Design and performance of a slotted bandpass quadrupole ion guide

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INTRODUCTION

Ion guides are designed to maximize sensitivity in tandem quadrupole mass spectrometers by efficiently transporting ions from the sampling orifice through the various pressure regimes to the first analytical quadrupole. Due to this, a significant ion current spanning a broad mass range reaches the first analytical quadrupole.

When resolving, quadrupoles only transmit ions with a given mass to charge ratio (m/z). Ions with an m/z outside of the transmission window of the quadrupole strike the quadrupole rods which leads to an accumulation of material on the quadrupole rods. Higher mass ions, being less volatile, significantly contribute to this contamination as they tend to stick to the surface of the quadrupole rods. The result is "ion burn", an example of which is shown in Figure 1. This contamination creates an insulating layer which allows charge to accumulate, which then affects the transmission efficiency of the quadrupole.

The symptoms of charging on the quadrupole rods vary from a general loss of sensitivity, for which the use of internal standards can provide some mitigation, to more subtle effects which can negate the effectiveness of internal standards.

Because of the fragile nature of analytical quadrupoles, service engineer intervention is typically required to rectify these issues, leading to significant unplanned downtime.

It would be advantageous to remove ions with a m/z significantly higher than the compound of interest before they reach the first analytical quadrupole.

Presented here is a slotted segmented quadrupole bandpass ion guide which employs resolving DC to reduce contamination on critical ion optics whilst maintaining the sensitivity and speed of a conventional ion guide. The key design features and their impact on performance are described.

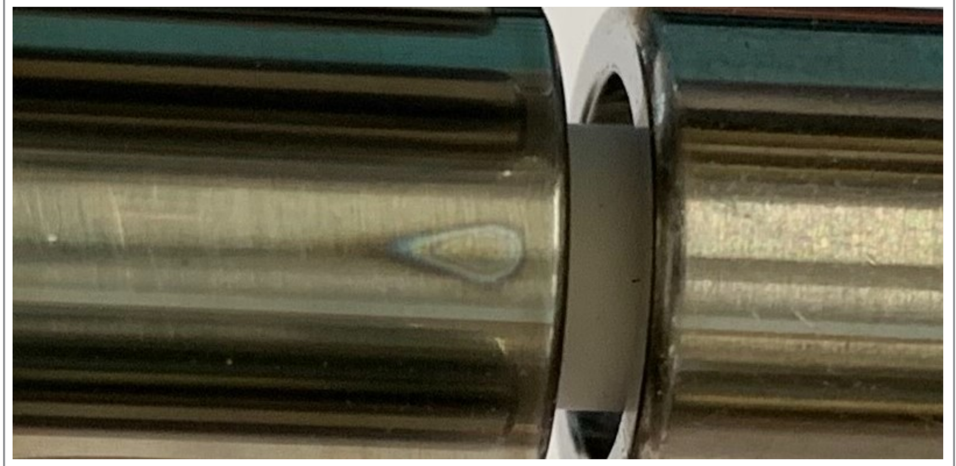

Figure 1. Typical evidence of ion burn on an analytical quadrupole

DESIGN

The slotted segmented quadrupole bandpass ion guide is located immediately after the first ion guide and operates in a pressure regime >1x10^{-4} mbar. It consists of three sections as shown in Figure 2.

The first section consists of a short RF-only segment which accepts ions from the first ion guide region. This is required to ensure ions are contained with the RF field before filtering is applied.

The second section consists of elements with slots in the centre of the quadrupole rods. Resolving DC is applied to these elements to remove the unwanted ions. Although ion guides are generally more tolerant to charge build up than the analytical quadrupole, charging will still occur eventually if high mass contamination is allowed to accumulate in this region. The slots in the segmented quadrupole elements allow resolved ions to pass through, therefore removing these contaminant ions from the ion path. A simulation demonstrating this effect is shown in Figure 3.

The final section consists of conventional segmented quadrupole elements to allow the ions to lose energy through collisional cooling and focus to centre-line of the guide. This maximises the ion transmission through the differential aperture to the analytical quadrupole.

Ion collisions with gas molecules in this pressure regime cause the ions to move relatively slowly through ion guides, adversely affecting the ability to perform fast Multiple Reaction Monitoring (MRM) experiments. To prevent this, a DC gradient is applied down the ion guide, where relatively small voltage drops are applied between each of the quadrupole segments, see Figure 2. The gradual axial field reduces the likelihood of unwanted fragmentation as may occur if a single, large offset were applied.

The key performance characteristics assessed were sensitivity, speed (fast MRM performance) and the effect of applying a bandpass on the system robustness.

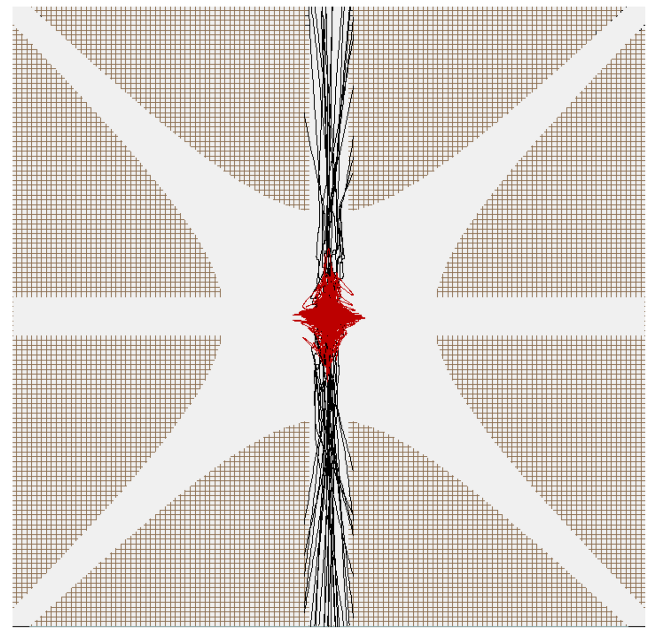

Figure 3. Simulation showing ion trajectory for stable ions (red) and un-stable ions (black) through a slotted bandpass ion guide.

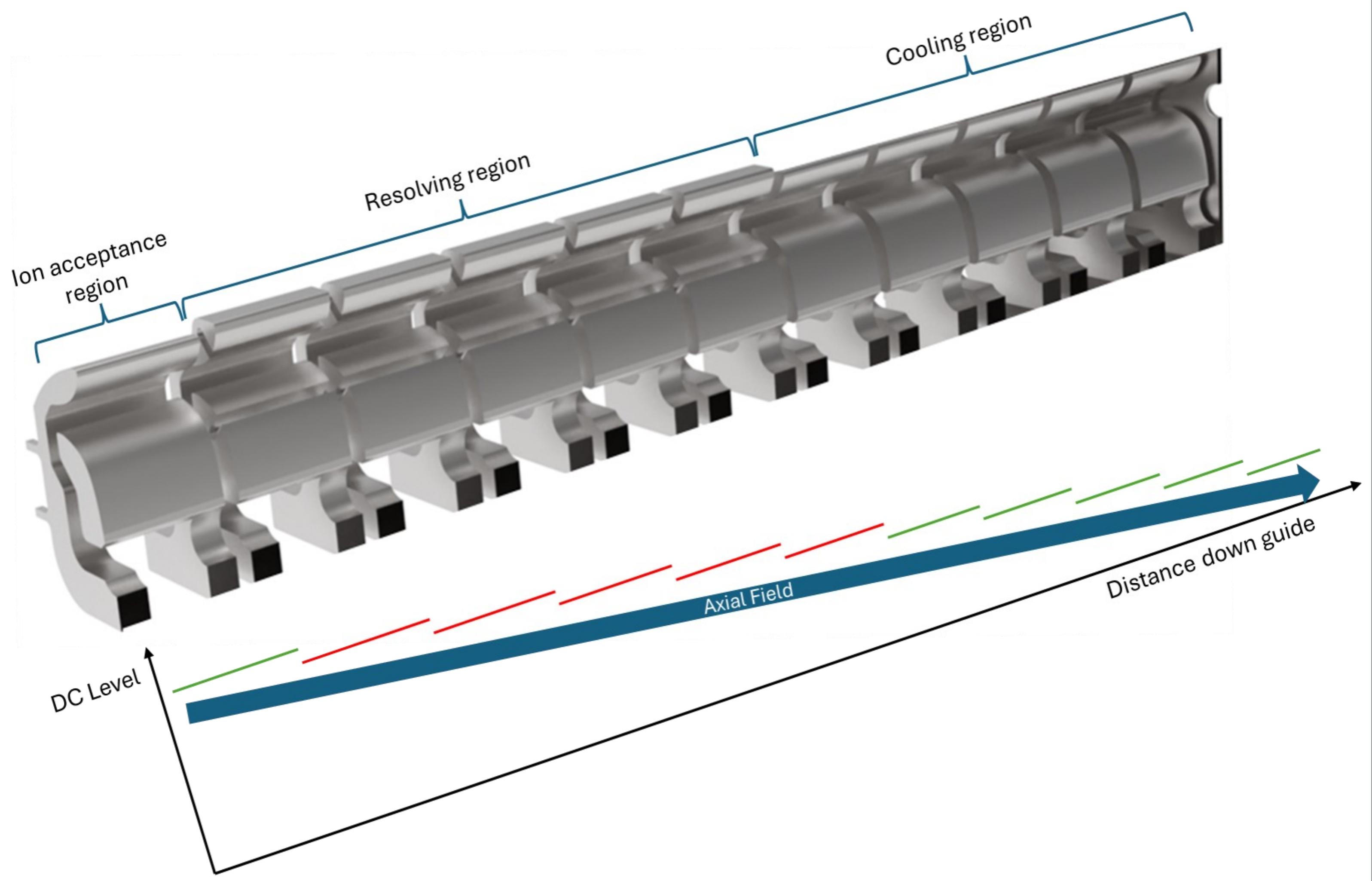

Figure 2. Application of an axial field to the sections of the slotted segmented quadrupole bandpass ion guide

SENSITIVITY

A mixture containing masses up to m/z 2000 was infused into a Xevo™ TQ-Absolute mass spectrometer equipped with the bandpass ion guide. The impact of applying a bandpass on transmission efficiency was evaluated by monitoring the transmission of a specific compound while progressively increasing the resolving DC. Figure 4 illustrates the effect of narrowing the bandpass window on the transmission of Sulfadimethoxine (311 m/z). The signal remained unaffected, even when the high mass cutoff was within 100 m/z of the target mass.

This procedure was repeated for various masses across the range to determine an appropriate resolving DC ramp to be applied when operating in Multiple Reaction Monitoring (MRM) mode.

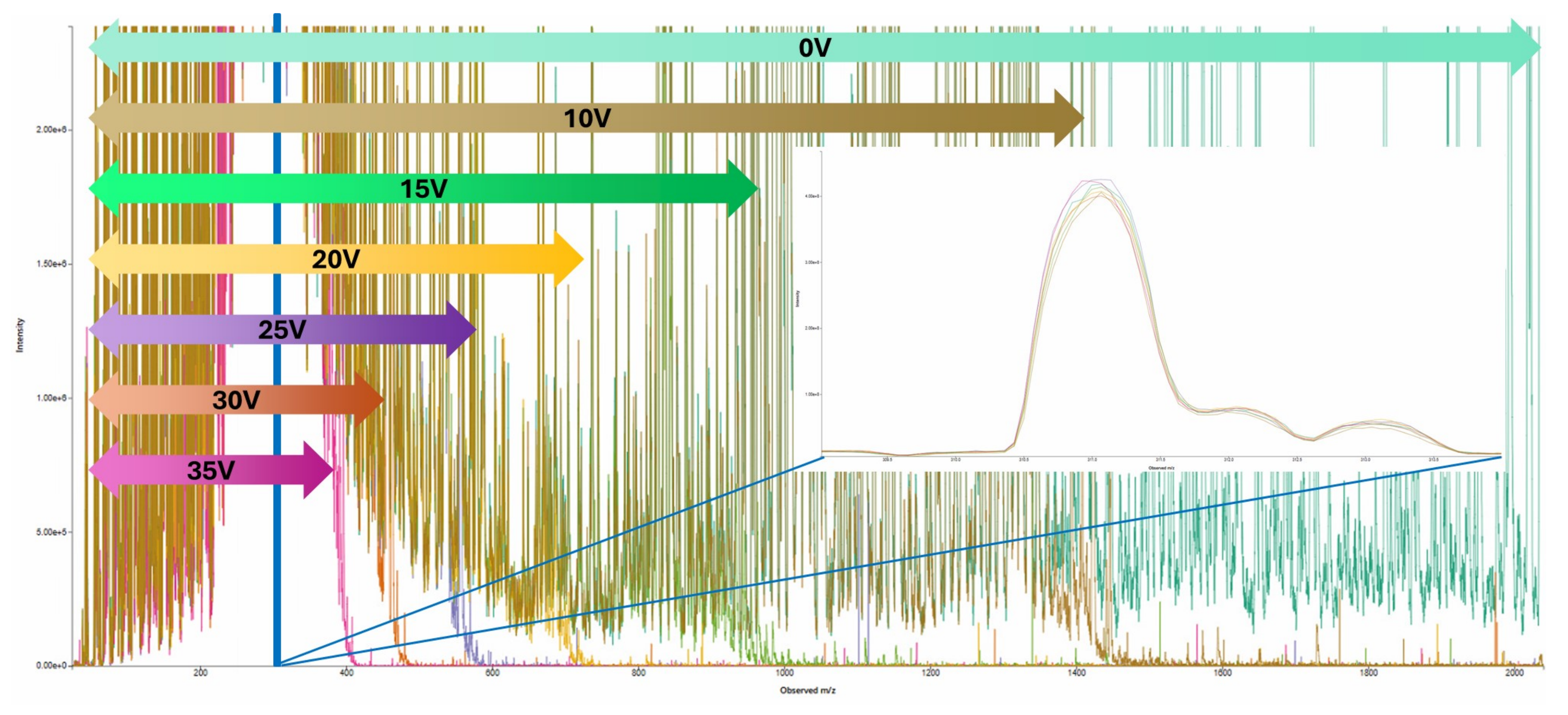

Figure 4. Overlayed spectra showing the effect of increasing resolving DC on the size of the bandpass and the transmission efficiency of Sulfadimethoxine (m/z 311).

SPEED

The effectiveness of the axial field allows for adjustment of the resolving DC for each transition based on the precursor m/z. To demonstrate this, a chromatographic multiresidue pesticide method was performed using different acquisition rates. Repeat measurements were conducted with 1µL injections of a 0.01µg/µL pesticide standard mix, comparing the peak areas of 14 pesticides with precursor m/z in the range 189 m/z to 404 m/z.

Data were acquired at a rate of 36 MRM/s (25ms dwell, 3ms inter-scan delay) and 500 MRM/s (1ms dwell, 1ms inter-scan delay). The relative areas for each pesticide were compared to assess the impact of acquisition rate on signal intensity.

Figure 5 illustrates an example chromatogram at both a comparatively slow acquisition rate of 36 MRM/s and a fast acquisition rate of 500 MRM/s on the same vertical scale. The average area difference for all pesticides was less than 2%, indicating minimal variation in peak areas despite the significant difference in acquisition rates.

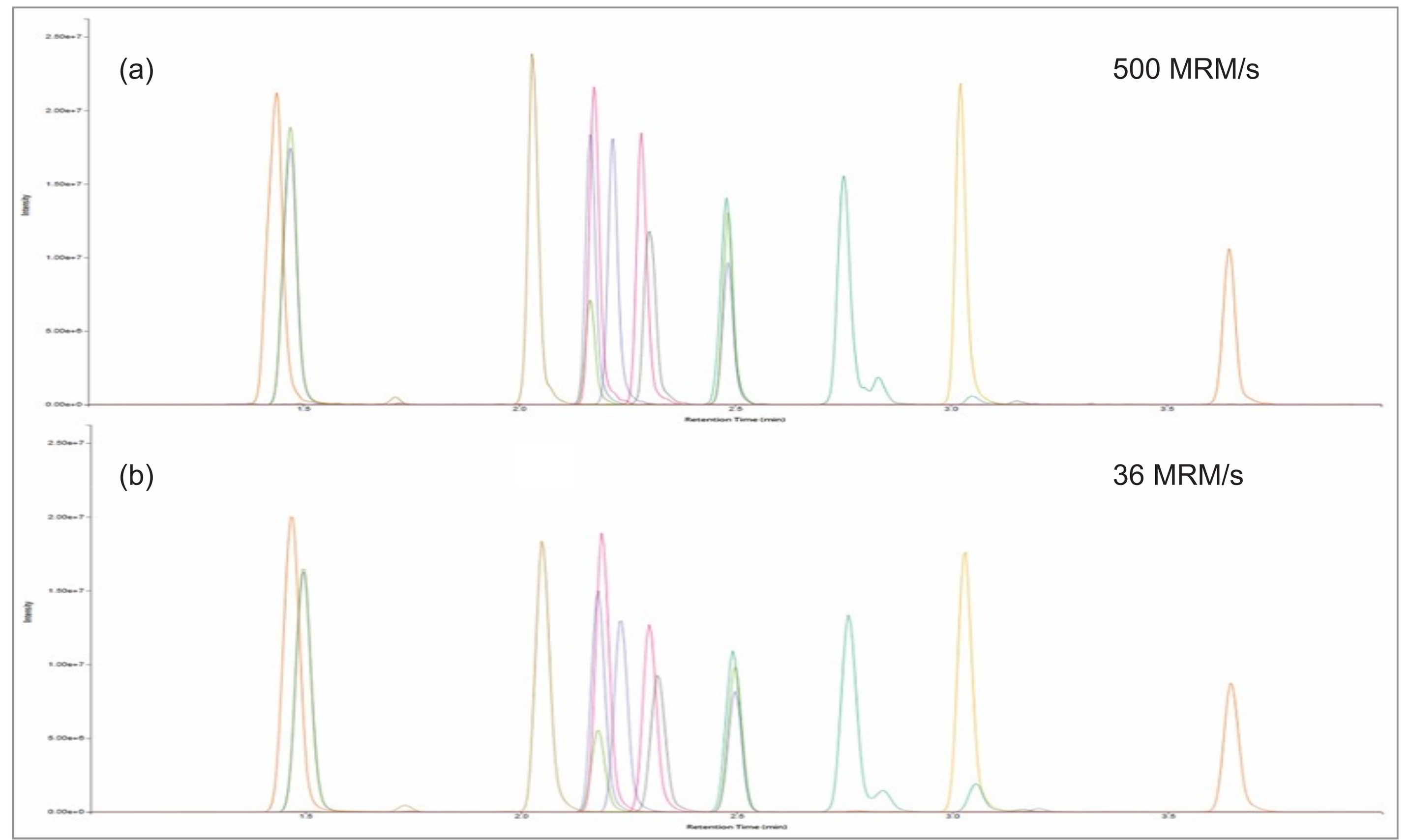

Figure 5. Chromatograms of 14 compounds in MRM mode (a) at 500 MRM/s using 1ms dwell, 1ms inter-scan delay, and (b) at 36 MRM/s using 25ms dwell, 3ms inter-scan delay.

ROBUSTNESS

A common symptom of charging in an analytical quadrupole is the increased time required for transmission efficiency to return to optimal levels following a large mass jump or polarity switch. Short term loss of sensitivity can be particularly problematic as internal standards do not always compensate for it, since the signal loss may only affect the quantitative and/or qualitative transition and not the internal standard.

To compare the performance of a slotted bandpass ion guide with a conventional ion guide, a contaminated soil matrix spiked with Fipronil desulfinyl (387 m/z) was infused into a Xevo™ TQ-Absolute instrument fitted with a conventional ion guide over several days. The characteristics of Fipronil desulfinyl transmission after a polarity switch were monitored every 24 hours until charging became evident. The instrument's ion optics were then cleaned, and the experiment was repeated using a slotted bandpass ion guide.

As shown in Figure 6(a), charging was evident within the first 24 hours on the standard ion guide and progressively worsened. Figure 6(b) demonstrates no charging on the bandpass ion guide even after 240 hours. Figure 6(c) illustrates the average change in transmission for the first 10ms after a polarity switch. For context, in an MRM experiment using 10ms dwell times, this would represent the sensitivity loss observed for the first transition after a polarity switch, with later transitions being less affected.

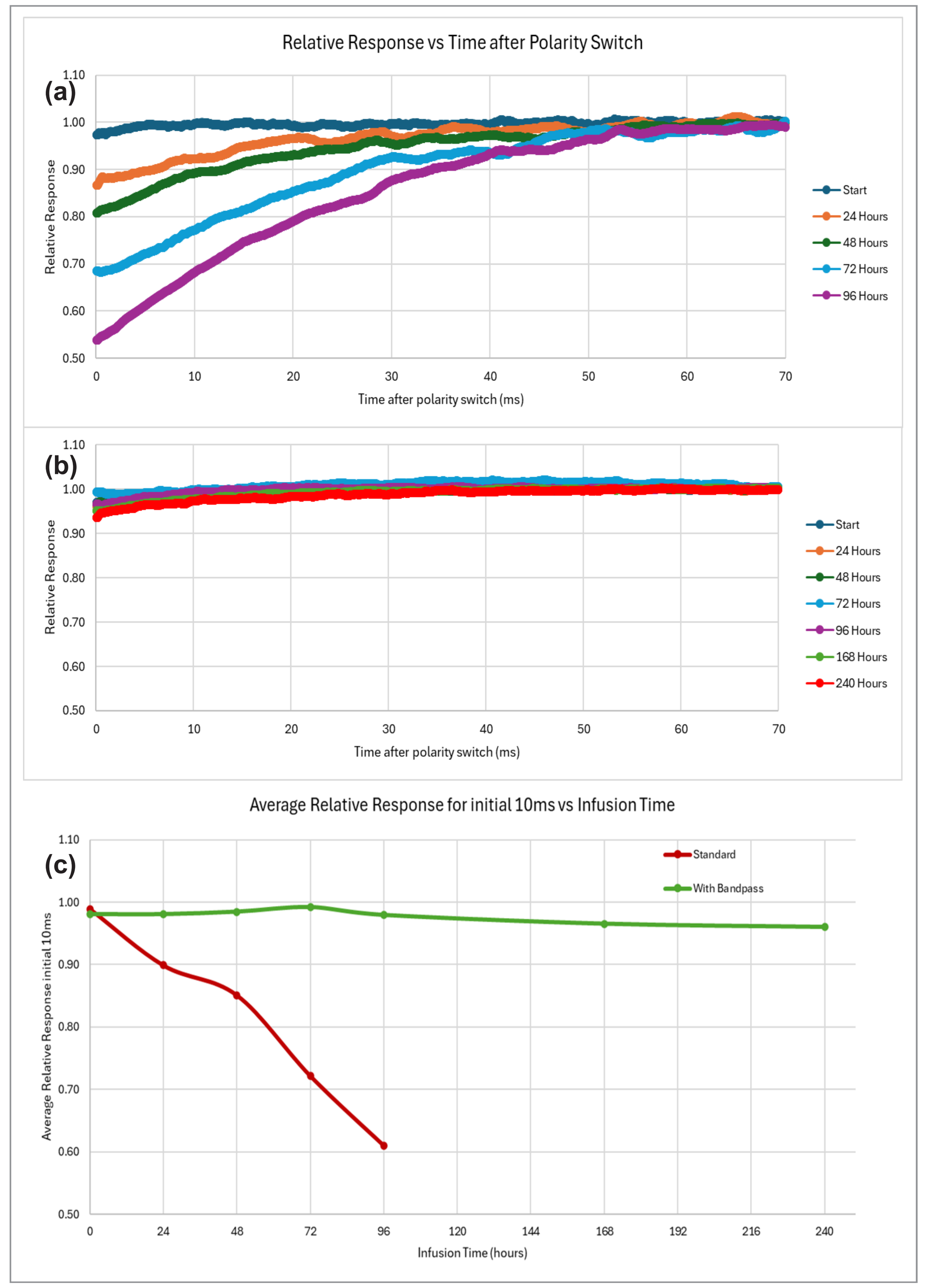

Figure 6. Response time after a polarity switch (a) on a conventional ion guide (b) on a slotted segmented quadrupole bandpass ion guide. (c) shows how the average response for the first 10ms varies over infusion time.

CONCLUSION

Accelerated tests show that the use of a slotted segmented quadrupole bandpass ion guide effectively protects the analytical quadrupole from contamination build-up and charging, increasing the time to failure by >10x.

Further testing demonstrated that, when combined with an axial field, these robustness improvements can be achieved without compromising sensitivity, even at high MRM acquisition rates.

The testing performed indicates the implementation of a slotted segmented quadrupole bandpass ion guide should improve instrument uptime and reduce the requirement for unplanned service interventions.