty cycles, a range of MRS centers were scanned. The counts at each MRS center were plotted to determine how the number of MRS Cycles and the proportion affect the number of mass windows.

Analysis

An explanation for this phenomenon is that delaying the MRS waveform (ie. mass 85) led to an alignment of the waveform that is very close to the later region of a nearby mass' MRS waveform (ie. 84.35). Figures 5 and 6 help prove this explanation. When an MRS waveform is centered at mass 44 and delayed by 200 turns (Ch 23), its AND combination (Logic 10) with an MRS waveform of 44.22 with 0 delay (Ch 7) has very little clipping; this shows that the waveforms are very similar and that it is very likely that a mass 44 waveform with a delay of 200 turns will allow masses of 44.22 to pass through due to waveform similarity. Additionally, figure 6 shows that using a waveform with a mass of 44.17, instead of 44.22, leads to significant clipping in the AND combination. Thus, figure 6 provides evidence that there is a separate mass window that includes the mass center 44.22 due the use of an MRS start delay.

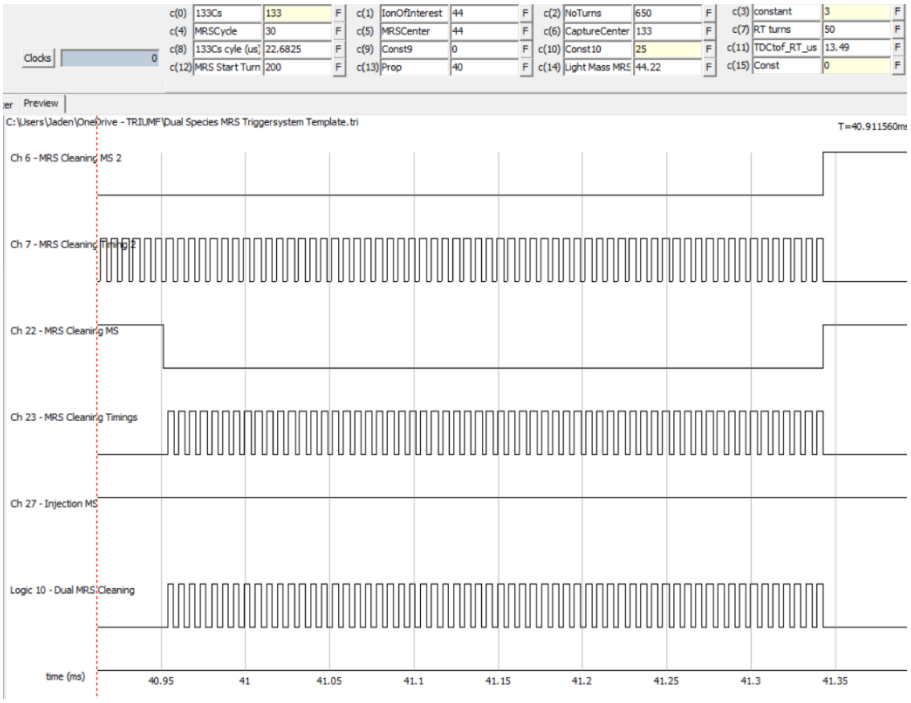


Figure 5: MRS Waveform AND Combination Mass 44 and 44.22 (settings: 40 Proportion, 30 MRS Cycles, 200 Start for 44 MRS waveform)

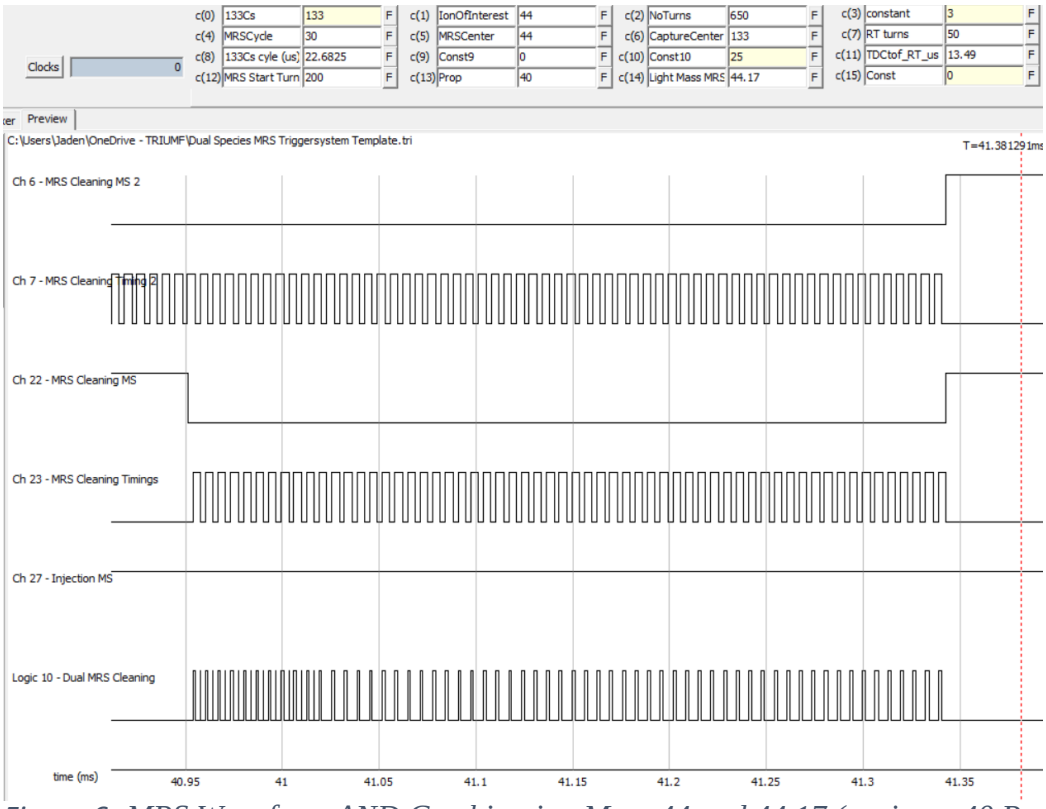


Figure 6: MRS Waveform AND Combination Mass 44 and 44.17 (settings: 40 Proportion, 30 MRS Cycles, 200 Start for 44 MRS waveform)

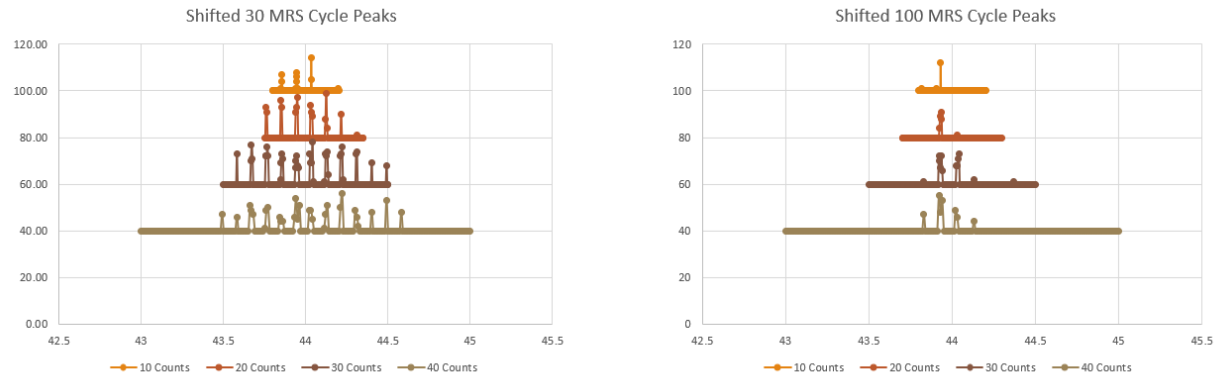


Figure 7: MRS Cycles and Proportion's effect on Peak mass windows (settings: start turn 200)

Please note that the 10 counts, 20 counts, etc.., represent the proportion settings. Also note that the counts for each proportion setting have been offset by different amounts for clarity.

Figure 7 shows that increasing the amount of MRS cycles (ie. from 30 to 100) leads to an overall decrease in the multiple peak phenomena. As MRS cycles are increased, the slight difference in alignment of the waveforms starts to become larger at later MRS cycles. This leads to the MRS waveform effectively blocking the unwanted species (ie. 44.22) and leading to a decrease in the number of peaks appearing. Alternatively, decreasing the proportion narrows the off time for each MRS waveform; this increases the probability of blocking the unwanted species and leads to a decrease in the peaks detected.

Results

The use of MRS start delay requires careful consideration of the mass detection goals. For instance, the MRS start delay should be considered if a scan or study requires a smaller proportion, larger amount of MRS cycles, and a very small mass window. Otherwise, please check for nearby species with MRS OFF to ensure that the correct masses are being examined when using the start delay.

2.5 MRS Centroid Investigation

The purpose of this investigation was to evaluate the potential of systematic uncertainty with altered MRS Cycles and Duty Cycle Settings. The results of this investigation are used to determine if further systematics investigations are necessary.

Procedure

For each MRS Cycles and duty cycles settings, a range of MRS centers were scanned, and a centroid was fit for each peak scanned. All improper gaussian fits were excluded due to high uncertainty.

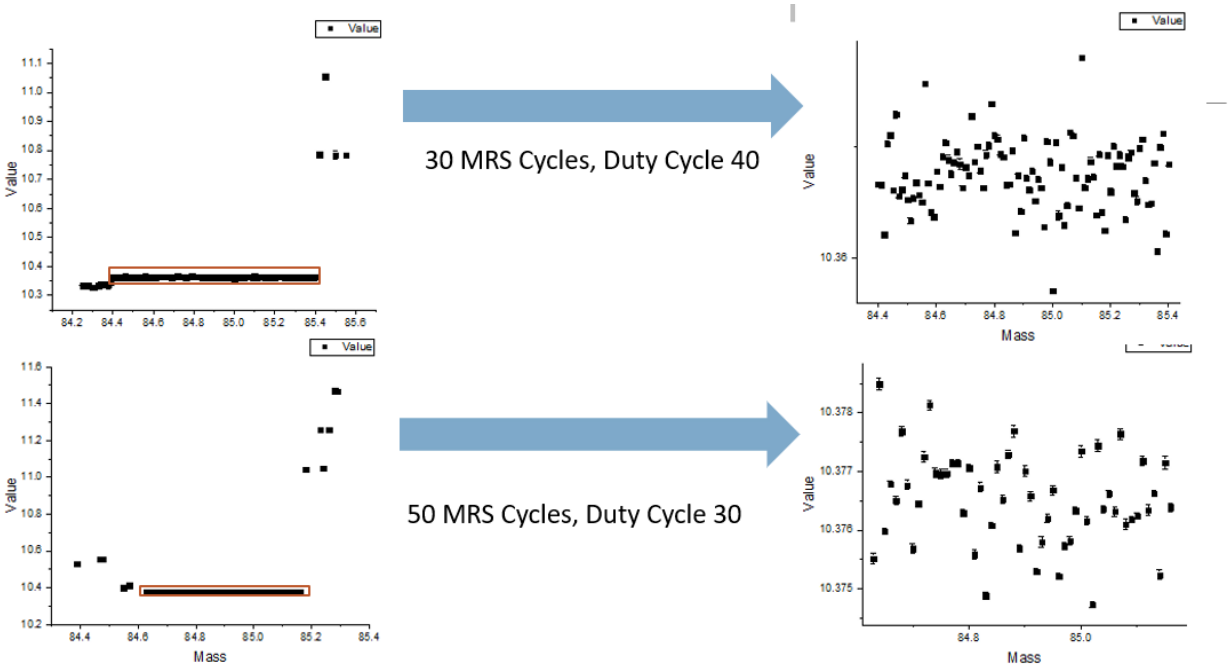


Figure 8: Gaussian Centroid vs. Mass Center for settings near 40 proportion and 30 MRS Cycles

Figure 8 displays the centroids detected at each mass center for two settings (30 MRS Cycles, 40 Proportional and 50 MRS Cycles, 30 Proportional). The apparently straight segment in the left graphs describe the main mass window for the specified settings. Centroids fitted on the borders of the mass windows appear to be having large shifts as they are likely seeing switching electric fields from the MRS electrode. The straight-line segment acts as the main mass window and is used to examine the systematic uncertainty potential. For the settings in figure 8, there appears to be an overall random spread when zoomed in. Thus, since there is no general trend, the deviations appear to be random – a sign that there is possibly little systematic uncertainty at the settings in figure 8. Alternatively, figure 9 displays clear trends (positive and negative slopes) in its zoomed in graphs for the straight segment. Since there are trends present, it is likely that there is some systematic uncertainty present at the following settings.

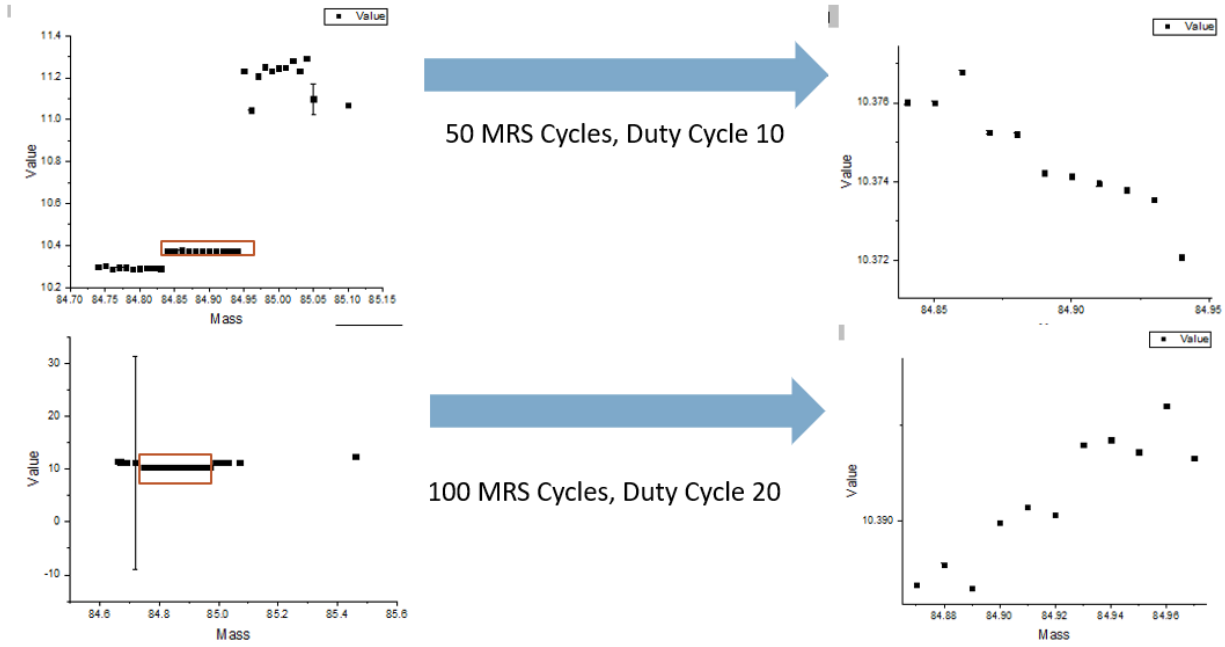


Figure 9: Gaussian Centroid vs. Mass Center for settings 10, 20 proportion and 50, 100 MRS Cycles

Results

According to figure 8 and 9, it appears that different setting ranges appear to have different effects on the amount of systematic uncertainty. Settings with lower proportions appear to have increases or decreases in the centroid values as the mass center changes; alternatively, settings with proportions near 30 and 40 appear to have a random spread of centroid values - representative of a constant centroid value being detected. The results in this section provide a motivation for a more in-depth investigation of the MRS systematics, where the systematic uncertainty can be quantified and used to determine optimal settings for re-trapping and mass measurement.

2.6 MRS ON-OFF Systematics

The purpose of this investigation was to effectively quantify the systematic uncertainty to determine optimal settings for re-trapping and mass measurement. The systematic uncertainty is defined as the mean change in centroids when the MRS is switched between ON and OFF.

Initial Procedure and Testing

Scans for multiple ON OFF peaks were conducted by delaying each scan and switching the MRS voltage ON and OFF for 100 samples each. The MRS is turned ON and OFF by using a scan delay and switching the voltage between 130 V and 0 V. The centroids of each ON-OFF pair were subtracted and plotted using a boxplot to describe the overall distribution and centering.

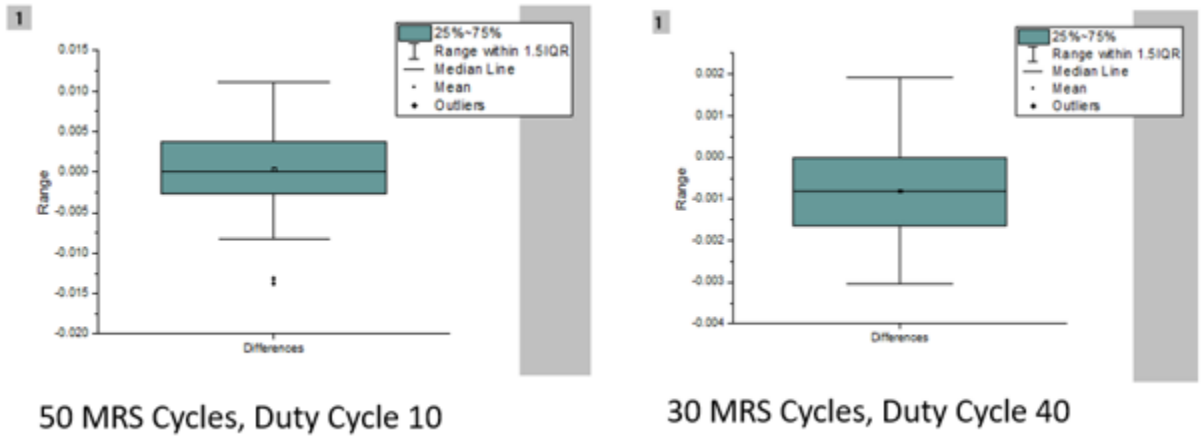


Figure 10: Centroid Differences Boxplots for the two settings of interest (section MRS Centroid Investigation)

Interestingly, figure 10 shows that the systematic uncertainty for the setting 50 MRS Cycles and 10 proportion is centered on zero, whereas 30 MRS Cycles and 40 Duty Cycles is centered on -0.001. This seems to contradict the previous section (MRS Centroid Investigation) and requires further analysis. The 50 MRS cycles and 10 proportion settings are used to conduct the same ON-OFF scans and analysis at three different mass centers: the left edge, the right edge, and the center of the mass window.

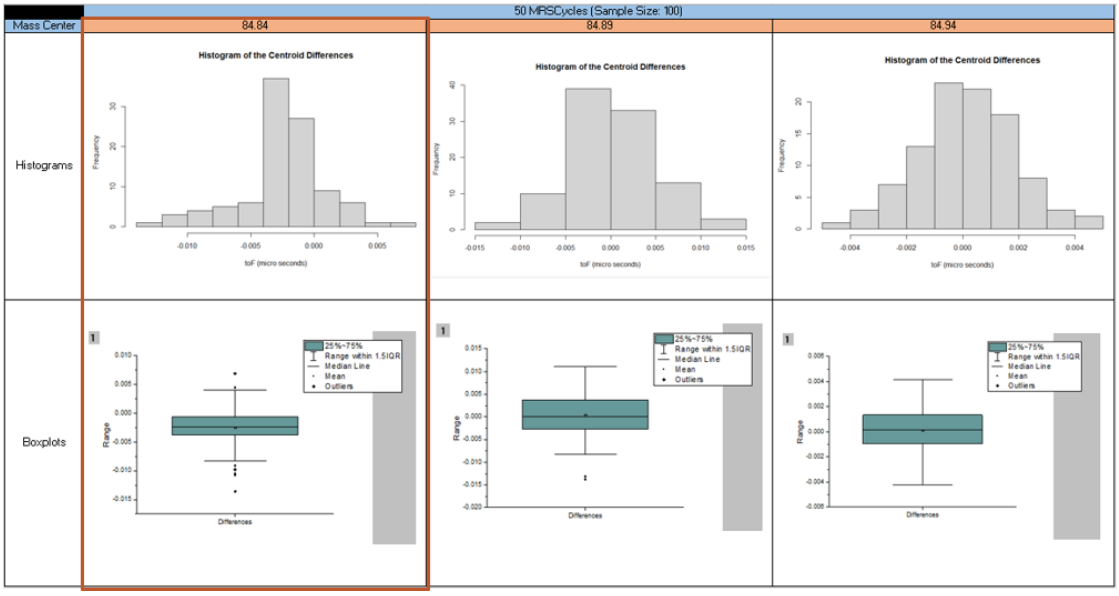


Figure 11: Centroid Differences Histograms and Boxplots for three different Mass Centers (Settings: 10 Proportion and 50 MRS Cycles)

Figure 11 shows that at mass centers 84.89 and 84.94, the systematic uncertainty appears to be centered at 0. However, at the left edge (84.84), the systematic uncertainty appears to be centered on -0.0025. Since there are only 100 samples for each distribution, using more samples will provide a much clearer result. Bootstrap distributions of differences were formed using the

difference samples at each mass center as the resampling populations. These bootstrap distributions were used for comparison with scanned distributions of larger sample sizes (500 samples of each ON/OFF). Due to high possibility of software issues with very long scans, a new procedure for scanning was developed. Instead of continuously switching the MRS voltage between 0 V and 130 V, a delay was added to the MRS so that it skips every second cycle.

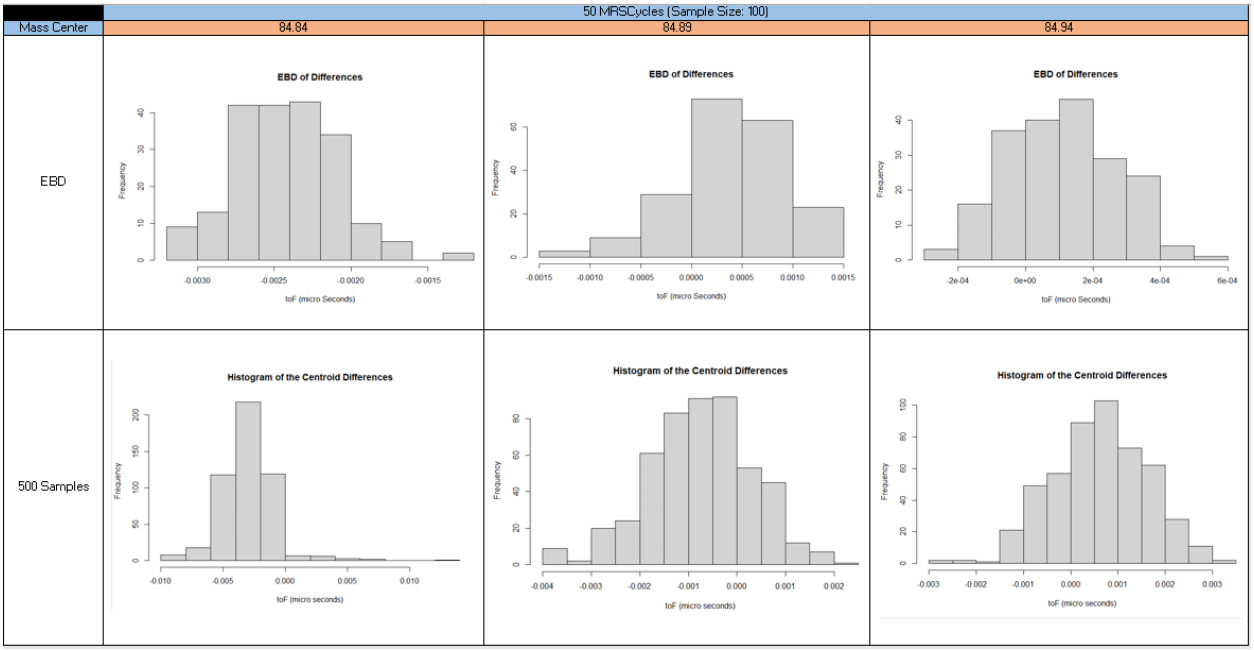


Figure 12: Comparison of Empirical Bootstrap distributions and 500 Sample distributions at each Mass Center (Settings: 10 proportional and 50 MRS Cycles)

Re-evaluating and Finalizing Procedure

Figure 12 shows that the variances and centers of the EBD's and 500 sample distributions are very different. Interestingly, the distributions on the left edge (84.84) appear to have a similar center and similar variance. Due to the large differences between the EBD and the 500 samples, it is evident that the change in procedure (delaying the MRS to skip every second cycle instead of changing between 0 V and 130 V) has affected the results greatly. It is likely that when changing between MRS electrode voltages, the voltages weren't stable during the scans. This is due to a pre-set scan delay time making some scans take place at voltages in between 0 V and 130 V. Due to the following issues, the new procedure of delaying the MRS to skip every second cycle was maintained for subsequent scans to ensure proper quantification of systematic uncertainty.

Systematic Uncertainty Evaluation

The systematic uncertainty throughout mass windows was evaluated at 10 different settings. Initially, it was evaluated at 0 MRS start turn and proportion of 30 (since 30 proportion provided a random spread in the previous section - MRS Centroid Investigation). Figure 13 shows that

using settings of 30 proportional and 50 MRS, the overall range of systematic uncertainty is well below 1 nanosecond (0.001 toF Difference). Please note that the error bars are based off a 95% confidence interval from a paired t-test. Since these settings have a mass window of about 0.6 mass units, these settings would be potential mass measurement settings. However, these settings are not ideal for re-trapping. Using the chart in figure 1, the following settings were chosen as they provided a mass window size near 0.1 mass units: (50 proportion, 800 MRS start, 30 MRS cycles) and (60 proportion, 800 MRS start, 30 MRS cycles).

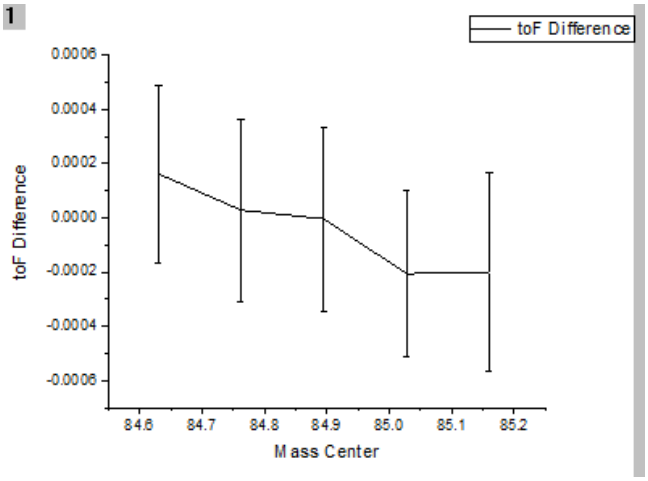


Figure 13: Mass Window Systematic Uncertainty Plot for Settings Proportional 30 and 50 MRS Cycles

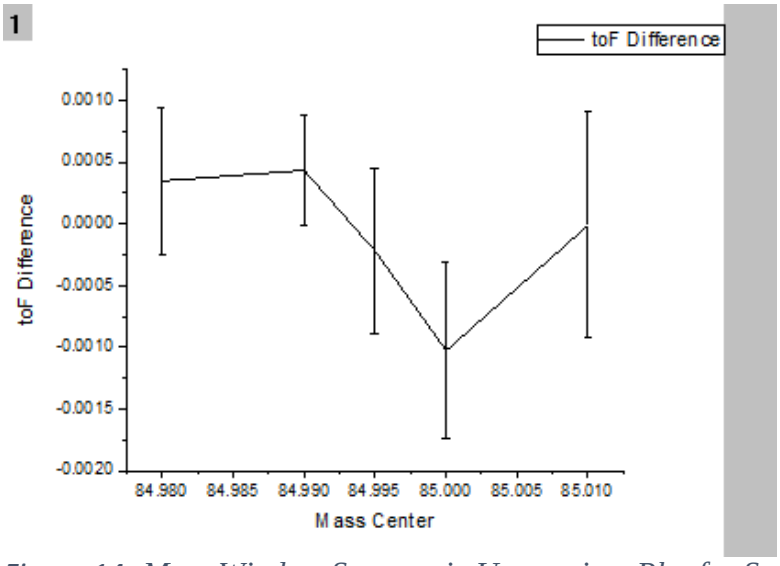


Figure 14: Mass Window Systematic Uncertainty Plot for Settings Proportional 50, 800 MRS start, and 30 MRS Cycles

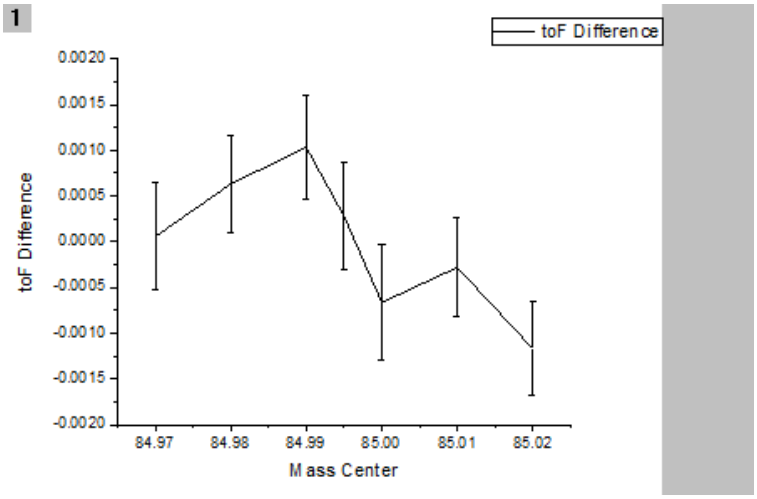


Figure 15: Mass Window Systematic Uncertainty Plot for Settings Proportional 60, 800 MRS start, and 30 MRS Cycles

Figures 14 and 15 show that the overall systematic uncertainty in each mass window appears to fluctuate around zero. The 50-proportion setting provides a smaller mass window (0.03) when compared to the 60-proportion mass window (0.05). Furthermore, the 50-proportion mass window appears to have a range of [-1.75 ns, 1 ns] which is slightly smaller than the setting with 60 proportion, [-1.75 ns, 1.75 ns]. It appears that a proportion between 35 to 50 and an amount of MRS cycles between 20 and 30, will minimize the systematic uncertainty. It is important to note that increasing the amount of MRS cycles tends to lead to increases in systematic uncertainty. Alternatively, the use of the MRS start delay does not appear to influence systematic uncertainty (as shown by figures 16) and can thus be used to effectively minimize mass window sizes. Also, proportions that deviate from the 35 to 50 range tend to increase systematic uncertainty; however, lower proportions can also be used to minimize window sizes at the risk of introducing more systematic uncertainty.

Re-trapping requires the use of less turns which limits the MRS start delay. In this paper, re-trapping will have a maximum number of turns set as 232. Thus, figure 16 shows an investigation of two small window settings at 200 MRS start turn and 500 start turn – which is used for comparison. Initially five mass centers were chosen for each mass window. However, since the MRS start doesn't seem to influence the overall shape of the graph (the systematic uncertainty), it can be kept at its maximum of 200.

As expected, the 10-proportion graphs appear to have slightly larger uncertainties near the centers of the mass windows. Also, it appears that the edges of the 10 and 20 proportion graphs appear to have very large uncertainties (greater than 2 nanoseconds). The two center graphs with more data points help provide more information on the systematic uncertainty curve – showing that the edges of the windows have high systematic uncertainties whereas the rest of the window contains systematic uncertainties that fluctuate around zero and are mostly smaller than 2 nanoseconds.

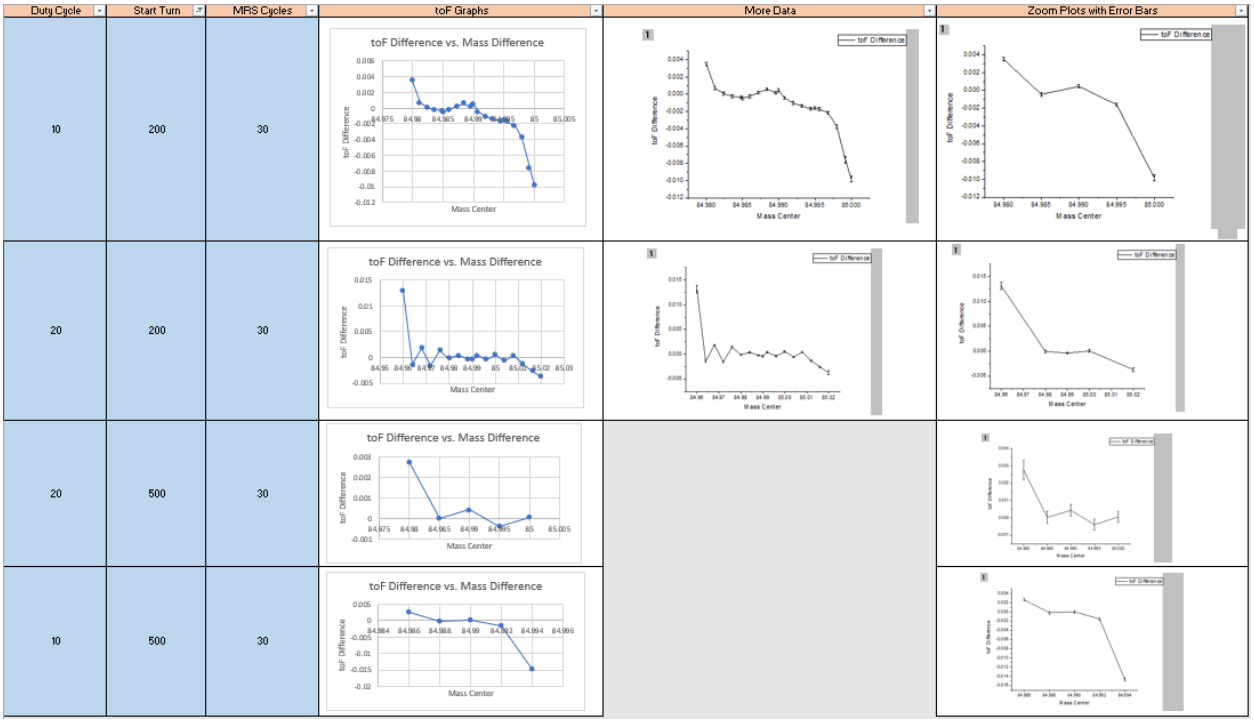


Figure 16: Re-trapping settings of Interest Mass Window Systematics Graphs

The recommended settings for re-trapping: proportion between 10-20, an MRS start of 200, and an MRS cycles setting between 20-30. It is important to stay away from the edges of the mass windows to avoid spikes in systematic uncertainty. Thus, a default setting of Mass window center $\pm$ 0.4(Mass window size) should be used to determine the maximum and minimum MRS center settings.

The true mass window is much smaller than expected (80% of scanned mass window). The mass window center tends to be about 84.99 for mass 85.

2.7 Conclusion

Through this investigation an effective procedure was developed for quantification of MRS systematic uncertainty. Additionally, a complete characterization of the MRS effectiveness and efficiency was completed to provide information on MRS settings, cleaning effectiveness (mass windows and systematic uncertainty), and efficiency (current drawn by MRS electrode).

The MRS provides separation up to a minimum window size of 0.0059 mass units. Thus, the MRS can possibly be used as an isobar separator. However, it should be used with extra caution as there are higher systematic uncertainties associated with lower proportions. Furthermore, increasing the MRS start delay is not always a viable option since it introduces the multiple peak detection phenomenon. The multiple peak detection phenomenon is especially problematic as it can introduce isobaric contaminants. The phenomenon can only be minimized by decreasing the proportion (which increases systematic uncertainty) or increasing the number of MRS cycles (which increases the current drawn and systematic uncertainty). Due to this trade-off, it is

suggested to attempt isobaric separation with MRS cycles between 30-50 turns, MRS start turn set to zero, and proportion between 20-40. It is possible to avoid the multiple peak detection phenomenon if there is a very little amount of other isobaric species present. Otherwise, using a smaller proportion should be the first action taken to minimize the multiple peak detection phenomenon as it also increases the separation strength (minimizing the window size).

	Systematic Uncertainty	Current Drawn	Mass Window	Multiple Peak Phenom
MRS Voltage	0	+	0 [1]	0
MRS Cycles	+	+	-	-
MRS Start	0	0	-	+
Proportion	+OUT	0	+	+

Figure 17: Causal Relationship Table for MRS Settings

[1]effects Mass window size of 85 Rb when Voltage is between 95 V and 105 V

Figure 17 displays the relationship between MRS settings and the system's separation effectiveness and efficiency. "0" represents no change, "+" represents a positive correlation, and "-" represents a negative correlation. Proportional may contain the word "OUT" after the sign - representing that the effect is only seen by leaving the 35-50 proportion range.

Type	MRS Cycles	Proportion	MRS Start	MRS Voltage (V)
Re-trapping	20-30	10-20	200	120-135
Mass Measurement	20-30	35-50	800	120-135

Figure 18: Suggested settings ranges for re-trapping and mass measurement

Figure18 provides the suggested ranges for re-trapping and mass measurement. Please note that these ranges are not definite and that slightly exceeding them should not lead to major changes. The MRS start for re-trapping is suggested to be the (MRS cycles + 2) subtracted from the maximum number of turns (in this case it is 200 given that the maximum number of turns is 232).

It would be beneficial to characterize the MRS's isobaric separation using the electron impact source (once it is commissioned). The electron Impact source is expected to provide higher rates of ionization, which will result in higher rates of isobaric pairs. These pairs can then be used along with the mass windows table to determine which settings lead to an effective isobaric cleaning through isolation of one species in the pair. This characterization will provide more detail into the settings that can be used to effectively minimize systematic uncertainty while also providing a reasonable amount of isobaric cleaning.

3 MRS Dual Species Isolation and Electron Impact Source

3.1 Overview

This section focuses on the implementation, testing and characterization of the Electron Impact Source and Dual Species Isolation using MRS.

The goals of this testing and characterization are to:

1. Evaluate the functionality and effectiveness of using the MRS for dual species isolation
2. Determine the new functionality and limitations associated with the new electron impact source
3. Compare the effectiveness and functionality of the electron impact source and the thermal ion source

The characterization of the electron impact source and the commissioning of dual species isolation using MRS will increase the overall toolset that can be used during experiments.

3.2 Thermal Ion Source

The thermal source uses heat to eject ionized species from a crystal source (figure 19). The ions then pass through a series of apertures and into the analyzer for mass separation and detection. The crystal is composed of several different species (ie. Rb, K, Cs) which are used as calibrant species. However, only small amounts of contaminants are ionized, leading to low counts at mass units without calibrant species. The hot cathode can be used to provide more heating, resulting in increased counts of calibrant species and contaminants. A list of all species present in the MR-ToF from mass 32 to 122, was developed to act as a reference during experiments (figure 20). Furthermore, the mass windows for 290 MRS settings were recorded (figure 21). The mass windows and the molecular identification effectively characterize the thermal ion source and the MRS effectiveness.

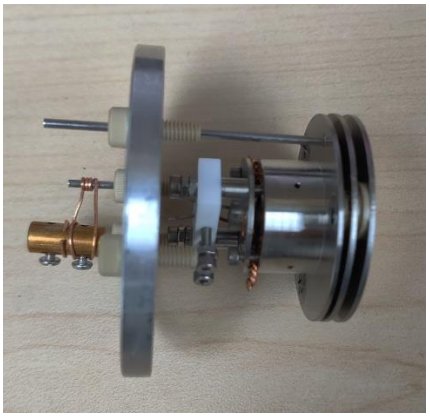


Figure 19: Thermal Ion source

Mass Charge Ratio (m/q)	Molecule	Turns
32	2O16:-1e ($^{16}O_2$)	510
32	1S32:-1e (^{32}S)	510
33	2H1:1C12:1F19:-1e ($^{12}C^{1}H_2{}^{19}F$)	510
33	1O16:1O17:-1e ($^{16}O^{17}O$)	510
33	1H1:2O16:-1e ($^{1}H^{16}O_2$)	510
33	1H1:1S32:-1e ($^{32}S^{1}H$)	510
34	2H1:2O16:-1e ($^{1}H_2{}^{16}O_2$)	510
34	1O16:1O18:-1e ($^{16}O^{18}O$)	510
34	2H1:1S32:-1e ($^{32}S^{1}H_2$)	510
34	1S34:-1e (^{34}S)	510
36	3C12:-1e ($^{12}C_3$)	510
36	1H1:1Cl35:-1e ($^{1}H^{35}Cl$)	510
37	1Cl37:-1e (^{37}Cl)	510
37	1H1:3C12:-1e ($^{12}C_3{}^{1}H$)	510
38	2H1:3C12:-1e ($^{12}C_3{}^{1}H_2$)	510
38	2C12:1N14:-1e ($^{12}C_2{}^{14}N$)	510
38	1H1:1Cl37:-1e ($^{1}H^{37}Cl$)	470
39	1K39:-1e (^{39}K)	375
39	3H1:3C12:-1e ($^{12}C_3{}^{1}H_3$)	375
40	1Ar40:-1e (^{40}Ar)	375
40	2H1:2C12:1N14:-1e ($^{12}C_2{}^{1}H_2{}^{14}N$)	375
40	3H1:2C12:1C13:-1e ($^{12}C_2{}^{13}C^{1}H_3$)	375
41	5H1:3C12:-1e ($^{12}C_3{}^{1}H_5$)	375
41	1H1:1Ca40:-1e ($^{1}H^{40}Ca$)	375
41	1K41:-1e (^{41}K)	375

Figure 20: Hot Cathode Molecule Identification Table

Mass	Voltage	MRSCycles (turns)	Upper	Lower	Width (mass vs. counts)	Current (MRS4_pos_U12) microA	Number of Turns	MRS Proportion	MRS Start
85	95	20	86.03	83.93	2.1	63.19	100	40	0
85	95	25	86.04	83.93	2.11	78.89	100	40	0
85	95	30	85.56	84.17	1.39	90.28	100	40	0
85	95	35	85.33	84.18	1.15	117.115	100	40	0
85	95	40	85.25	84.48	0.77	129.5	100	40	0
85	95	45	85.25	84.48	0.77	134.1	100	40	0
85	95	50	85.25	84.63	0.62	141.1	100	40	0
85	95	55	85.25	84.63	0.62	157.15	100	40	0
85	95	60	85.25	84.63	0.62	166.45	100	40	0
85	95	65	85.09	84.63	0.46	183.45	100	40	0
85	95	70	85.09	84.63	0.46	191.65	100	40	0
85	100	20	85.72	83.93	1.79	66.265	100	40	0
85	100	25	85.56	84.01	1.55	83.43	100	40	0
85	100	30	85.56	84.32	1.24	97.055	100	40	0
85	100	35	85.45	84.32	1.13	109.95	100	40	0

Figure 21: MRS settings and Mass Windows Table

3.3 Electron Impact Source

The electron impact source is an ion source designed to increase gas ionization through collision with electrons. More precisely, a Tantalum band is heated to release electrons. The electrons accelerate down an electric field gradient created by the Repeller and nearby apertures. The electrons then collide with and ionize the gas particles. The electron impact source and the thermal ion source will increase the counts of ionized species in the MR-ToF. This will enable the creation of isobaric pairs which can be used to further evaluate MRS cleaning and systematic uncertainty. Additionally, with the introduction of SF_6 gas, more calibrant species will be introduced; this will improve calibration and accuracy of mass measurement. Figure 22 shows the overall design of the electron impact source.

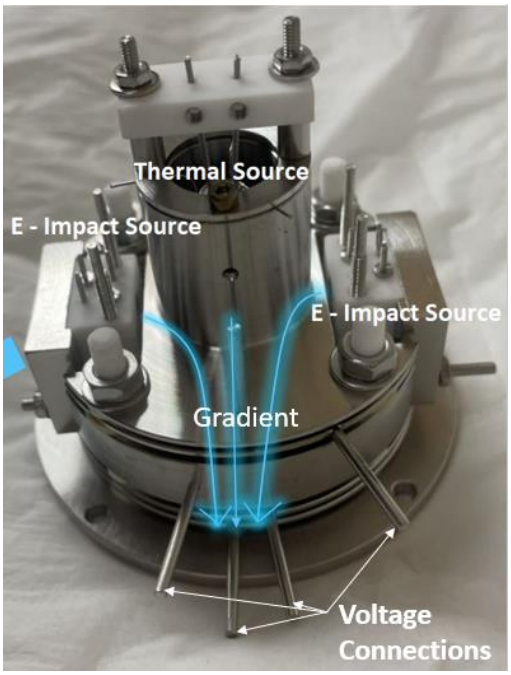


Figure 22: Electron Impact Source

Electron Impact Source – Thermal Ionization Rates

The electron impact source's voltages are first tuned to maximize ionization rates. This initial tuning is used to evaluate ionization rates based on source heating. The ion rates for Cesium, Rubidium, and Potassium are measured at various heater currents (Figure 24). The Cesium rate was the highest rate and appeared to saturate immediately. The Potassium rate required much more heating to appear. Figure 23 shows that the rate of each species increases exponentially until saturation, when heater current is increased. Please note that a new tuning was applied when measuring Cesium rates below 1 A; This shift to the left in the graph (approximately 0.02 A) can be applied to the other species' curves to approximate the rates present with the new tuning. Additionally, the rate of Rubidium at different switchyard pressures was measured and graphed (Figure 25 and Figure 26). As the pressure was increased, the rate of Rubidium increased. The Rubidium rate increased at a high rate until the Rubidium rate approached saturation. Applying more MRS cycles and measuring the Rubidium rate against pressure showed that the overall rate of Rubidium decreased due to an increase in MRS cycles.

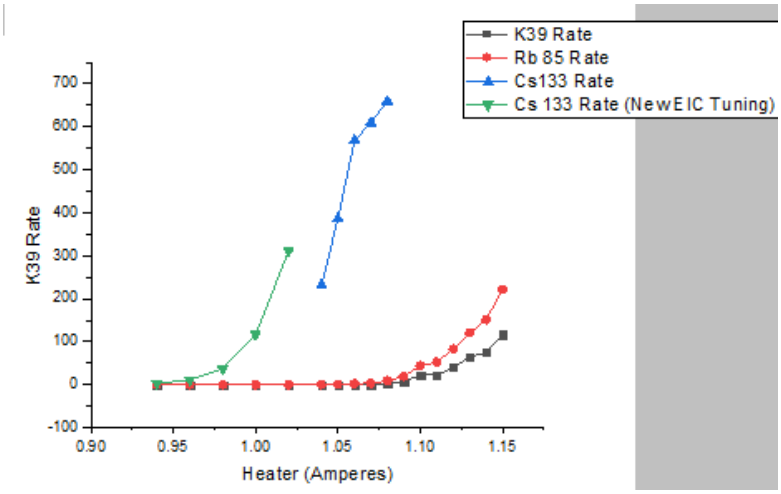


Figure 23: Ion Species Rates and Heater Current Graph

Heater (Amperes)	K39 Rate	Rb 85 Rate	Cs133 Rate	Spectrums	RFQ U	RFQ Switchyard	RFQ Trap	microPirani Pressure (mbar)	Flow Rate	Turns	MRSCycles	Injection Trap U404 (V
0.94			3.48824	60	9	9.4	9.5	3.08E-02	62	500	0	1300
0.96			11.5822	60	9	9.5	9.5	3.09E-02	62	500	0	1300
0.98			36.7423	60	9	9.5	9.5	3.09E-02	62	500	0	1302
0.98			38.1733	60	9	9.5	9.5	3.09E-02	62	500	0	1300
1			116.442	60	9	9.5	9.5	3.11E-02	62	500	0	1300
1.02			310.7	60	9	9.5	9.5	3.10E-02	62	500	0	1300
1.04		0.533333333		60	6.5	6.5	6.5	2.45E-02	62	500	0	1300
1.04			231.33333	60	9	9.5	9.5	2.45E-02	62	500	0	1300
1.05		1.433333333		60	6.5	6.5	6.5	2.45E-02	62	500	0	1300
1.05			385.86667	60	9	9.5	9.5	2.45E-02	62	500	0	1300
1.06		2.883333333		60	6.5	6.5	6.5	2.42E-02	62	500	0	1300
1.06			568	60	9	9.5	9.5	2.42E-02	62	500	0	1300
1.07		3.533333333		60	6.5	6.5	6.5	2.42E-02	62	500	0	1300
1.07			609.65	60	9	9.5	9.5	2.42E-02	62	500	0	1300
1.08	4.45			60	4.5	3.5	4	2.86E-02	62	500	0	1300
1.08		9.133333333		60	6.5	6.5	6.5	2.86E-02	62	500	0	1300
1.08			659.35	60	9	9.5	9.5	2.86E-02	62	500	0	1300
1.09	7.4666667			60	4.5	3.5	4	2.79E-02	62	500	0	1300
1.09		19.7		60	6.5	6.5	6.5	2.79E-02	62	500	0	1300
1.1	22.533333			60	4.5	3.5	4	2.76E-02	62	500	0	1300
1.1		43.93333333		60	6.5	6.5	6.5	2.76E-02	62	500	0	1300
1.11	22.383333			60	4.5	3.5	4	2.71E-02	62	500	0	1300
1.11		52.68333333		60	6.5	6.5	6.5	2.71E-02	62	500	0	1300
1.12	40.9			60	4.5	3.5	4	2.70E-02	62	500	0	1300
1.12		83.28333333		60	6.5	6.5	6.5	2.70E-02	62	500	0	1300
1.13	64.583333			60	4.5	3.5	4	2.70E-02	62	500	0	1300
1.13		120.4666667		60	6.5	6.5	6.5	2.70E-02	62	500	0	1300
1.14	75.45			60	4.5	3.5	4	2.84E-02	62	500	0	1300
1.14		151.35		60	6.5	6.5	6.5	2.85E-02	62	500	0	1300
1.15	116.75			60	4.5	3.5	4	2.80E-02	62	500	0	1300
1.15		221.3166667		60	6.5	6.5	6.5	2.82E-02	62	500	0	1300

Figure 24: Ion Species Rates and Heater Current Table (Blue – new EIC Tuning)

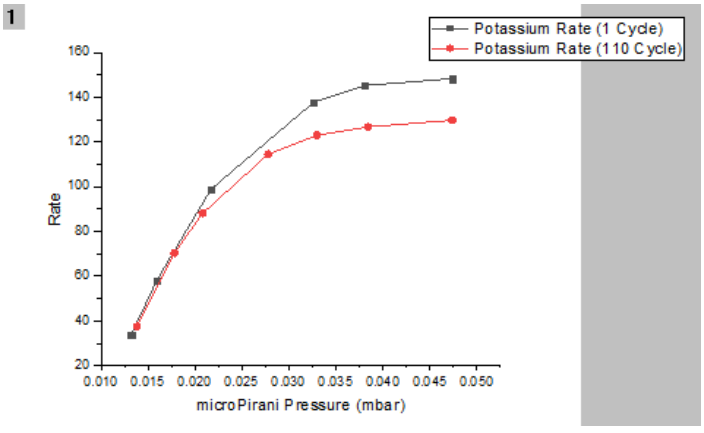


Figure 25: Rubidium Rate and Switchyard Pressure Graph

IG1 Pressure (tor)	Flow Rate	microPirani Pressure (mbar)	Potassium Rate	Heater Current	Turns
1.26E-05	60.5	1.38E-02	37.4	1.15	110
1.00E-05	59.7	1.78E-02	70.3	1.15	110
7.50E-06	58.9	2.08E-02	88.1226	1.15	110
1.44E-05	62	2.78E-02	114.505	1.15	110
1.75E-05	62.9	3.30E-02	123.034	1.15	110
2.12E-05	63.7	3.84E-02	126.675	1.15	110
2.70E-05	64.6	4.74E-02	129.686	1.15	110
7.10E-06	58.1	1.32E-02	33.7581	1.15	1
9.00E-06	59.7	1.59E-02	57.9692	1.15	1
1.00E-05	61.2	2.17E-02	98.8333	1.15	1
1.74E-05	62.9	3.26E-02	137.631	1.15	1
2.08E-05	63.7	3.80E-02	145.2	1.15	1
2.70E-05	64.6	4.74E-02	148.278	1.15	1

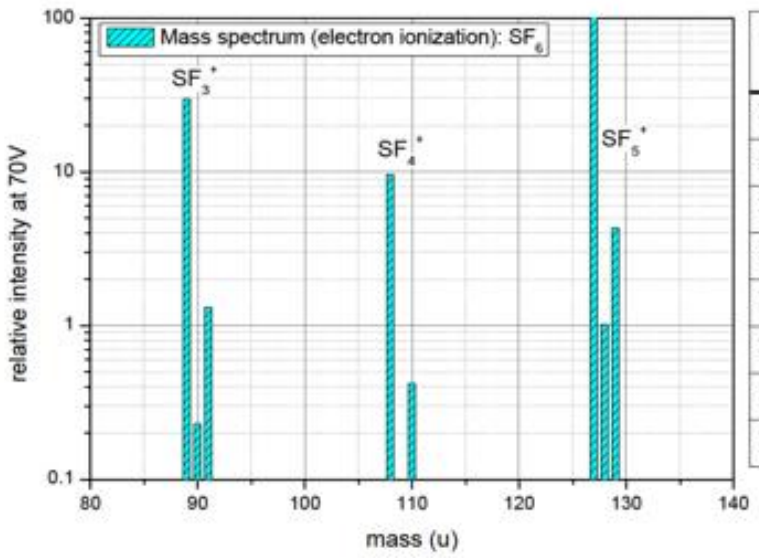
Figure 26: Rubidium Rate and Switchyard Pressure Table

Electron Impact Source Calibrant Species

The electron impact source provides Cesium, Rubidium, and Potassium as calibrant species using thermal ionization of the source crystal. Once the electron impact source is completely commissioned, it is expected to provide Sulfur-Fluorine calibrant species using electron impact ionization. Figure 27 provides a graphical description of the potential Sulfur-Fluorine calibrant masses up to mass 150. The FRS Ion Catcher at GSI produced a total of 9 calibrant species using the electron impact source and Sulfur Hexafluoride gas (Figure 28). Figure 28 will act as an expectation for calibrant species once the electron impact source is commissioned.

Expected Calibrant Masses of SF_6 Gas Ionization							
		F					
		1	2	3	4	5	6
S (Stable Isotopes)	32	51	70	89	108	127	146
	33	52	71	90	109	128	147
	34	53	72	91	110	129	148

Figure 27: Potential Sulfur-Fluorine Calibrant Species



Molecule	Mass [amu]	Relative intensity
SF_3^+	89	29.6
SF_3^+	90	0.230
SF_3^+	91	1.31
SF_4^+	108	9.56
SF_4^+	110	0.416
SF_5^+	127	100
SF_5^+	128	1.01
SF_5^+	129	4.33

Figure 28:Calibrant Species in the FRS Ion Catcher at GSI, Germany

3.4 Electron Impact Source and Thermal Source Comparison

The thermal ion source limits the types of calibrant species present, making it challenging to accurately measure masses at masses with no calibrant species present. Alternatively, the electron impact source will ionize SF_6 gas to yield a larger range of calibrant species. The characterization of the thermal ion source will be compared to the characterization of the electron impact source to describe the effectiveness and experimental potential of the electron impact source. The comparison between the two sources will be based on molecular species provided and their respective rates.

3.5 MRS Dual Species Isolation

The Mass Range Selector uses a square Voltage waveform applied to the MRS analyzer electrodes to deflect unwanted species. During Lo segments of the waveform, the MRS permits ions, especially the ions of interest, to pass through. Alternatively, when the MRS is on Hi, ions are deflected and eventually cleared. The MRS Hi voltages are generally set to 130V, and the driver signal is provided by the Altera De2 board which is connected to the MAC trigger system.

To use the MRS as a dual mass separator, the trigger scheme MRS waveforms for both MRS settings are combined using an AND gate and then outputted by the FPGA. The AND combination is chosen as it ensures that the MRS waveform is Hi (blocking) only when both species are outside the MRS region; otherwise, the MRS electrodes remain Lo to ensure that neither species of interest is being blocked. The main concern with MRS waveform combination is generating peaks shorter than 5-30 nanoseconds as it may put the FPGA in a

broken/indeterminate state. It may also result in voltage spikes that draw large amounts of power. Thus, a testing procedure using the MRS Dual Species Isolation Simulator is developed to ensure safe testing that gradually checks all possible waveform states (figure 29). Please note that the testing procedure requires high ionization rates provided by the Electron Impact Source and so will not be completed until the Electron Impact Source is commissioned. Figure 30 provides a sequential list of MRS settings that were determined for effective and safe dual species isolation testing.

Order	Test	Procedure	Goal	Outcome
1	MRS DSI Simulator Scans	Conduct scans from mass 60 to 100 with different proportions and MRS Cycles. Create a list of mass pairs with unique waveform traits that may be problematic (ie. contains a Hi segment shorter than 10 nanoseconds).	Determine and create a list of all potentially problematic waveform traits.	A list of mass pairs and MRS settings was created for exhaustive testing of Dual Species Isolation.
2	FPGA Output Signal Investigation	The output MRS waveform signal (Logic Box 10) was displayed using an oscilloscope. Short segments (ie. belwo 20-30 ns) were located and analyzed.	Determine the effectiveness of the FPGA in outputting short segments smaller than 200 ns.	Segments smaller than 50 ns were hard to recognize. Segments smaller than 10 ns were clipped and barely noticeable due to rise and fall times
3	MRS Pulser Output Investigation	The same short segments of waveforms with a minimum segment length of 200 ns to waveforms with a minimum segment length of 4 ns were analyzed sequentially at a Hi of 5V.	Characterize the output of the Pulsers for Hi segments smaller than 200 ns.	Segments smaller than 50 ns were not generated. Some segments were slightly clipped but all segments appeared ideal for MRS operation.
4	Dual Species Isolation Functionality	The MRS Pulsers' output was set to a 130V Hi and the mass seperation functionality was analyzed through MAc. The investigation started with the Rb 85 and 87 species. Then the list of mass pairs from test 1 was used.	Determine the effectiveness of using the MRS for dual species isolation. Ensure funcitonality for combination waveforms with short segments and various normalized on times.	The MRS was able to effectively isolate all mass pairs provided. However, low counts made it challenging to judge the effectiveness of certain settings. Normalized on times appeared to have an affect on the minimum number of MRS cycles for effective isolation.
5	Investigation of Functionality using the EIC	The Electron Impact source will be used to provide more calibrant species to investigate mass pair combinatinos which previously had low counts in test 4	Further evaluate effectiveness along with effects of normalized on time and waveform frequency.	This test is still to be completed upon the commissioning of the electron impact source.

Figure 29: MRS Dual Species Isolation Testing Procedure

Mass 1	Mass 2	Proportion	MRS Cycles	Min Count	Normalized On Time	Cleaning	Reason
88	85	40	30	149	61	Yes	Gradual decrease of minimum peak length to ensure safe and effective cleaning.
133	85	40	30	154	59		
41	39	40	30	54	57		
44	39	40	30	109	58		
88	87	40	30	2394	69	Low counts	Characterize cleaning of a mass pair with a large minimum peak length.
133	87	40	30	109	59	Yes	Determing if cleaning is possible with a large mass difference.
85	41	40	30	19	59	Not possible - RFQ settings	
69	32	40	30	4	58		
85	39	40	30	124	59		
41	32	40	30	34	60	Yes	Evaluate cleaning using waveforms with peaks smaller than 50 ns.
57	39	40	30	4	60		
98	81	20	30	9	79	Low counts	Test effects of frequency on cleaning since waveform is periodic.
95	96	40	30	2644	71	Yes - Low Counts	Deterine cleaning effectiveness with large mass pairs with high minimum peak lengths and normalized counts.
96	97	40	30	2674	71		
97	98	40	30	2704	71		

Figure 30: MRS Settings List for Testing

3.6 Conclusion

The introduction of the electron impact source will improve mass measurements through the introduction of new species calibrants. It will also enable a more detailed investigation into the MRS's potential as an isobar separator. Finally, it will provide increased ionization rates for completion of MRS Dual Species Isolation Testing.

Once the Electron Impact Source is commissioned, an investigation of the calibrant species and molecular contaminants will be conducted for source characterization and comparison with the thermal source. The Electron impact source will then be used to provide isobaric mass pairs at high enough rates for an investigation of MRS effectiveness using the MRS Settings (figure 30) and Mass Windows Table (figure 21). Finally, the Electron Ion Source will be used to provide higher molecular rates for thorough evaluation of MRS Dual Species Isolation.

4 MRS Dual Species Isolation Mass Range Scanner Analysis

4.1 Overview

The MRS Dual Species Isolation Simulation Software was used to characterize the appearance of waveform features (such as 4 ns peaks) in a range of mass pairs. The data was graphed and analyzed to determine feature trends based on proportion, MRS cycles, and mass pairs. These trends were then applied to generate a sequential testing list (figure 30). The trends also provided an overall description of the cleaning efficiency of the MRS in dual species isolation mode.

4.2 Dual Mass Scanner: MRS Cycles

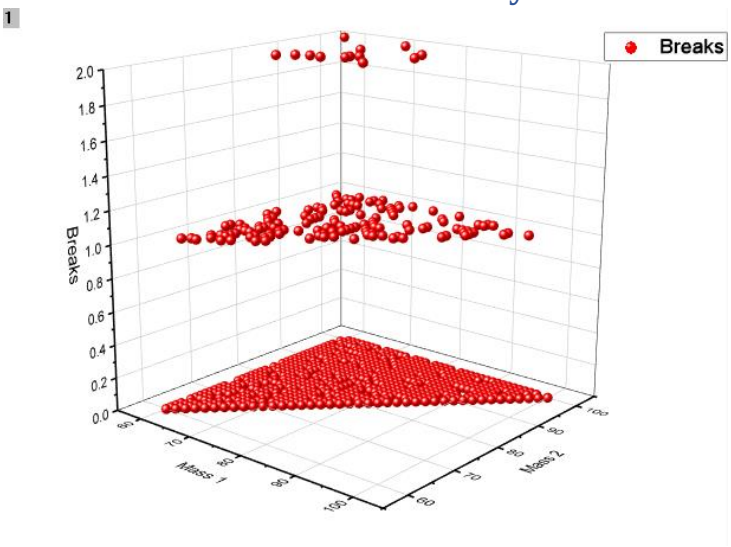


Figure 31: Adjacency Breaks with settings 40 Proportional, 40 MRS Cycles, 10 Adj. Break, window [60, 40, 100]

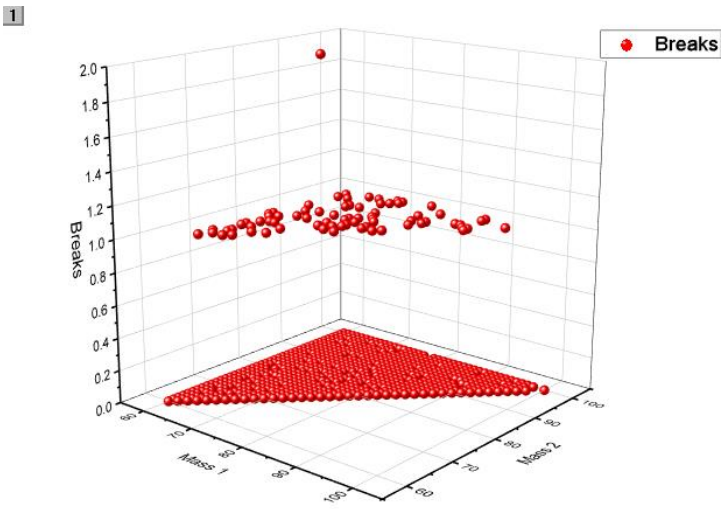


Figure 32: Adjacency Breaks with settings 40 Proportional, 20 MRS Cycles, 10 Adj. Break, window [60, 40, 100]

It is expected that increasing the MRS cycles will prolong the waveforms and thus increase the probability that the combination waveform will have peaks that are below the adjacency break limit. This is shown through figure 31 and figure 32 as decreasing the number of MRS cycles from 40 to 20 resulted in reduced mass pairs with single and double breaks. Thus, increasing the MRS cycles will likely result in having a higher number of peaks that fall below the adjacency break limit. Figure 33 shows this relationship by summing the total number of breaks for each MRS setting. The single break counts appear to start increasing linearly with low amounts of MRS cycles, whereas the double breaks appear to remain zero throughout.

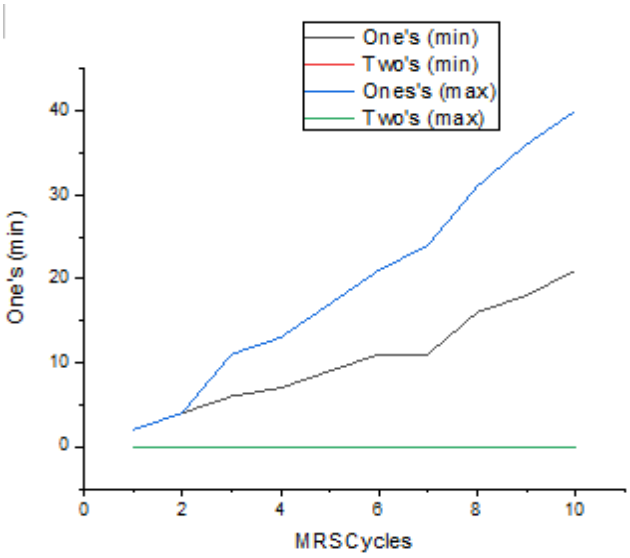


Figure 33: Adjacency Breaks Summation with settings 40 Proportional, 1-10 MRS Cycles, 10 Adj. Break, window [60, 40, 100]

4.3 Dual Mass Scanner: Proportion

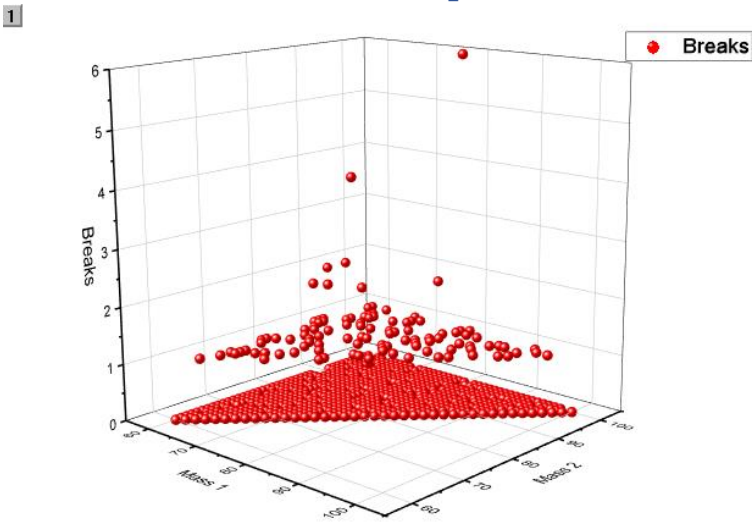


Figure 34: Adjacency Breaks with settings 20 Proportional, 30 MRS Cycles, 10 Adj. Break, window [60, 40, 100]

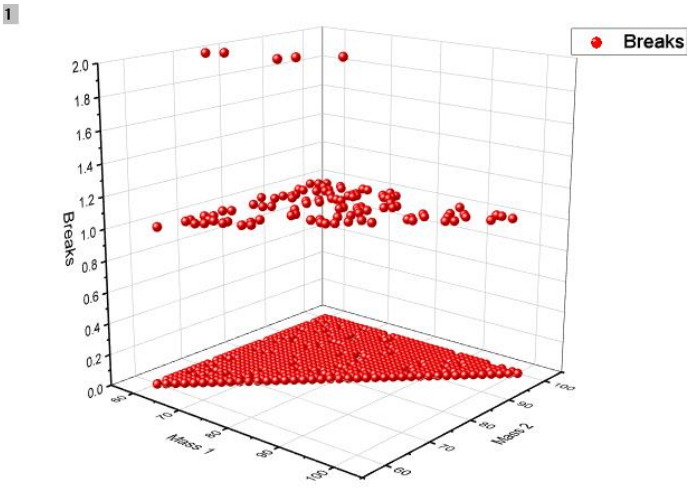


Figure 35: Adjacency Breaks with settings 10 Proportional, 30 MRS Cycles, 10 Adj. Break, window [60, 40, 100]

Proportion does not seem to have a predictable influence on the overall number of breaks. Increasing the proportion is expected to increase the number of breaks since the MRS waveform on times will become smaller. However, the overall alignment of the waveforms changes, resulting in an unpredictable trend for the number of breaks. In figure 34, it is shown that a 20 proportion and 10 Adjacency Break setting will result in a couple of mass pairs having 3 to 6 breaks. However, proportions of 10 (figure 35), 19, 21, 20, 50, and 60 fail to show breaks greater

than 2; also, the overall distribution of breaks appears to be unpredictable for each setting. Interestingly, the mass pair with 6 breaks at 20 proportion has a minimum break of 0.

4.4 Dual Mass Scanner: Switches

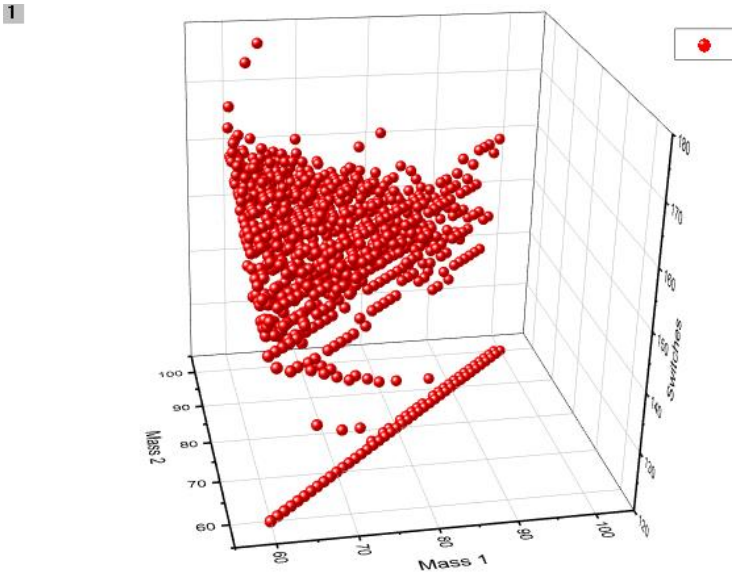


Figure 36: Switches with settings 21 Proportional, 30 MRS Cycles [60, 40, 100]

The switches for a waveform appear to increase as the difference between mass pairs increases. This is expected as smaller masses will have multiple Hi and Lo peaks during a Hi peak of the larger mass. As a result, the AND logic combination will split the Hi peak of the larger mass into smaller peaks. When the masses are equal, the switches remain at 120 which is the number of MRS cycles multiplied by 4 since there are two Hi to Lo peaks in each MRS cycle. Figure 36 shows an example of the switches for different mass pairs. It is possible for a switch to be less than the expected minimum (4*MRS cycles). However, it is very unlikely as the alignment would have to be nearly perfect so that the number of lost peaks (through alignment) is greater than the number of new peaks.

4.5 Dual Mass Scanner: On Time

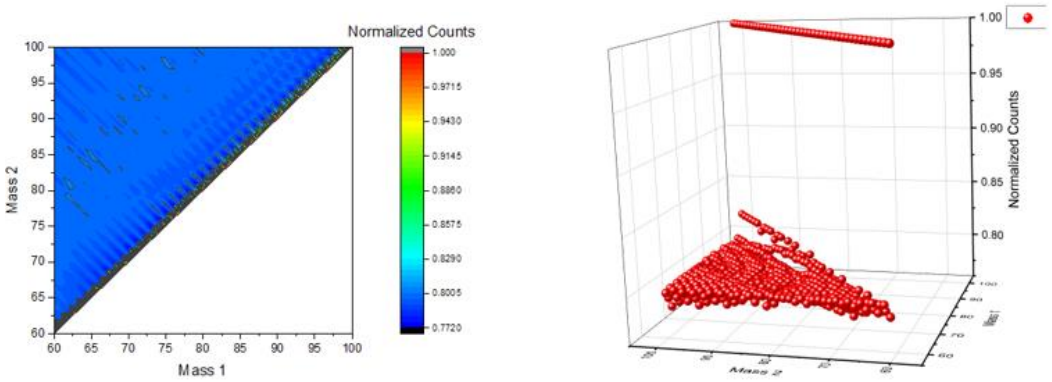


Figure 37: Normalized on Time with settings 20 Proportional, 30 MRS Cycles, window [60, 40, 100]

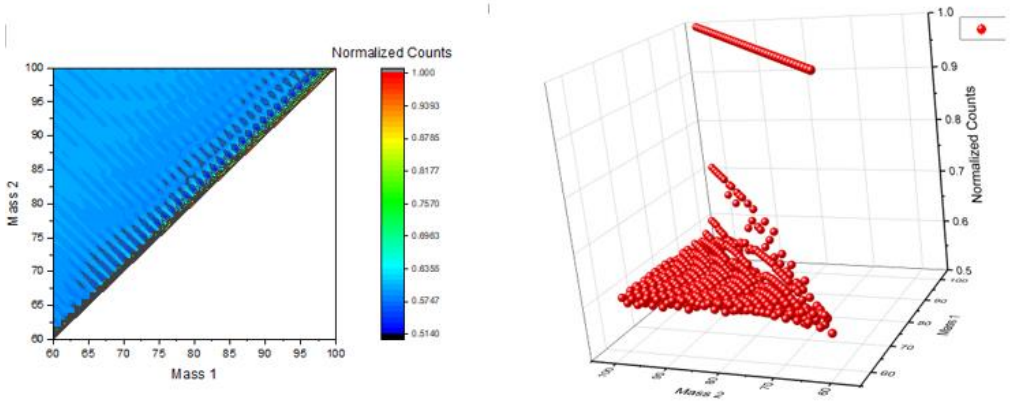


Figure 38: Normalized on Time with settings 40 Proportional, 30 MRS Cycles, window [60, 40, 100]

The Time On acts as a strong statistic for MRS cleaning being performed in the new mass pair MRS combination waveforms. The Normalized Time On is the Time On of the mass pair divided by the Time on of the MRS cycle for the larger mass. The larger mass is chosen as it is the maximum on time for a mass pair MRS combination. The amount of MRS cleaning that is lost can be seen through the normalization of the on times.

Figures 37 and 38 show the overall normalized on times being very similar for most of the mass pairs. It is important to note that heavier mass pairs (greater than 80) that are closer to the normalization line (mass 1 = mass 2) tend to have larger efficiencies. Also, decreasing the proportion leads to less off time for each waveform and a higher chance of increased on time in the mass pair waveform due to increased overlapping probability and the use of the AND combination logic. As shown in figures 37 and 38, decreasing the proportion appears to offset the graph upwards (except for the normalization line).

4.6 Dual Mass Scanner: Minimum Counts

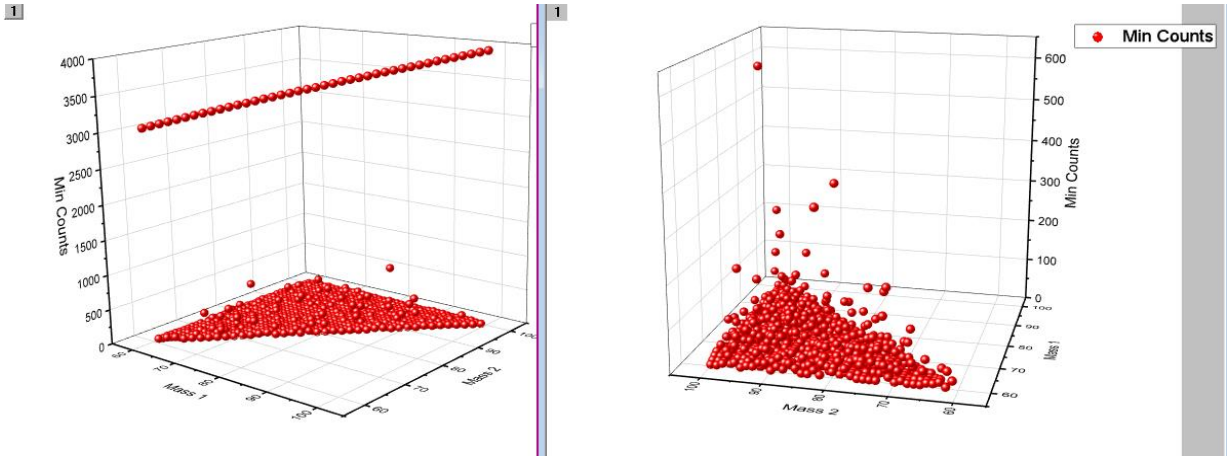


Figure 39: Minimum Counts with settings 40 Proportional, 180 MRS Cycles, window [60, 40, 100]. Zoomed in graph is on right side.

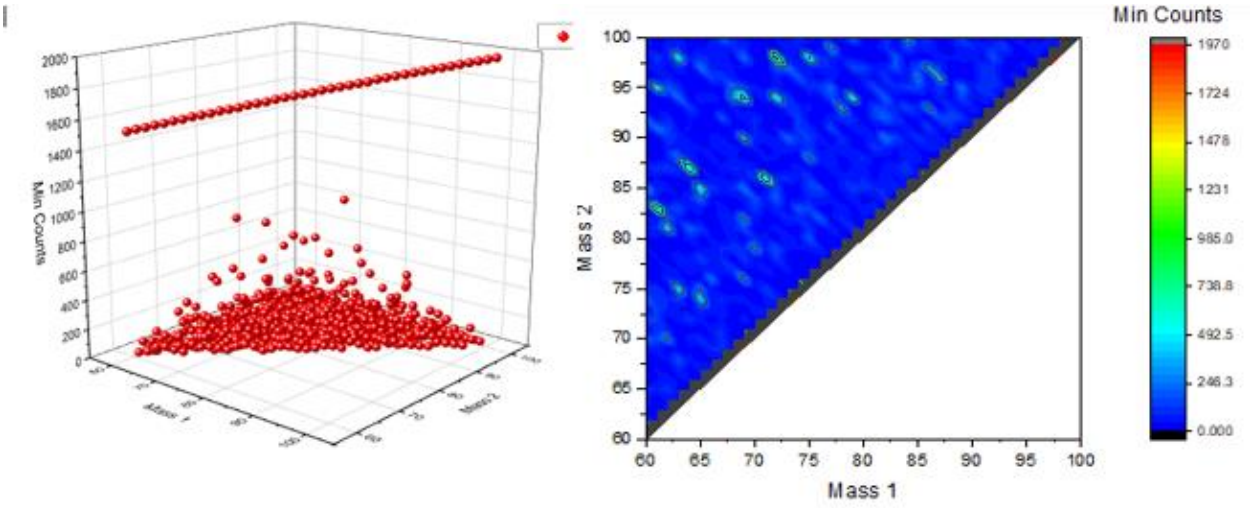


Figure 40: Minimum Counts with settings 20 Proportional, 30 MRS Cycles, window [60, 40, 100]

The minimum counts represent the smallest peak width present in each MRS dual mass combination waveform. As the number of MRS cycles increases there is more on time for a smaller peak width to appear. Thus, lower MRS cycles will reduce smaller peak widths. These changes in minimum counts are shown in figures 39 and 40. It is noted that there is no general trend in the spread of minimum counts. Also, most minimum counts appear to be smaller than 1000 nanoseconds, except for the mass pairs near the normalization line at certain settings such as 40 proportion and 30 MRS cycles. Coupling the minimum counts and the normalization of the on-time results acts as a strong indicator for mass pair waveforms with strong overlap.

4.7 Dual Mass Scanner: Adjacency Breaks

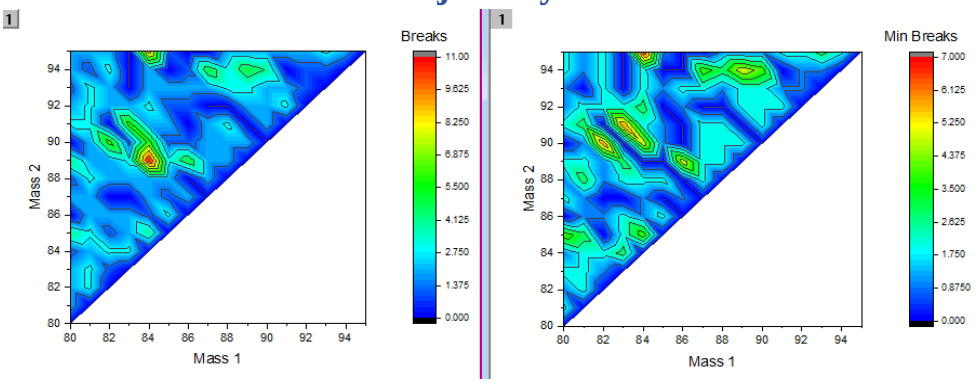


Figure 41: Adjacency Breaks with settings 40 Proportional, 30 MRS Cycles, 25 adj. Breaks, window [20, 70, 133]

Figures 41 and 42 show that increasing the adjacency break criteria from 10 to 25 greatly increases the number of peaks (breaks). Since most of the minimum counts lie below 50 nanoseconds, it is expected have a strong increase in peaks. This effect is evident in both the minimum and maximum breaks, as shown in figure 41.

4.8 Dual Mass Scanner: Full Range Scan

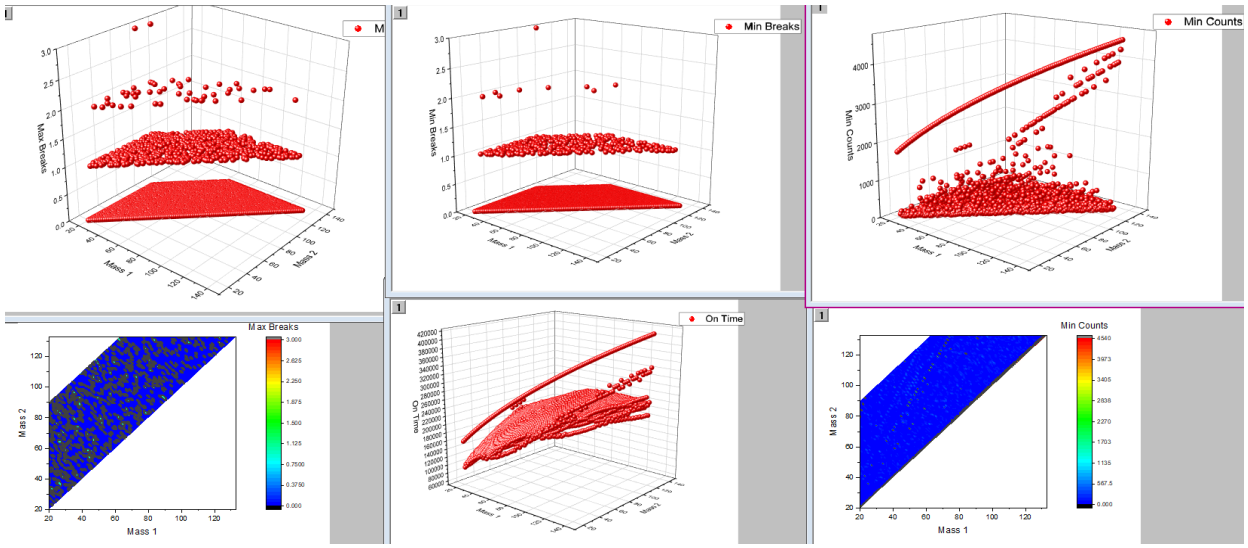


Figure 42: Graphs with settings 40 Proportional, 30 MRS Cycles, 10 adj. Breaks, window [20, 70, 133]

Figure 42 displays a set of graphs detailing the results of a full range scan from mass 20 to mass 133 with a 70-mass window. The max and min breaks graphs show that the amount of mass pair breaks does not exceed two, while also showing large density of single breaks and zero breaks. The Minimum counts shows that the mass pairs with largest minimum peak width are the mass pairs closest to the normalization line (mass 1 = mass 2). The On Time plot shows a very smooth surface that follows the overall curve of the normalization line.

5 MRS DSI Simulation Software Development and Optimization

5.1 Overview

The overall development and optimization of the MRS Dual Species Isolation (MR DSI) Software will be discussed in this section. MRS Dual species isolation can be used to isolate two separate masses in the MR-ToF. To use the MRS as a dual mass separator, the trigger scheme MRS waveforms for both MRS settings are combined using an AND gate and then outputted by the FPGA. The AND combination is chosen as it ensures that the MRS waveform is Hi (blocking) only when both species are outside the MRS region. The main concern with MRS waveform combination is generating peaks shorter than 5-30 nanoseconds as it may put the FPGA in a broken/indeterminate state or possibly result in voltage spikes that draw large amounts of power.

The goal of the MRS DSI is to simulate MRS trigger system waveform merging for various settings (masses, proportion, MRS cycles). The combined MRS waveforms will be analyzed to output data on the waveform's characteristics (i.e., minimum peak length, number of peaks shorter than a specific length, total on time (blocking time), etc.). The software will provide users with the ability to scan mass pair ranges and output the data/characteristics for each mass pair. Apart from mass pair scans, further testing such as frequency characterization will be discussed.

Please note that the source code link is in the MR-ToF ELOG submission – (0103) MRS Dual Species Isolation Software. The executable file is in the "useful stuff" folder, which is located in the TRWIN MR-ToF DATA folder. Please download the full "MRS Dual Species Simulator" folder for proper execution.

5.2 Development

5.2.1 Waveform Abstract Data Type

The software structure is built upon the abstract data type, Waveform. Through the implementation of Waveform, an MRS waveform with a specific resolution can be constructed from a specified mass, number of MRS cycles, and proportion. Waveform also contains a constructor that combines two Waveforms using an AND logic gate. If the AND is changed to another logic gate such as OR, it should be immediately noted. Then the wave graphing tab (displayed on GUI) should be used to output the MRS waveform datapoints (timings and subsequent columns representing the first mass, second mass, and combination waveforms) to compare graphs using a graphing software.

Representation Invariant

Wave only contains 0's or 1's and is non-null. Each wave element has a corresponding timing. The list of timings is in ascending order and all timings are unique.

Abstraction Function

A 2D wave represented through digital values and times. Wave contains values of 1 corresponding to Hi/Blocking and 0 corresponding to Lo/Passing. Each value is separated by a

specific time interval in nanoseconds - calculated using the specified resolution. The list of timings contains the corresponding time (in nanoseconds) for each value of the wave.

Waveform Alterations

The representation invariant and abstraction function must always be met for waveform to execute properly. If any changes to waveform are made, the representation invariant and abstraction function should be checked to ensure proper functionality. Also, the testing suite (located in the tests package) should be executed after making any changes to the source code. The checkrep function can be used in new function/constructor implementations if a representation violation is possible, otherwise an exception should be thrown if it is inefficient to check the representation invariant. A new test should be added to the testing suite if a new constructor, observer, or function is implemented into Waveform. Finally, the SpecViolation or the Representation Violation can be thrown if a specification is violated, or if the representation invariant does not hold.

Generating Waveforms

The MRS waveforms created by the Waveform constructors are developed in line with the MAc trigger system calculations and approximations. For instance, the trigger system rounds down all MAc values for on time and delay time to the nearest fifth. This becomes problematic when time delay of channel 23 (square wave generator) is used in the time delay of channel 22 (On time interval generator); as a result, the rounded channel 23 value is used in the channel 22 time delay formula. This results in double rounding and an overall 5 nanosecond inaccuracy in the channel 22 time delay. This finding likely has almost no effect on MRS accuracy as it rarely occurs; however, this inaccuracy can be avoided by implementing the channel 23 time delay formula instead of referencing the channel 23 time delay formula in the channel 22 time delay formula.

When MRS waveforms are on Hi and the Channel 22 time on ends (rising edge), the MRS waveform continues until the Hi switches to a Lo. This MRS waveform extension is accounted for in the software. Please note that test cases were constructed in the testing suite to ensure the software is in line with the trigger system's waveform construction.

5.2.2 Pulse Generator

The pulse generator class was developed for waveform merging analysis. Its main functions are pulseScheme and adjacent Lengths. It also contains additional functions: getSuggestedTimeSale and normFactor.

The pulseScheme function combines two MRS waveforms of different masses. It then iterates through the combined waveform and gathers statistics such as the smallest peak size, number of peaks smaller than a specified length, the total on/blocking time. The output of pulseScheme is shown in figure 43. Please note that the normFactor provides the on time for the MRS waveform

of the heavier mass. This acts as the maximum on time an MRS combination waveform can have.

Element	Output Statistic
0	the number of peak lengths under a user provided length limit (edges are counted as 0)
1	the number of times the waveform switches between Hi and Lo
2	the number of peak lengths under a user provided length limit (edges are counted as indeterminate)
3	the number of peak lengths under a user provided length limit (edges are counted as 0 and 1.
4	the total Hi/blocking time of the waveform (in nanoseconds)
5	the length of the smallest peak
6	the length of the second smallest peak
7	the time at which the smallest peak's falling edge takes place
8	the time at which the second smallest peak's falling edge takes place
9	100 x (onTime)/(normFactor of heavier mass)

Figure 43: pulseScheme Output List

The adjacent Lengths function combines two MRS waveforms. It then iterates through the combined waveform and outputs a list of Hi/Lo segment lengths. The first entry in the array is the length of the first segment of the waveform (normally the Lo delay time). All subsequent entries are in order so that every second entry is normally Hi. Most importantly, the last segment is not included as it depends on the timescale and is not a valuable part of the waveform.

The function, get Suggested Time Scale, is used to minimize the window size of MRS waveforms. This function is especially helpful when scanning multiple mass pairs as it reduces the amount of data points for each waveform – increasing the speed of the program greatly. The function norm Factor provides an on time for normalizing the on time of a dual mass waveform.

5.2.3 Wave Grapher

The Wave Grapher class provides functions that output various waveform characteristics. Some of the characteristics are used to determine the overall effectiveness of the waveform. Other outputted characteristics can be used for visual testing or for outputting parts of the waveform for further analysis.

The single Mass Pair Wave Grapher function is a good diagnostic tool for determining if the waveforms are being properly formed. It also helps in testing out new logic combinations of waveforms (ie. OR). The function will provide 4 columns in a text file. The first column is the timings of each value in nanoseconds. The second, third, and fourth columns are the values for the heavier mass, lighter mass, and combination of masses. Once outputted, the text file can be

imported into excel and then graphed using Origin. Since text files are limited in size, waveforms up to about 1.5 million data points can be constructed. Please note that using a resolution other than 1 ns to graph large waveforms will result in rising and falling edge inaccuracies.

The checkAdjLengths function will write the lengths of each Hi and Lo segment to a specified file (figure 44). The function uses the adjacentLenghts function in the Pulse Scheme class to generate the list of lengths. Then it outputs a file with a column of lengths. This function is especially useful when testing out the combination waveform on the MR-ToF system. After displaying the output waveform signal from the FPGA, it is possible to use the list of lengths to determine the exact location of a peak in the oscilloscope output. This makes it possible to determine if certain peaks are being attenuated, or irregularly outputted based on their lengths. This enables proper testing and characterization of the FPGA output signal.

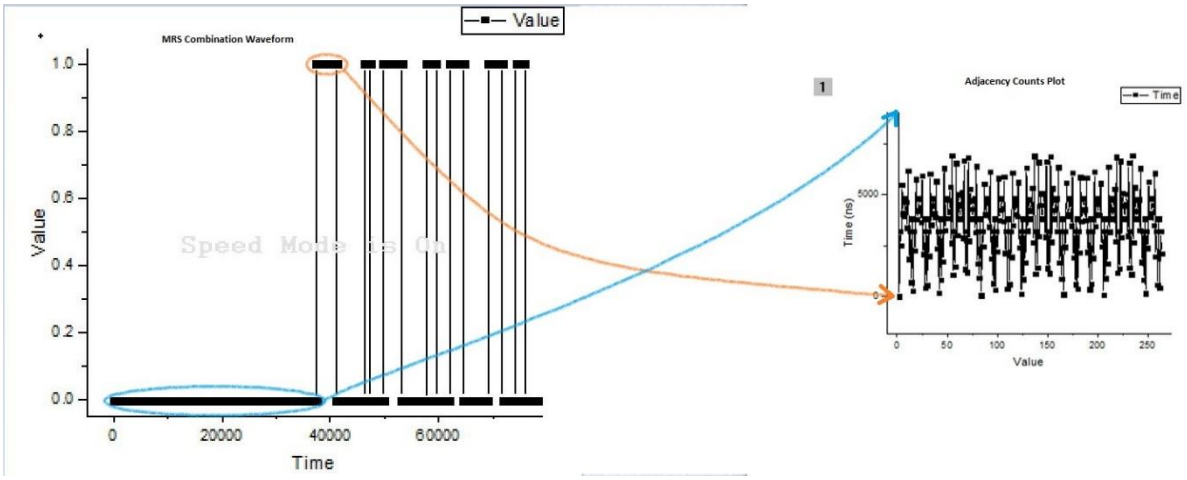


Figure 44: checkAdjLengths Waveform and Output

The testFreq and write Values Of Interest functions are specifically designed for FFT analysis. These functions are discussed in the FFT Investigation section.

The get Norm On Time function was mainly developed for GUI usage. The function returns the normalized on time (deflecting time) for a single MRS waveform combination. It is useful in quantifying the cleaning effectiveness of the dual MRS waveform.

The graph Generator function is a sequential implementation of the Dual MRS Mass Scanner (Dual MRS Waveform Statistics section) and is provided as a back up. The graph generator can only output the mass pairs, the adjacency breaks in normal mode, and the number of switches. This implementation was kept at a basic development as its processing time is very long - in the range of minutes to hours.

5.2.4 Dual MRS Waveform Statistics

The Dual MRS Waveform Statistics class contains the Dual MRS Mass Scanner which scans a range of mass pairs and provides statistics on each mass pair's MRS waveform combination. This function runs in parallel due to its long processing time. The user specified mass range is displayed in figure 45 – users can change the scan area by altering the parameters: minimum mass, maximum mass, and window. All statistics are organized into columns and written into a specified file. Figure 46 provides a list on the column numbers, column titles, and the outputted statistics. Additionally, the user may choose to only output the mass pairs and their respective normalized on times (columns 1, 2, and 10).

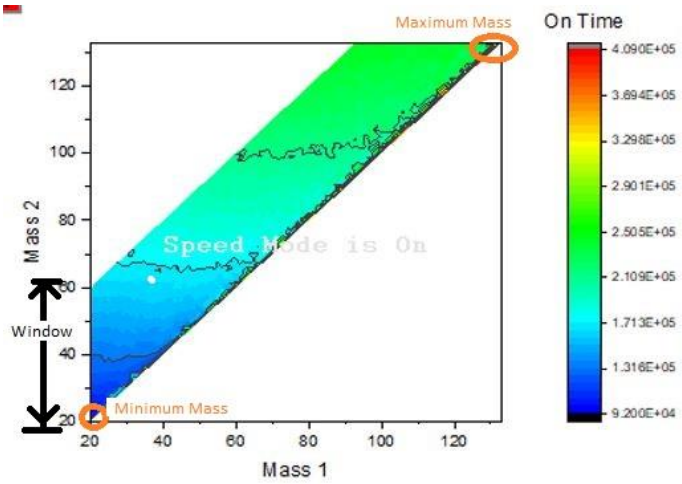


Figure 45: DualMRSMassScanner Scanning Region

Column	Title	Output
1	M1	The first mass in the mass pair (x-axis of figure 45)
2	M2	The second mass in the mass pair (y-axis of figure 45)
3	Mi	Maximum amount of adjacency breaks (indeterminant mode)
4	Br	Number of adjacency breaks in normal mode
5	Ma	Minimum amount of adjacency breaks (inclusive mode)
6	OT	Total On time of combined MRS waveform in nanoseconds
7	Sw	Total number of switches between Hi/blocking and Lo
8	Mc	Smallest peak length in the combined MRS waveform
9	Ss	Second Smallest Peak length in the combined MRS waveform
10	%C	The normalized on time – 100 x (onTime)/(normFactor of heavier mass)

Figure 46: DualMRSMassScanner Output List

5.3 Optimization

The Dual MRS Mass Scanner was constructed so that it can run in parallel. It uses the executor service to create a thread pool that has the same size as the number of processors available. The

executor service then enters all mass pairs into a blocking queue – a queue that is accessed by open threads. Each thread will then create a new instance of Grapher and run the parallel processes. In Grapher's run function, each thread creates a waveform combination and analyzes it using the pulse scheme function. The outputted pulse scheme values are then written to a user specified text file using the write To File function in the write File class. The creation and analysis of the waveforms are done in parallel while writing the data is done sequentially to avoid data races (using synchronization).

Termination of the executor service after scan completion becomes a problem when it is added to the queue. The termination command usually terminates all threads before closing the file. As a result, data in the file writer's buffer are lost. Thus, the executor service is shutdown in the write File function to avoid this problem. Once a thread writes the data for the maximum mass pair, the executor service will then run 15 extra mass pairs but will not record their values. Once a thread completes the last waveform analysis (not recorded), the thread will then start a delay timer before closing the file. This provides enough time for other threads to complete their task, accounting for the possibility that one thread takes more time to complete a recorded waveform analysis. Occasionally a thread may take more time than the extra cycles and delay time allotted when completing a waveform analysis; this results in the loss of one set of statistics for a combined waveform. However, using the parallel version is worth the risk as the speed up is large, approximately 2 times faster. Please note that if the GUI provided is not used to execute the Dual MRS Mass Scanner, then an exit function should be added below the close file function in the write File class.

A greater speedup is expected when running the program on a computer with more than 8 processors. However, having more processors than the total number of mass pairs being scanned increases the probability of terminating threads that are still analyzing mass pair MRS waveforms of interest. One potential solution to this problem is using the Future interface. However, Future would also increase the complexity of the program and can possibly lead to a slightly longer computation time. Since a computer with more than 8 processors is unavailable, the Future class will not be used in this version of the MRS simulator software. Thus, it is important to maintain a scan size that is approximately twice the size of the number of processors (at least a window of 4).

Amdahl's Law and Speedup

Speedup is the ratio of the sequential runtime to the new optimized (parallelized) runtime. A speedup of 2 describes the new optimized program as two times faster. Amdahl's rule (figure 47) shows that the speed up can be determined using the proportion of the program parallelized and the number of processors used.

The proportion of parallelization is determined using speedup measurements conducted. These speedup measurements are determined from the runtimes of the sequential and parallel programs. Please note that the extra 15 seconds in the parallel program will not be used in the Amdahl's Law calculation as it remains constant - its effect negligible as scan size increases.

Figure 48 shows the results of the speedup measurements and Amdahl's law calculations for two different scan sizes. Both scans provide similar results as expected. Since the proportions of parallelization are similar for both scans, figure 49 uses the average proportion of 0.6095 to display the overall effect on speedup as the number of processors increases. It is important to note that as the number of the processors goes to infinity, the speedup reaches a maximum of about 2.56. Thus, using 8 cores appears to be the most reasonable implementation as it provides a speed of about 2 and minimizes the possibility of data loss due to thread termination. However, if a speedup of approximately 2.5 is needed, then it is suggested to use about 30-50 cores.

$$S = \frac{1}{(1-p)+\frac{p}{N}}$$

S *is the Speedup*

p *is the Proportion of Parallelization*

N *is the number of Processors*

Figure 47: Amdahl's Law

Mass Range	Window	Cores	Sequential Time (s)	Parallel Time (s)	Speedup	Proportion of Parallelization	Maximum Speed Up
40-80	40	7	135.00	65.00	2.0769	0.6050	2.5316
20-100	80	7	602.00	285.00	2.1123	0.6140	2.5907

Figure 48: Speedup Measurements and Amdahl's Law Calculations

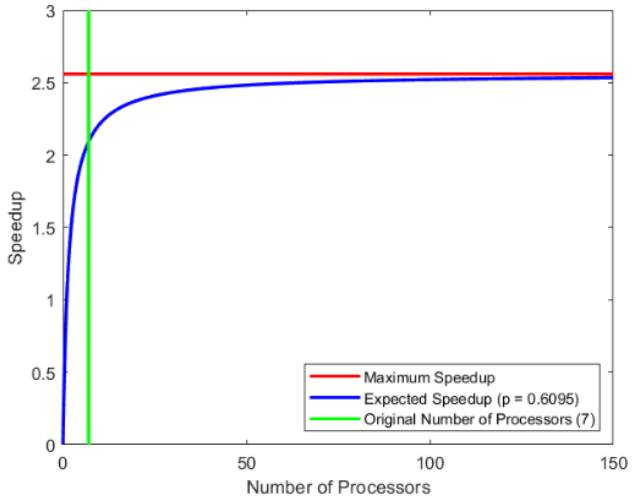


Figure 49: Speedup optimization using Number of Processors

5.4 MRS Dual Species Isolation Simulator GUI

The MRS Dual Species Isolation Simulator GUI provides users with the ability to conduct mass range scans along with other function such as adjacent lengths for a single mass pair. The GUI was developed to provide useability without having knowledge of Java or having to use an IDE. Furthermore, it makes it simple to get data for wave graphing and further FFT investigation (see FFT Investigation Section). Figure 50 displays the start up window of the GUI.

The single Norm On Times tab provides a normalized on time for the MRS combination of the mass pair (please see the Wave Grapher section). However, the tab first requires two masses, a proportion, and the amount of MRS cycles.

The adjacent lengths tab will write the lengths of each Hi/Lo segment, for a mass pair MRS waveform combination, to a text file (please see the WaveGrapher section). The FFT VOI tab will remove the first and last Lo segments, effectively removing any delay (please see the FFT Investigation Section). The waveform graphing tabs will write the timings and the values of the heavy mass, lighter mass, and combination MRS waveforms to a text file (please see WaveGrapher section). All three tabs require the same parameters as the single Norm On Times tab. However, after clicking the Generate button, the user must also choose a location and name for the text file.

The Mass Pair Scanner requires the same parameters (scanning range, proportion, MRS cycles) and provides the same output (text file of data) as the Dual MRS Mass Scanner in the Dual MRS Waveform Statistics class. For further information on output and input parameters please see the Dual MRS Mass Scanner section. Figure 45 provides a simple visualization for setting the scanning range. Figure 51 shows the mass pair scanner tab. Please note that the cancel button only exits the program when running a scan. Also, if Norm On Times Only is selected, the program will output only the mass pairs and their respective normalized On Times. The location and name for the text file must also be chosen after clicking the save button in order to start the scan. Once the scan is started, the progress bar will display the mass pairs that have been completed. The program finishes once the loading bar stops (below the progress bar). Sometimes, the progress bar may show “Done!” – this may not happen due to thread usage. Thus, the loading bar should be used as the main sign for scan completion.

The GUI was developed using the DualSpeciesMRSSim.form (layout planner) and the Dual Species MRS Sim Java class. The java class holds a main function that runs the GUI. The GUI closes when the window is closed or when the cancel button is pressed during a scan in the Mass Pair Scanner tab.

If an incorrect number is entered, the program will immediately inform the user that an incorrect value was entered. However, if large masses (greater than 100) and a high number of MRS cycles (larger than 50) are used, the results may not be accurate due to large size of the waveforms leading to memory problems. Please note that the program will not output an error as this problem is dependant on the specific mass and MRS cycles used.

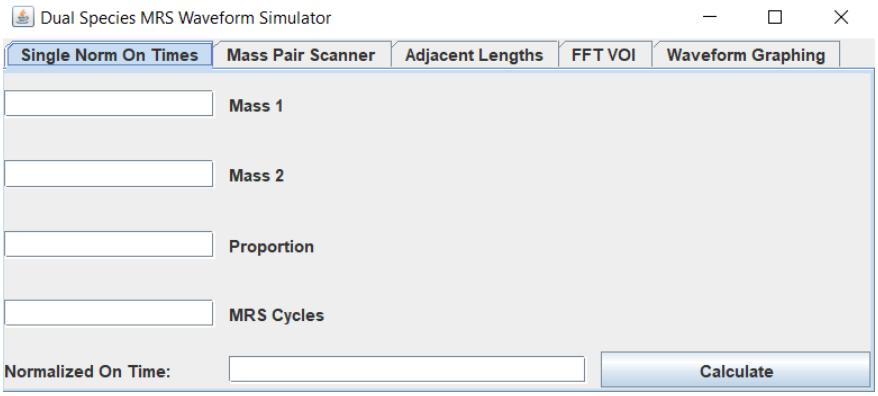


Figure 50: Startup window: Single Norm on Times Tab of GUI

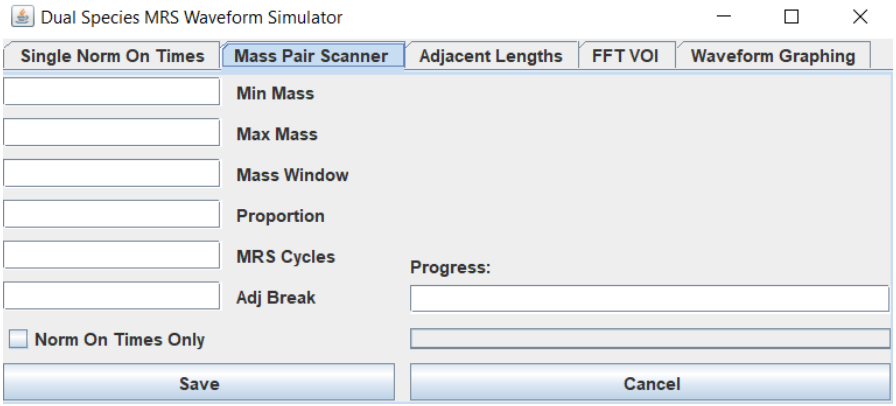


Figure 51: Mass Pair Scanner Display

Parameter	Specification (X represents parameter)
Min Mass	X > 0
Max Mass	X > Min Mass
Mass Window	X > 0 AND X ≤ Max Mass – Min
Mass 1	X > 0
Mass 2	X > 0
Proportion	0 < X < 1
Adj Break	X > 0
MRS Cycles	X > 0 (X is suggested to be smaller than 50 for heavy masses)

Figure 52: GUI Parameter Specifications

Figure 52 shows the specifications that should be followed for proper usage of the MRS Dual Species Isolation Simulator GUI. If these specifications are not followed, an error message will be provided. Please note that suggested specifications do not throw an error message.

5.5 FFT Investigation

An investigation into the frequency of the dual MRS waveform was conducted for further characterization of the combined waveforms. The overall goal of the FFT analysis was to determine if the dual MRS waveform can be modelled by frequencies. If definite frequencies were provided by the investigation, it would enable the development of a model that mathematically describes the dual MRS waveform. As a result, it would enable calculation of the times when certain peaks occur; this will help in optimizing MRS cleaning.

The initial investigation consisted of finding mass pairs with 3 or more peaks that were smaller than the adjacency break limit of 10. The timings of each peak were recorded and then the interval between each peak timing was determined using the testFreq function. Initial results for masses 98 and 81 at 20 proportional showed that the five intervals generated were all the same. This provided a sign that there might be a specific frequency that characterizes the dual MRS waveform. More waveform combinations were tested using the same procedure. A few waveforms had intervals that were not equal and most of the waveforms had two to three different intervals that were repeated. Thus, there was still potential that a frequency characterization of the dual MRS waveforms was possible. Furthermore, the AND combination mimics multiplication – if two frequencies are multiplied, the generated waveform consists of the combination of two new frequencies. Thus, it is likely that using not enough MRS cycles resulted in waveforms that only contained unique interval sizes.

On a side note, it was noticed that waveforms which had the same intervals appeared to have nonzero adjacency breaks in indeterminant mode and zero adjacency breaks in inclusive mode (figure 53). Other waveforms with repetitive sets of intervals contained nonzero adjacency breaks in both modes, but the adjacency breaks were not equal. Therefore, it is likely that since certain waveforms only had the intervals based off their minimum lengths, the periodicity was noticed (figure 54). This is because only one specific length can be deemed an adjacency break in indeterminant mode and not an adjacency break in inclusive mode. Therefore, it is likely that certain intervals were not based on timings where a unique point in length occurred (a length that only occurs once every period). Thus, if there is multiple interval repetition, it is possible that the actual periods are based on a sum of intervals, or that there are not enough MRS cycles used.

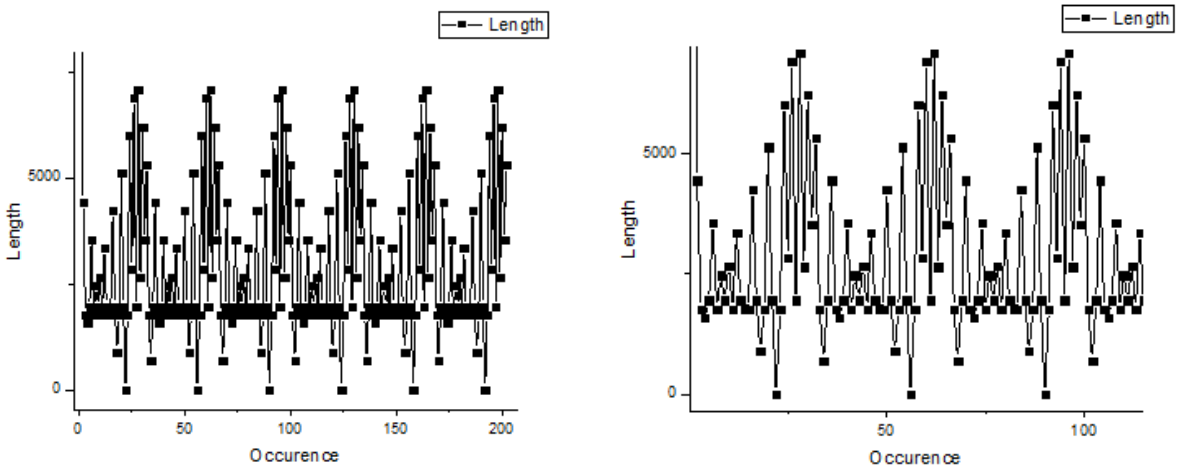


Figure 53: Adjacent Lengths graph for Mass combination 81 and 98 at 20 proportion (Zoomed-in on right)

Figure 53 shows that the MRS waveform combination of 81 and 98 at 20 proportion was periodic. Additionally, its minimum occurred periodically at a length of 9. Since the minimum was a 9. If the rising edges and falling edges were counted, then it would be transformed into 11 – which is greater than the adjacency break setting of 10. However, when the rising and falling edges were not counted, the length remained smaller than 10 - each minimum was counted as a peak.

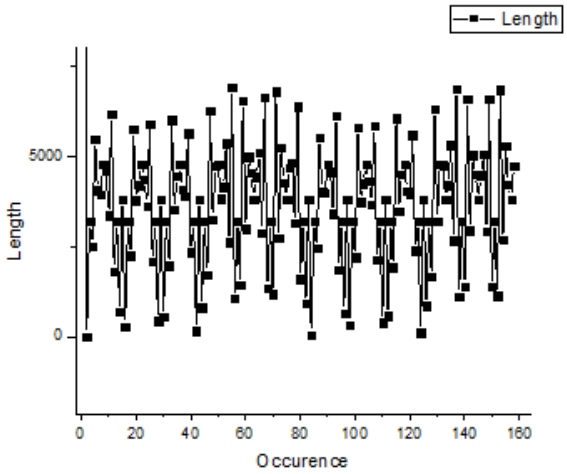


Figure 54: Adjacent Lengths graph for Mass combination 66 and 94 at 40 proportion

After the initial investigation, the write Values Of Interest function was used to output the dual MRS waveform without the starting delaying and the ending Lo segment. This clipped waveform was then imported into a Jupyter notebook where an FFT of the waveform was conducted and plotted. The 0 frequency was omitted as a digital waveform is always seen as a 0.5 offset waveform. Interestingly, the plot for the mass combination 98 and 81 at 20 proportion shows

distinct frequencies (figure 55). Therefore, it is very likely that this MRS waveform combination can be modelled using frequency. When the MRS waveform combination for masses 94 and 66 at 40 proportion were plotted using the same procedure (figure 56), it appeared that there was a lot of spectral leakage - an indicator that the provided waveform is non-periodic in the provided interval. Thus, it is likely that this mass combination at 40 proportion has period that is longer than the 30 MRS cycles used. For further analysis, an FFT with windowing, using the Hann function, was conducted to reduce spectral leakage and to provide more information on potential frequencies.

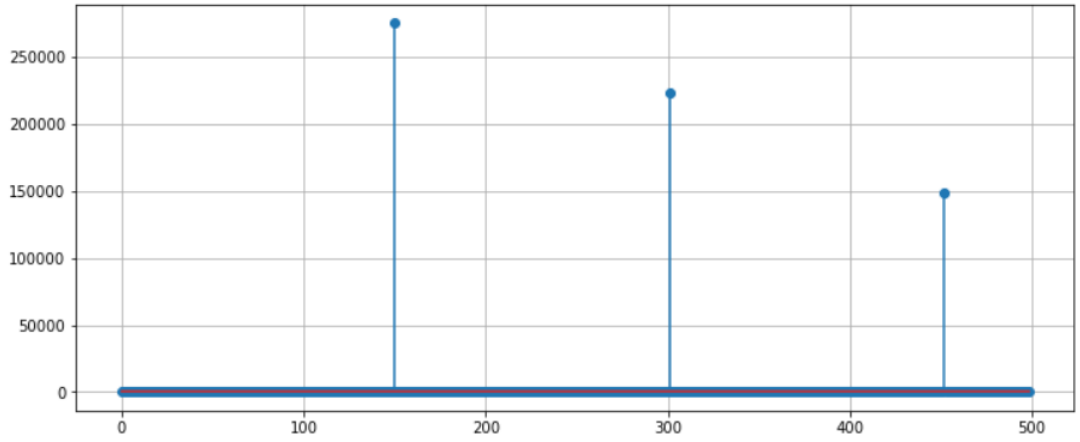


Figure 55: FFT Plot of Dual MRS Waveform with masses 98 and 81 at 20 proportion

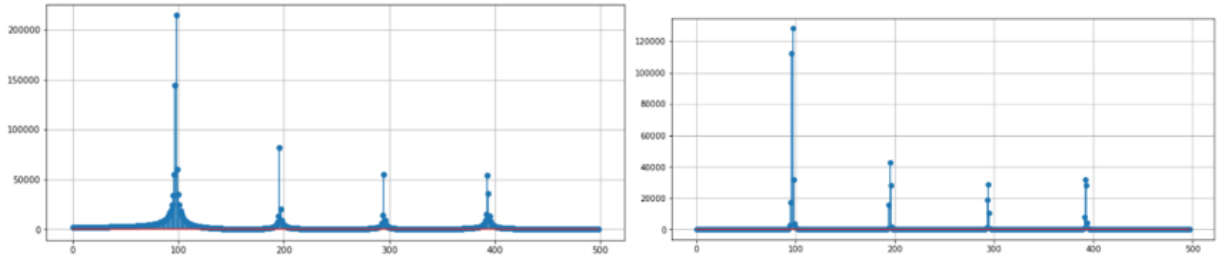


Figure 56: FFT Plots of Dual MRS Waveform, masses 94 and 66 at 40 proportion, without windowing (Left) and with windowing (Right)

The FFT investigation has displayed that it is possible that all MRS waveforms eventually become periodic. However, this behaviour is heavily dictated by the amount of MRS cycles used. This is because some waveforms can have periods that are larger than the MRS on time – making it hard to determine potential frequencies. Using windowing, it is possible to narrow the range of potential frequencies and reduce spectral leakage. This enables better characterization for waveforms that do not experience periodicity in the provided MRS cycles. For further characterization, it is suggested that the MRS cycles are extended until the output text file

reaches the size limit. Through this extension, it would be possible to characterize more MRS waveforms using frequency while also further clarifying the possibility that all waveform combinations are periodic.

5.6 Overall Software Structure

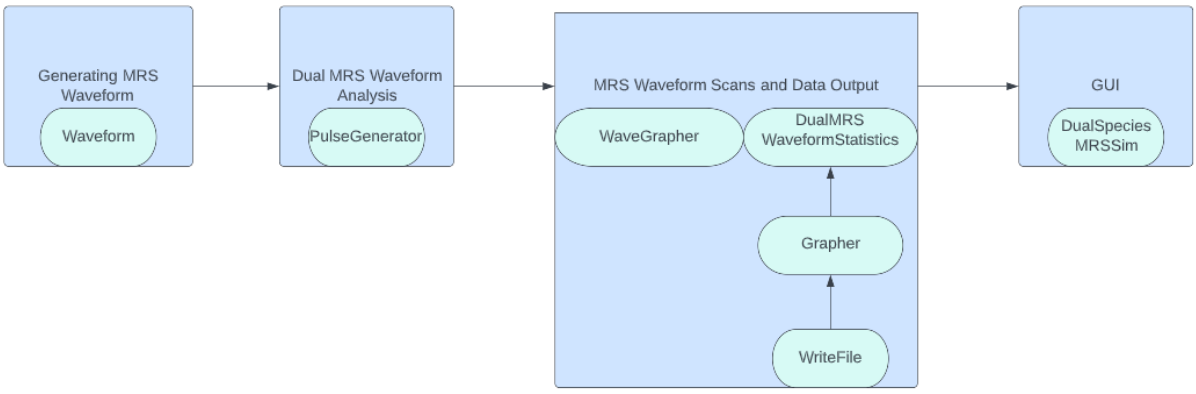


Figure 57: Overall Dual MRS Waveform Structure

Figure 57 describes the overall structure of the MRS Dual Species Isolation Software. Please note that figure 57 does not describe the class hierarchy and is only used to explain the overall process of simulating the waveforms. The blue boxes represent a specific process in simulating or analyzing the MRS waveform. Each process contains green boxes which represent the classes used. Since Dual MRS Waveform Statistics contains a parallel function, it requires Grapher and WriteFile for parallel execution. Through this execution process, the waveforms are simulated efficiently while also providing accuracy in the nanoseconds.

6 Conclusion

A thorough understanding of the principles and factors affecting MRS effectiveness, accuracy, and efficiency were developed through a complete MRS investigation. In addition, dual species isolation using the MRS has been added to the experimental toolset – enabling more MRS functionality. With the addition of the Electron Impact Source, a full characterization of dual species MRS is planned to be completed. This will help determine new functionality and potential limitations of MRS dual species isolation.

7 Glossary

Adjacency Breaks - The minimum number of the same adjacent Hi's or Lo's (in nanoseconds) for the waveform to be considered stable.

Blocking/Deflecting - Setting the MRS electrodes to Hi to block unwanted species.

Full range scan - A scan from mass 20 mass to mass 133 with a window of 70.

Inclusive mode – Counting the rising and falling edges of the dual MRS waveform as 0 and 1.

Indeterminant mode – Counting the rising and falling edges of the dual MRS waveform as indeterminant.

Mass pair ranges - A range of mass pairs - normally used in scans. The mass pairs are scanned in the shape of a trapezoid (based on user settings) on a mass-mass graph.

Maximum breaks/breaks - The number of breaks when the rising and falling edges are considered indeterminate (not counted).

Minimum breaks - The number of breaks when the rising and falling edges are counted as Hi and Lo.

Minimum counts - The minimum peak width of an MRS waveform.

MRS Center - The time calibration for the MRS Duty Cycle.

MRS settings - A general term for proportion, MRS cycles, MRS start, and MRS Voltage.

MRS start - The turn number that the MRS starts at in the mass separation cycle.

Normal mode – Counting the rising and falling edges of the dual MRS as only 0.

Passing - Setting the MRS electrodes to Lo to allow species to pass.

Peak - A mass window that appears in a mass unit with multiple windows.

Primary setting of interest – The optimal MRS setting that has the least systematic uncertainty associated with a mass window small enough to distinguish between two isobaric species.

Proportion/Proportional – The percentage of time off in the MRS duty cycle (ie. 40 proportion represents a duty cycle that is 40 percent Lo and 60 percent Hi).

Secondary setting of interest - The optimal MRS setting that has the smallest mass window associated with a systematic uncertainty less than 1-2 nanoseconds.

Switches - The total number of rising and falling edges for an MRS waveform.

Window settings - [minimum mass, window, maximum mass]. Please refer to the Software overview documentation attached for a graphical description of the window.