Practical Quadrupole Theory: Digital Quadrupoles vs. Traditional Sinusoidal Operation

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Introduction

Recent work by other groups has demonstrated great promise in extending the mass range and mass resolution of resolving quadrupoles by using 'Digital Quadrupoles', i.e. the operation of quadrupoles using square and rectangular waves instead of the traditional sine wave.

Typical digital quadrupole implementations utilize fast switching between two potentials, typically requiring fast response FETs switching high voltages with high currents across a capacitive load (the quadrupole, cables, and internal capacitance of the FETs themselves). The heat generated by this high-speed switching ultimately results in limiting the practical operating voltage to a few hundred volts peak to peak.

In this work, a broadband amplifier is used to apply higher voltage (to 600 Vpp), non-ideal rectangular waves to a quadrupole comparing performance to traditional sinusoidal operation.

Experimental

A quadrupole mass spectrometer was configured with a Brink type EI ion source mounted onto a 12 mm round rod quadrupole of 12 inch length, using an electron multiplier as the detector. The 12 inch long quadrupole length was selected to allow more cycles of ion motion (improved resolution) for the ions than our standard 8 inch long quadrupole, since the Astraea system has a maximum of 500 kHz operating frequency. Perfluorotributylamine (FC-43) was used as the analyte molecule since it has a well characterized periodic collection of mass peaks.

Data acquisition was effected using the Ardara Technologies Model 121 Tempus quadrupole data acquisition system and the GAA Custom Electronics Astraea Hybrid Precession Waveform Generator with the high voltage relay option (0 to 100 V_{op}, 200 V_{pp} effective, 50 to 500 kHz, with 0.001% duty cycle granularity and a few ppm duty cycle jitter). (See Figure 1.) Each Astraea scan typically included acquisition of ten data points for each m/z, with each data point representing 50 RF cycles at a given RF frequency. Acquisition at higher masses (lower RF frequencies) resulted in longer 'dwell' times per data point

Data acquired using the Astraea system, used its internal function generator to provide the precise waveform duty cycle, with the quadrupole high voltages originating from the Astraea box itself, connected to the quadrupole RF feedthrough using 12 inch RG-62 cables with BNC connectors on one side, and SHV on the other. The short length RG-62 cables were selected to minimize the capacitive load added to the system to ~6.7 pF.

Zero-to-peak voltages of 2.5 volts to 100 volts were utilized with Astraea, with the operating voltage limited by the operating voltage required to pass the lightest ion in the selected mass range at the maximum frequency of the power supply (500 kHz). For the 12 mm rod diameter quadrupole used in these experiments, this calibrates to ~0.5 Vop per amu at 500 kHz, with the Astraea empirically calibrated to a value of 5.372 mm, with a q of 0.706.

Data acquisition using the Ardara Technologies Model 121 Tempus data acquisition system utilized an inexpensive arbitrary waveform generator (RIIAI Model FY2300, 20 MHz, 14 bit, with 0.01% duty cycle granularity) to generate sine waves, rectangular waves, and arbitrary waveforms. This allows direct performance comparison between traditional sine waves, digital (rectangular waveforms), and arbitrary waveforms.

These waveforms were input into an Ardara Technologies Model 158 Broadband Amplifier, which provided the high voltage RF outputs. The Broadband amplifier was modified to remove its input low pass filter to allow amplification of higher harmonics, allowing a square wave to be more square than sinusoidal, and replacing the standard twin solenoidal output inductor with a toroidal inductor.

Since the Broadband amplifier uses an N-to-1 transformer to amplify the high voltage RF, while the average of the two phase outputs is zero for a 50:50 duty cycle, for other duty cycles, the peak-to-peak voltage will be correct, but not centered on zero volts DC, like the 50:50 duty cycle case. To correct for this offset, mass programmed DC 'Compensation Voltages' were added to the RF outputs to bring the average of their two states back to zero volts DC. This 'Compensation Voltage' was implemented by using the standard resolving DC in the Ardara Technologies Model 129 Quadrupole Power Supply controller, by calibrating a mass programmed DC offset 'Compensation Voltage' to maintain that the high voltage output waveform centered around zero volts for all masses, with a slight additional DC resolving voltage with increasing mass to maintain unit mass resolution across the mass range. The modified broadband amplifier had a maximum RF output of 600 Vpp at 500 kHz, with a slightly overdamped rise time 'trapezoidal' waveform, not an idealized square wave. (See Results and Discussion section.)

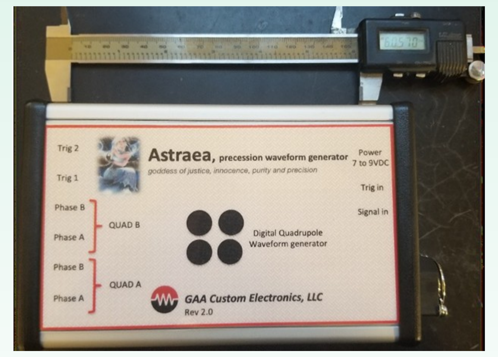


Figure 1. GAA Custom Electronics Astraea Hybrid Precession Waveform Generator

Results and Discussion:

Astraea Digital Quadrupole Performance:

The Astraea data acquisition system utilizes a user-selectable fixed amplitude (0 to 100 V_{op}), calibrated to the user input Mathieu parameter 'q', (0.706 was chosen in this work), with an $r_0$empirically determined for the 12 mm round rod system to be 5.372 mm, based on the built in theoretical mass calibration that Astraea uses.

During initial testing, the 0 to +5 volt control waveform was accidentally connected to the quadrupole, resulting in nice resolved spectra across the mass range for 5 V_{pp}, (2.5V_{op}), even with ugly ringing on the measured drive voltages due to mis-matched impedances. After verifying that the power supply was not damaged, this spectrum was reproduced with the high voltage outputs set tot 2.5 V_{op}, as shown in Figure 2 below.

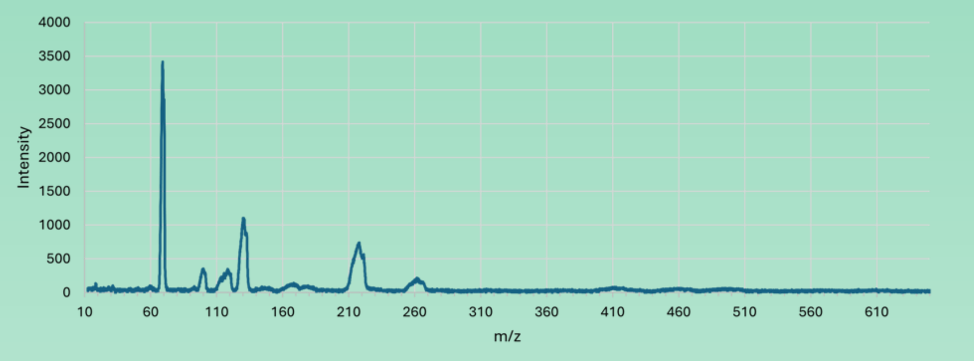


Figure 2. Astraea constant resolution frequency scan of perflurotributylamine from 10 to 650 amu with 2.5 V_{op} (5 V_{pp}). Calculated frequencies ranged from 345.79 kHz (5V_{pp} at 10 amu) to 42.89 kHz (5V_{pp} at 650 amu). Duty cycle 61.2% to 39.8%.

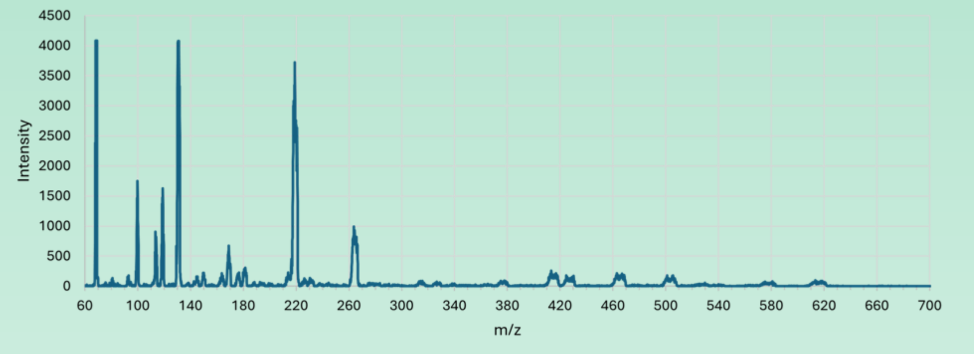


Figure 3. Astraea constant resolution frequency scan from 60 to 650 amu with 25 V_{op} (50 V_{pp}). Calculated frequencies ranged from 446.41 kHz (50V_{pp} at 60 amu) to 135.63 kHz (50V_{pp} at 650 amu). Duty cycle 61.125% : 39.875%.

Transmission as a function of mass resolution for Perflurotributylamine m/z 219 using Astraea near 467.33 kHz with various duty cycles shows a relative transmission of ~25% at unit mass resolution, which is comparable to traditional sinusoidal performance at 500 kHz.

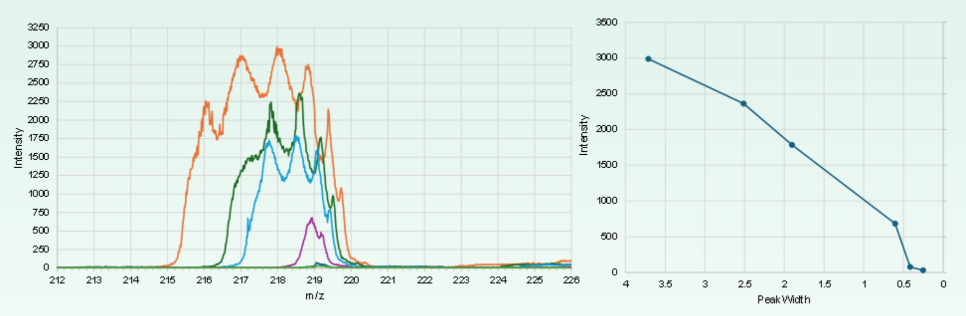


Figure 4. Peak shapes for m/z 219 at various duty cycles, with Resolution-Transmission curve showing relative transmission of ~25% at unit mass resolution. This was an Astraea frequency scan from 210 to 230 amu with 100 V_{op} (200 V_{pp}). Calculated frequency at m/z 219 is 467.33 kHz. Duty cycle varied from 60.75:39.25 to 61.125:38.875

Hybrid Digital / Broadband Analog Performance:

The modified Ardara Technologies Model 158 Broadhead power supply was configured with a Quadrupole Power Supply Controller, controlled by the Tempus Data Acquisition system. This configuration allows for a mass programmable DC voltage with adjustable range from -50 to +50 VDC, well beyond the range required for these experiments.

This configuration allows for constant frequency scans, with RF amplitude varied as a function of mass, with a voltage range to over 500 Vpp at 500 kHz. Mass calibration was approximately 1 V_{pp} per amu at 500 kHz, yielding ~500 amu mass range at 500 kHz.

Using a square wave input with 60:40 duty cycle, the high voltage outputs showed apparent DC offsets, even though the input DC voltages were at ground, and the resulting mass spectra looked like RF-only spectra.

A DC 'Compensation Voltage' was added to each RF pair with equal and opposite DC voltages, calibrated empirically to result in unit mass resolution for the various mass peaks across the mass range.

The resulting 'Compensation Voltage' adjusted high voltage waveforms appeared to be centered around 0 volts, similar to the outputs of the Astraea system, which forces the waveforms to center around ground (or a user selected pole bias) by its very nature, since the voltages are direct driven DC voltages through FET switches.

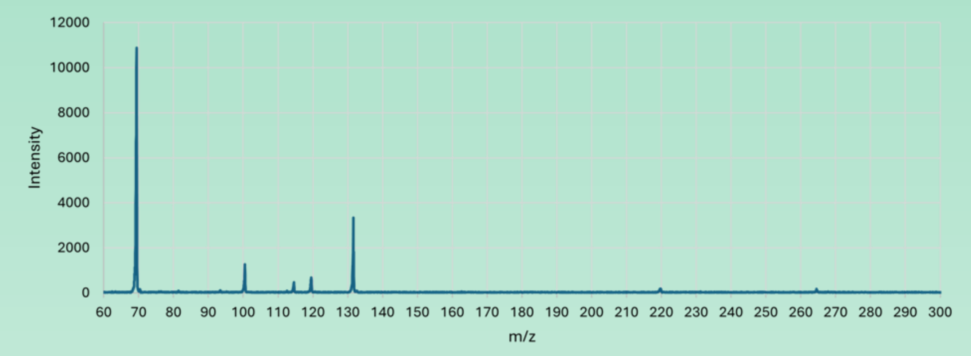


Figure 5. Mass scan from 50 to 300 amu with a fixed frequency 500 kHz 60:40 duty cycle analog rectangular wave, with peak-to-peak voltage increasing with increasing mass. (Voltage scan, not frequency scan. The DC Compensation Voltage was manually calibrated across the mass range to provide unit mass resolution.

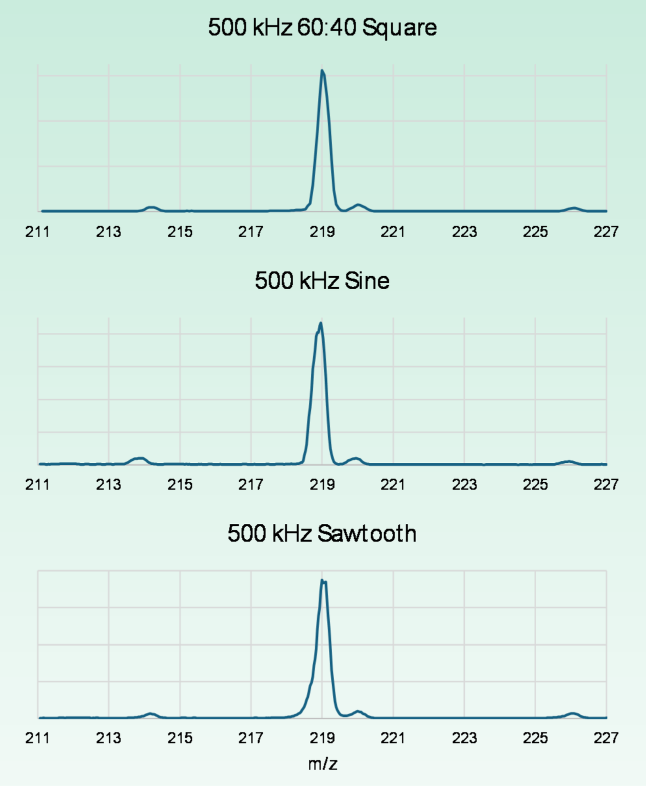


Figure 6. Mass scans of perfluorobutylamine m/z 219 showing better than unit mass resolution at 500kHz, driven by a traditional sine wave, rectangular wave with 60:40 duty cycle, with Compensation Voltage, and an arbitrary wave form (ramp), with Compensation voltage. Peak shape, resolution and absolute sensitivity are barely distinguishable between these three operating modes.

Resolution-Transmission Curves:

Perfluorotributylamine m/z 219 was measured using voltage scans on the broadband amplifier for 500 kHz Sine wave inputs, and 500, 400, and 300 kHz rectangular wave inputs with 60:40 duty cycle. Compensation voltage was adjusted to vary resolution for each spectrum, and spectra were gathered with 4, 2, 1, and 0.7 amu peak widths, as well as the highest resolution before the peak disappeared (ultimate resolution).

Peak height was measured along with peak width for each spectrum, with the resulting resolution-transmission curves compared.

Ion energy of 8 eV was used to maximize sensitivity, and the same tune and multiplier voltage was used for all scans, allowing direct comparison of absolute sensitivity between the different frequencies.

A dramatic loss in absolute sensitivity was seen as RF frequency is reduced, especially at unit mass resolution, with a loss of a factor of about 20% when RF frequency was reduced from 500 kHz to 400 kHz, but another factor of 40 loss in sensitivity at 300 kHz. Below 300 kHz, m/z 219 couldn't be resolved from m/z 220.

Peak to peak voltage for m/z 219 at various RF frequencies:

RF Frequency (kHz)	Vpp	Intensity at ~4 amu fwhm	Intensity at 0.7 amu fwhm
500	228.9	9000	2200
400	146.5	~7000	1750
300	82.4	3500	~40

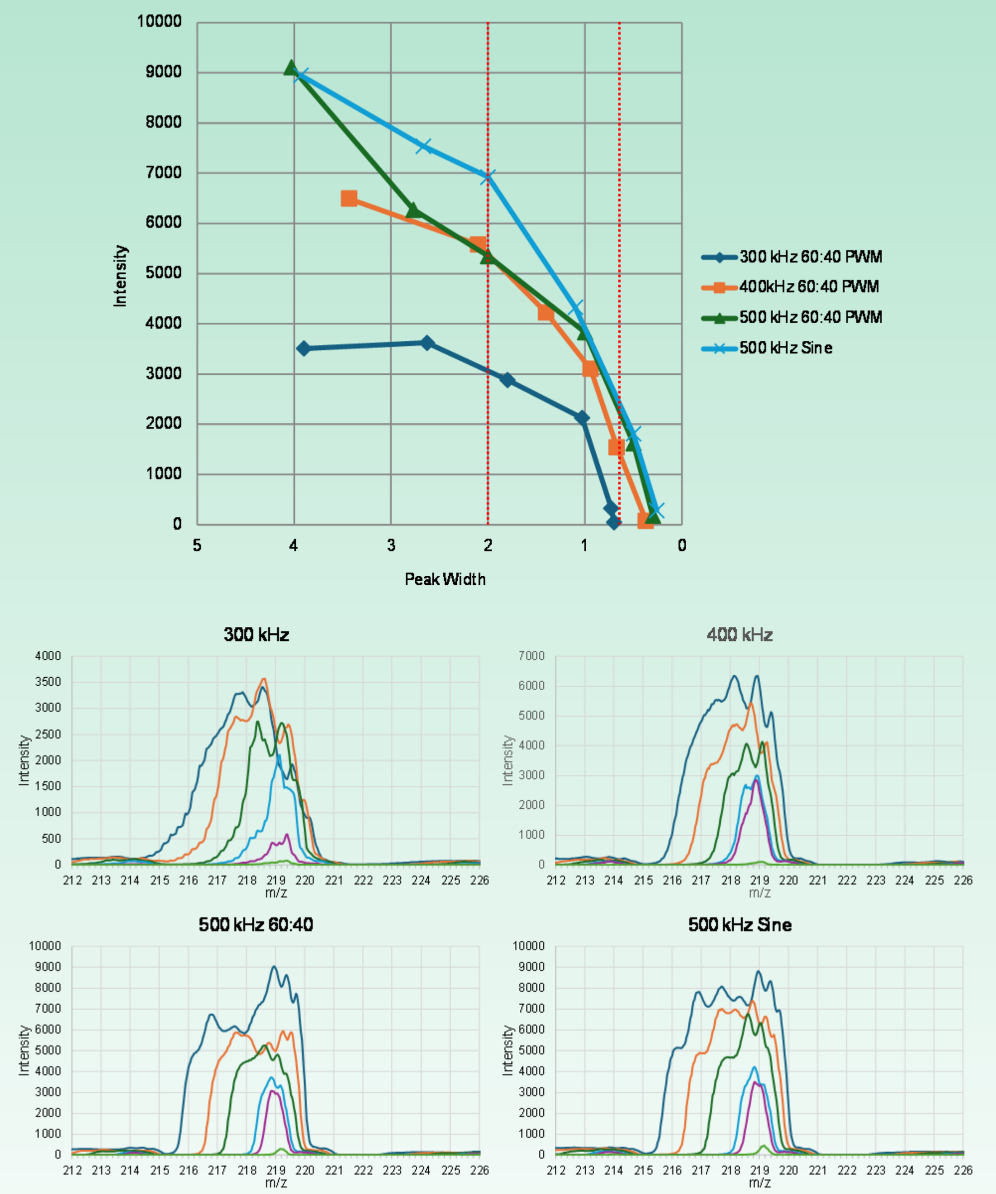


Figure 7. Evolution of peak shape, and Resolution-Transmission curves for 500 kHz Sine wave drive, 500 kHz, 400 kHz, and 300 kHz rectangular waves. Lower RF frequencies did not yield unit mass resolution.

Waveform Discussion

There is no magic in using digital waveforms to operate a quadrupole mass filter.

The resulting field strength is the same for a given set of RF and DC amplitude, regardless of whether the field is derived from sinusoidal or digital waveforms.

The RF and DC voltages used in the Mathieu equation 'a' and 'q' parameterizations can be calculated with the V_{rf}calculated as V_{rms} of the rectangular waveform multiplied by the square root of two, and the V_{dc} can be calculated from the PWM of the peak-to-peak waveform.

Thus the traditional stability diagram can be used for digital waveforms with these parameterization adjustments.

The resulting RF to DC ratio for a 61.2:39.8 rectangular wave is thus 6.315 to 1, approaching the 5.958 ratio at the tip of the stability diagram (a=0.23699, q=0.706).

The Compensation Voltage required to bring the rectangular wave to center around 0 V, (or the applied pole bias), match the negative of the PWM voltage given by the duty cycle.

Furthermore, almost any arbitrary waveform that can yield a non 50:50 duty cycle can be used to create a PWM resolving DC voltage, and a Compensation Voltage can be found for almost any duty cycle to yield resolving performance in the standard first stability region.

The following figure show the oscilloscope captures of the waveforms used in figure 6.

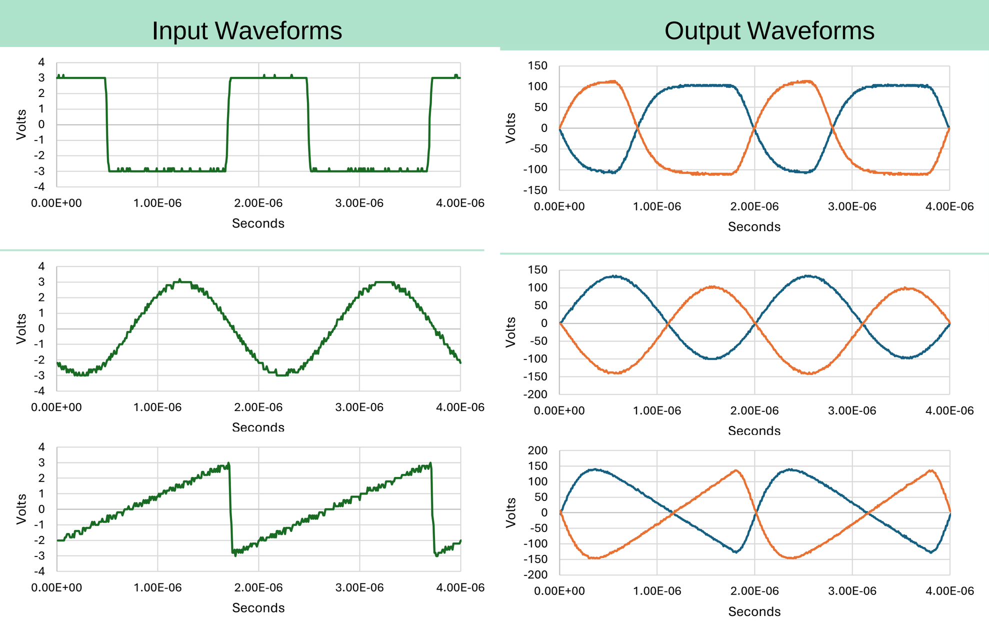
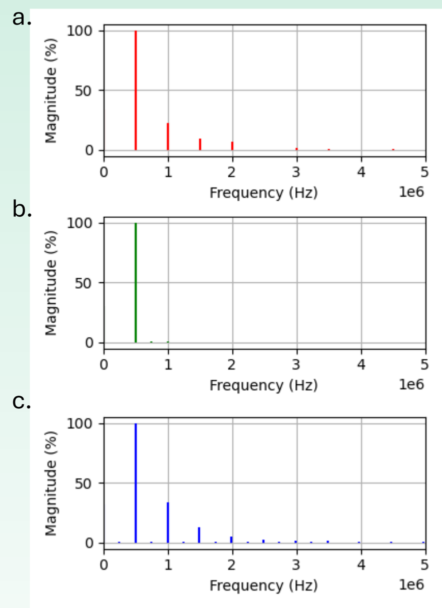


Figure 8. Input waveforms and high voltage outputs for three different applied waveforms.



The square wave input to the broadband amplifier becomes distorted by the poor high frequency response of the analog amplifier, to yield a trapezoidal-looking high voltage output. DC compensation voltages were applied to both RF outputs to bring their centerline back to 0 volts DC.

The sine waveform high voltage output shows the resolving DC offsets, and its FFT shows negligible harmonic content.

The ramp waveform high voltage outputs had enough harmonic frequency content to generate the pulse-width modulated resolving DC.

Figure 9. Fast Fourier Transforms of the high-voltage outputs from the 500 kHz square wave input (a.), the 500 kHz sine wave input (b.), and the 500 kHz sawtooth wave input (c.)

Conclusions:

The following conclusions are based on experiments in the normal first stability region, and are expected to hold true for alternate stability regions.

The field is the field is the field! - Using a digital waveform to drive a quadrupole mass filter results in the same field, with the same equations of motion, the same stability diagram and the same physics as sinusoidal operation. The calculations for VRF_{op} and $V_{dc}$to plug into the Mathieu equation are different but easy to determine.

Varying the duty cycle to create a pulse width modulated resolving DC voltage is equivalent to adding a resolving DC 'Compensation Voltage'.

Digital quadrupole performance does not require perfect rectangular waveforms. For a given RF frequency, mass peak shape, resolution, and sensitivity are almost indistinguishable between sinusoidal operation, idealized digital rectangular wave operation, imperfect rectangular waveforms, and random digital arbitrary waveform operation.

Fixed voltage, RF frequency scans can extend the mass range of a quadrupole, but with constant resolution, (peaks get proportionally wider proportional to mass number), instead of the more commonly seen constant peak width quadrupole mass scan seen with fixed frequency voltage scans.

The Astraea data system allows segmented programming of different duty cycles at different RF frequencies to allow for improved mass resolution as different masses are scanned, but changing the duty cycle to increase mass resolution as RF frequency is reduced to extend mass range, will still result in reduced sensitivity.

By definition, scanning RF frequency with fixed peak-to-peak amplitude and fixed duty cycle results in reduced ultimate resolution and absolute sensitivity, as RF frequency is reduced to extend the mass range. At m/z 219, sensitivity at unit mass resolution (0.7 amu fwhm) reduces by a factor of ~55 between 500 KHz and 300 kHz operation.

A practical limitation of a pure digital quadrupole power supply using FET's is the potential over-heating of the FET's as voltage, and/or RF frequency is increased. This has limited the practical implementations of digital quadrupoles to hundreds of volts.

A hybrid digitally-controlled, analog-amplified power supply can operate over wider range of operating voltages and frequencies, and has the additional benefit of allowing the use of constant RF frequency while varying the RF amplitude to control mass position. Higher voltage, (>500 V_{pp} 500 kHz), higher frequency operation for a given m/z results in better resolving power and higher sensitivity. Perfect waveforms are not essential.

If an analog amplifier is used which inductively or capacitively couples the input waveform to the RF outputs, then each output waveform will have a DC offset, in which the centerline of the output waveform will 'float' from ground by the pulse width modulated DC, yielding an RF-only spectrum. A DC 'compensation voltage' equal to the negative of the PWM DC voltage will bring the waveform back to centered around ground (or the selected pole bias offset).

When used in the standard first stability region, digital quadrupole power supplies are compatible with quadrupoles with pre-filters, since capacitively coupling the RF to the pre-filter removes the PWM DC voltage, and results in RF-only operation.

Using a traditional quadrupole control system, unit mass resolution is possible using a digital waveform with constant duty cycle by use of mass programmed 'compensation voltage', (resolving DC), since duty cycle and 'compensation voltage' are scale-able to each other, and are thus interchange-able.

The use of a digital quadrupole power supply promises to dramatically extend the mass range for existing systems with a simple, easy-to-use interface, especially useful for the mass selecting quadrupole in a hybrid system, where unit mass resolution is not required.

The Astraea Hybrid Precession Waveform Generator with integral high voltage pulser provides great flexibility across a very wide mass range, providing resolution greater than 20 even with 2.5 V_{op} RF voltage, and better than unit mass resolution for a range of masses well above the 219 amu data shown when 100 V_{op} is applied.

The Astraea data system allows segmented programming of different duty cycles at different RF frequencies to allow for improved mass resolution as different masses are scanned. However, increasing mass resolution as RF frequency is reduced to extend mass range, will still result in reduced sensitivity.

Using an unmodified Ardara Technologies Model 158 Broadband Amplifier with sinusoidal input waveforms instead of digital waveforms allows a much higher output voltage (to 1800 Vpp at 100 kHz), resulting in an even wider mass range extension than 200 Vpp operation, promising higher absolute transmission as well, since higher frequencies can be used at higher voltages to get to the desired mass.

If a fixed high mass range is desired, a standard Ardara Technologies Model 151 High Q Head, with fixed resonant frequency could be configured for low frequency operation (as low as 100 or 200 kHz), with more than 4,000 Vpp outputs.

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