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Impact of injection potential on measured ion response for digitally driven mass filters

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ABSTRACT

Digital Waveform Technology (DWT) has recently evolved to provide sufficient duty cycle resolution necessary to create a purely digital waveform-based mass filter. Digital operation provides a number of options that remain extremely challenging for sinusoidal waveform technology (SWT) driven systems. One of those options is collecting ions in a gas-filled digital ion guide/trap and subsequently axially injecting the collected ions in a temporally-short and spatially-focused packet into the digital mass filter (DMF). This work explores the effects of trapping ions before mass analysis. In particular, it focusses on the measured response of the ion distribution as a function of axial ejection conditions while maintaining identical trapping conditions. The ejection energy was varied showing changes in the ion distribution that corresponded to desolvation, multimeric dissociation and small molecule from the higher charge states. This study shows that duty cycle-base ion ejection from into an axial potential well and out of the same well of a gas-filled linear quadrupole is essentially equivalent in terms of energy imparted to the ion. However, the energizing mechanism of the ejection process is radial rather than axial. Sampling issues of the trapped ions from the gas-filled quadrupole were analyzed and discussed.

1. Introduction

The concept of using rectangular waveforms to operate an ion guide or mass filter originated with Richards in 1973 [1]. Unfortunately, it was another good idea that had to wait for the technology to catch up. It was not until a quarter of a century later, in the late 1990s, that the development of direct digital synthesis (DDS), high voltage field effect transistors (HV-FET) and field programmable gate arrays (FPGA) provided the necessary foundations for digital waveform technologies applied to mass analysis. DDS served to generate accurate and precise low voltage square waveforms while FPGAs functioned to rapidly alter these waveforms on time scales compatible with *m/z* manipulation. HV-FETs were required to amplify the waveforms to the high voltages needed to operate these digital devices. Finally, in 2001, Shimadzu introduced the first square waveform driven 3D ion trap at the ASMS meeting in Chicago [2]. They developed this technology over the next 5 years [3–6] without producing a commercial product.

In spite of the years of development, three core aspects of DWT were not fully explored even though they are, in our opinion, game changing. These features are: first, phenomenal frequency resolution [7], second, the ability to rapidly change the axial [8] and radial [9–11] stability of the ions, and third is the agility of the waveform generator [11,12]. Agility, in this case, is defined by the number of waveforms that can be applied before switching to another set of waveform conditions. Digital waveform generators (DWFG) can often do this after only one period of the waveform. These features allow new methods of axially and radially trapping, ejecting, isolating, exciting and shuttling ions around that greatly expand the capabilities of ion traps and guides in comparison to sinusoidal waveform technology (SWT).

More recently, our group invented another method of producing rectangular waveforms using a comparator and an 18-bit digital to analog converter (DAC) [13]. The idea was to compare the amplitude of the sine wave output of the DDS with a fixed potential output of the DAC. The comparator output provides the low voltage rectangular waveforms. Fig. 1 illustrates the waveform generation process. The sine wave is depicted in blue and the DAC created voltage for comparison with the sine voltage is depicted in orange. In this case, when the sine wave amplitude is greater than the DAC input voltage, the comparator outputs a high and a low voltage when the sine amplitude is less, thereby yielding the rectangular wave output (red trace). The precision of the DAC and the threshold level of the comparator define the duty cycle resolution to roughly

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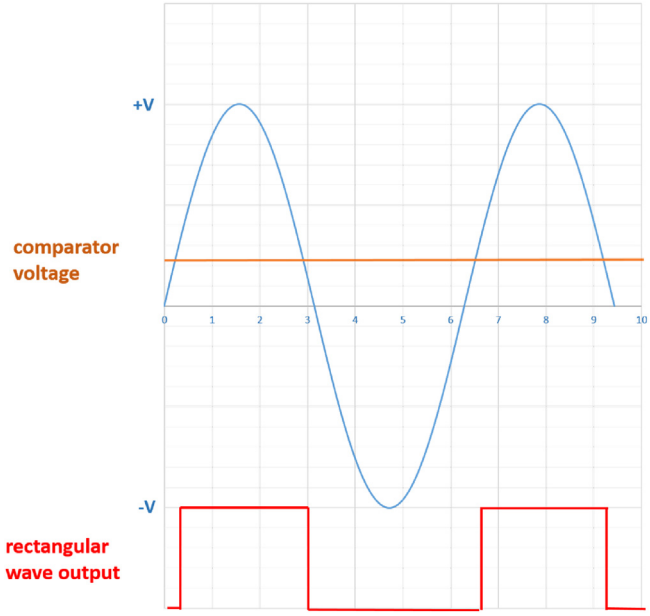

Fig. 1. Illustration of voltage comparator-based rectangular waveform generation is high resolution duty cycle control.

10 ppm and makes a purely digital mass filter feasible. The duty cycle and the frequency of the waveforms can be changed essentially instantaneously with the minimum application time of the new waveform defined by the speed with which the new waveform information can be down loaded to the DAC and the DDS, respectively.

This DWFG provides unprecedented control of the duty cycle not only for the DMF but also for the gas-filled ion guide that precedes it. Exact duty cycle control of the guide allows the ions to be precisely manipulated while they are axially trapped and ejected. In a previous publication, we examined the effect of axial trapping potential on DMF generated spectra while using the duty cycle to keep the DMF injection beam energy constant [14]. This work continues the systematic investigation of the effect of the duty cycle based ion manipulation by varying the injection energy into the DMF on the mass spectra to determine the response of the measured ion populations.

2. Experimental

In this work lysozyme was used to demonstrate DWT-based ion trapping followed by mass filter analysis of intact proteins. It was purchased from Sigma Aldrich Company (St. Louis, MO) and used without further purification. 50% methanol/ 50% water (both HPLC grade and both from Fisher Chemical, Waltham MA) was used to dissolve the lysozyme and produce a 6 μM solution. No acid was

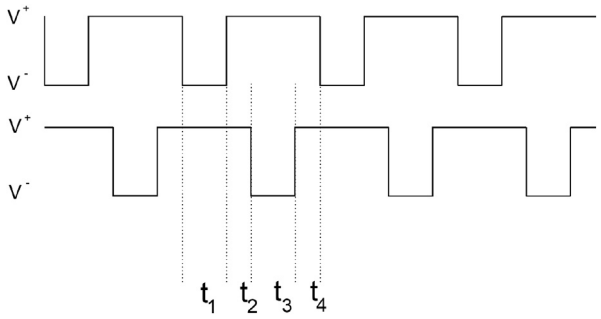

Fig. 3. An example of a generic ejection waveform that defines the waveform fractions, t_n, of constant potential along the central axis.

added to the solution in order to maintain the mass distribution in lower charge states.

The instrument used in this effort is depicted in Fig. 2. The sample was introduced by electrospray ionization using the commercial fused silica capillary 30 ± 2 μm tip (New Objective Co.) with an applied potential of +2600 V relative to the pinhole inlet. Sample solutions were pneumatically pushed through the capillary at 1 psig. Ions enter the instrument through a 300 μm diameter thin plate orifice and expand within a digitally-operated ion funnel operated at 500 kHz and 48 Vp-p with a −50 V DC potential across the funnel in a differentially pumped chamber at approximately 1.3 Torr [15]. The AC and DC fields of the funnel collimate and push the ions toward the exit orifice and into a digitally-operated ion guide at ~10 mTorr.

The guide is driven by a pair of high voltage waveforms, one for each electrode pair. The duty cycle of each waveform is defined by the percentage of the cycle that the waveform is in the high state. The waveforms applied to each pair of electrodes of a quadrupole guide or filter are defined by a pair of duty cycles. For axial trapping waveforms, the duty cycle values add to less than 100%, whereas duty cycle values for ejection add to greater than 100%. In these experiments, the trapping duty cycle and the trapping time were held constant so that the trapped ion population was always consistent for each set of spectra. In some cases, the trapping time was adjusted to avoid detector saturation. The ejection axis potentials were varied at 1, 10 and 20 V at a constant 80/80 ejection duty cycle to demonstrate their effect on measured ion distribution.

The duty cycle derived axis potential is defined as a time-weighted average of the DC axis potentials during a waveform cycle. In the case of our waveform generator, there are four waveform fractions of constant potential along the central axis of the quadrupoles, t_1 through t_4, as shown in Fig. 3. t_1 and t_3 are defined by the fractions of the period where the electrodes are at V^+ and V^- and vice versa, where V^+ and V^- are the positive and negative potentials supplied to the high voltage pulsers. t_1 and t_3 form the quadrupolar portion of the waveform period. t_2 and t_4 define the fractions of the waveform period when both electrode pairs are at

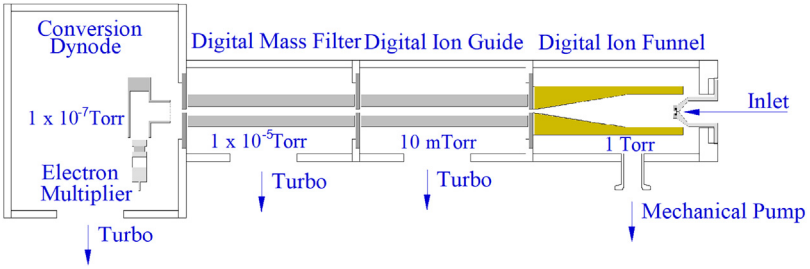

Fig. 2. Dual quadrupole instrument illustration.