

Improving mass spectrometer robustness using a slotted bandpass ion guide

Authors: Benjamin Jones, David Gordon, Kate Whyatt
Affiliations: Waters Corporation, Wilmslow, UK

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.

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. 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.

An example of how the internal standard compensation can be compromised is shown in Figure 1. Figure 1 (a) shows how the sensitivity for negative ions changes upon a polarity switch on a clean system where the sensitivity has reached an optimum (X) before the negative ion transitions are acquired. As the system becomes compromised, the time taken to achieve maximum sensitivity in negative ion increases as shown in Figures 1(b) and 1(c). In each case the Quan ion response reduces (to Y), yet the internal standard is not affected so will not provide compensation for this loss in response, leading to failing QCs and incorrect Quan/Qual ion ratios.

ION GUIDE

A slotted segmented quadrupole bandpass ion guide can be used to remove the unwanted high mass ions before they reach the analytical quadrupole. It consists of three sections as shown in Figure 2(a). 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. An illustration showing this effect is shown in Figure 2(b). The final section consists of conventional segmented quadrupole 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

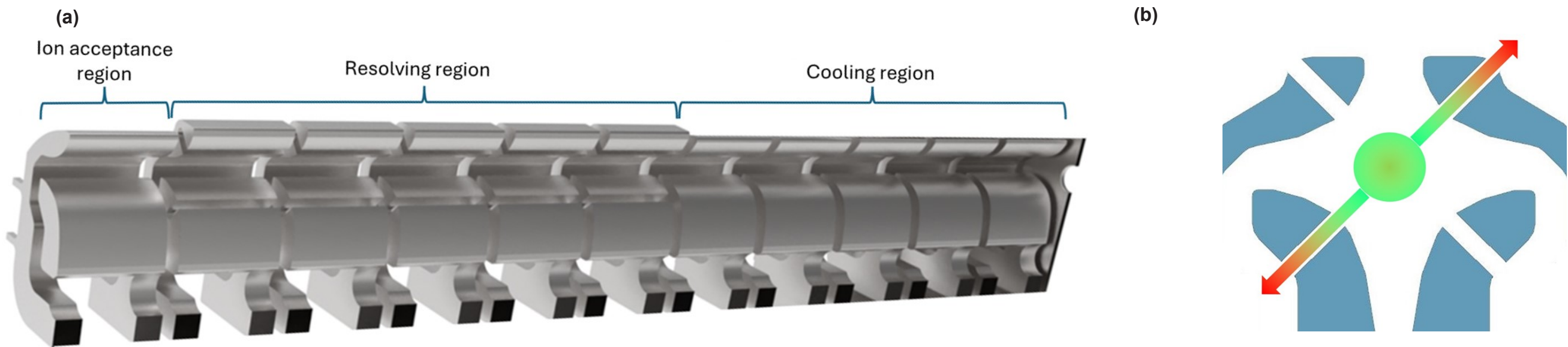


Figure 2. Image of the slotted bandpass ion guide showing (a) the three sections of the ion guide, and (b) an illustration of the path of the resolved high mass ions.

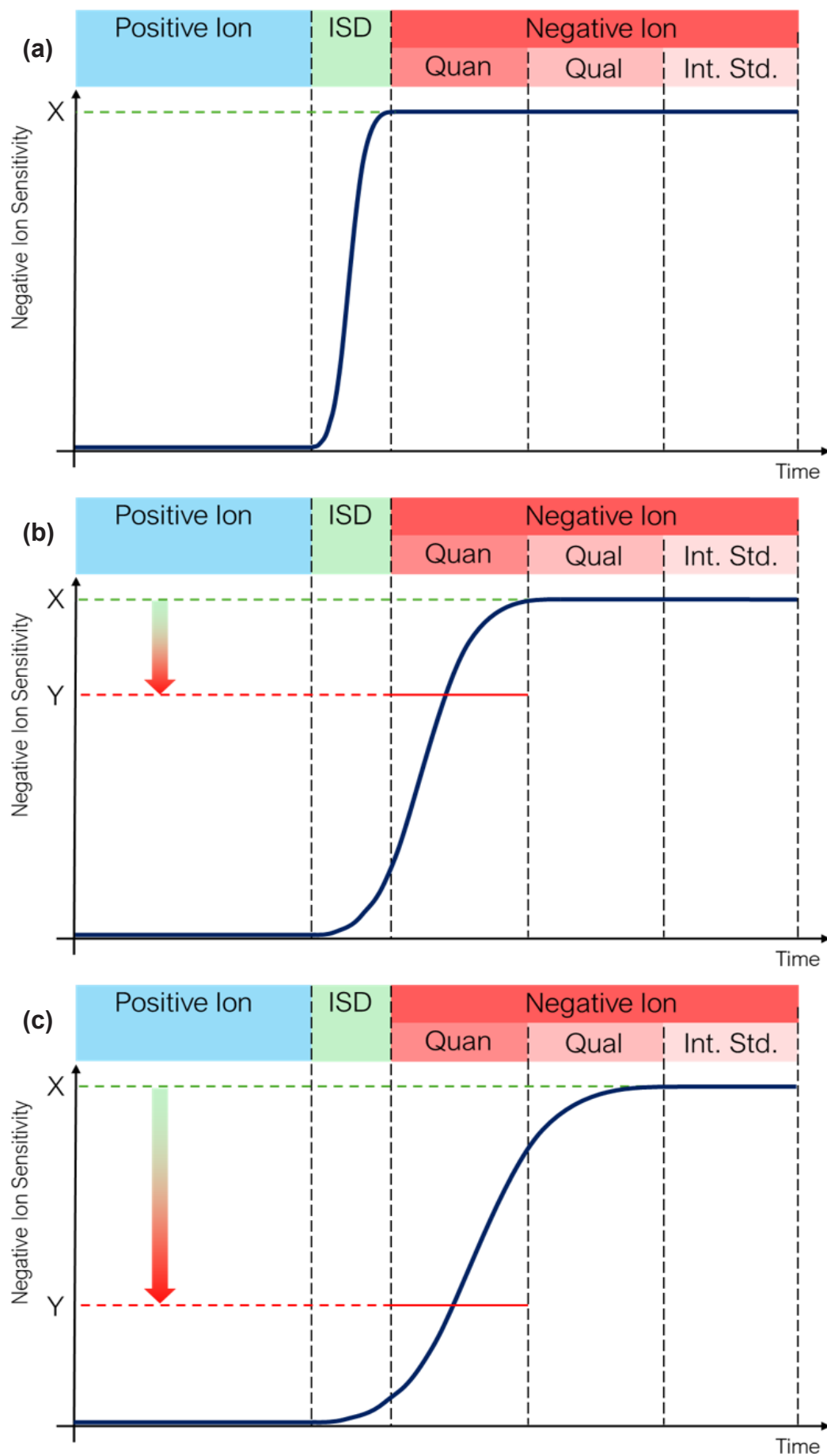


Figure 1. Indication of the effect of charging on the analytical quadrupole on response time for negative ions.

METHODS

A system consisting of a Waters™ ACQUITY™ H-Class with a Xevo™ TQ-XS mass spectrometer was used for this study.

Sample Preparation

5g of homogenised fish feed sample was placed in a 50-mL plastic centrifuge tube. The sample was extracted with 20 mL of 80:20 Acetonitrile:H₂O containing 0.5% of Acetic Acid and 0.2% of Formic Acid (v/v). Then the sample was placed on a roller for 20mins, vortexed for 1min and centrifuged for 6 min at > 5000g. The fish feed extract was then filtered through 13 mm I.D., 0.45 µm syringe filter. 10mL of the supernatant was diluted with 90mL of de-ionised water. This was then spiked with mixture containing the compounds shown in Table 1.

Compound	Ionization Polarity
Acetominaphen	ESI+
Caffeine	ESI+
Sulfadimethoxine	ESI+
17-alpha-Hydroxyprogesterone	ESI+
Verapamil	ESI+
Chloramphenicol	ESI-

Table 1: Compounds spiked into fish feed matrix at 10pg/µL.

LC Method

Column: ACQUITY™ UPLC™ BEH™ C18 Column, 130Å, 1.7 µm, 2.1 mm X 50 mm
MP A: 1mM Ammonium. Acetate in H₂O with 0.5% Acetic Acid, 0.1% Formic Acid
MP B: Methanol with 0.5% Acetic Acid, 0.1% Formic Acid
Flow Rate: 0.7mL/min
Injection volume: 5µL
The gradient is shown in Table 2.

Gradient Time (min)	%A	%B	Curve
0.00	90%	10%	Initial
1.00	5%	95%	6
4.00	5%	95%	6
5.00	90%	10%	6

Table 2: Gradient table.

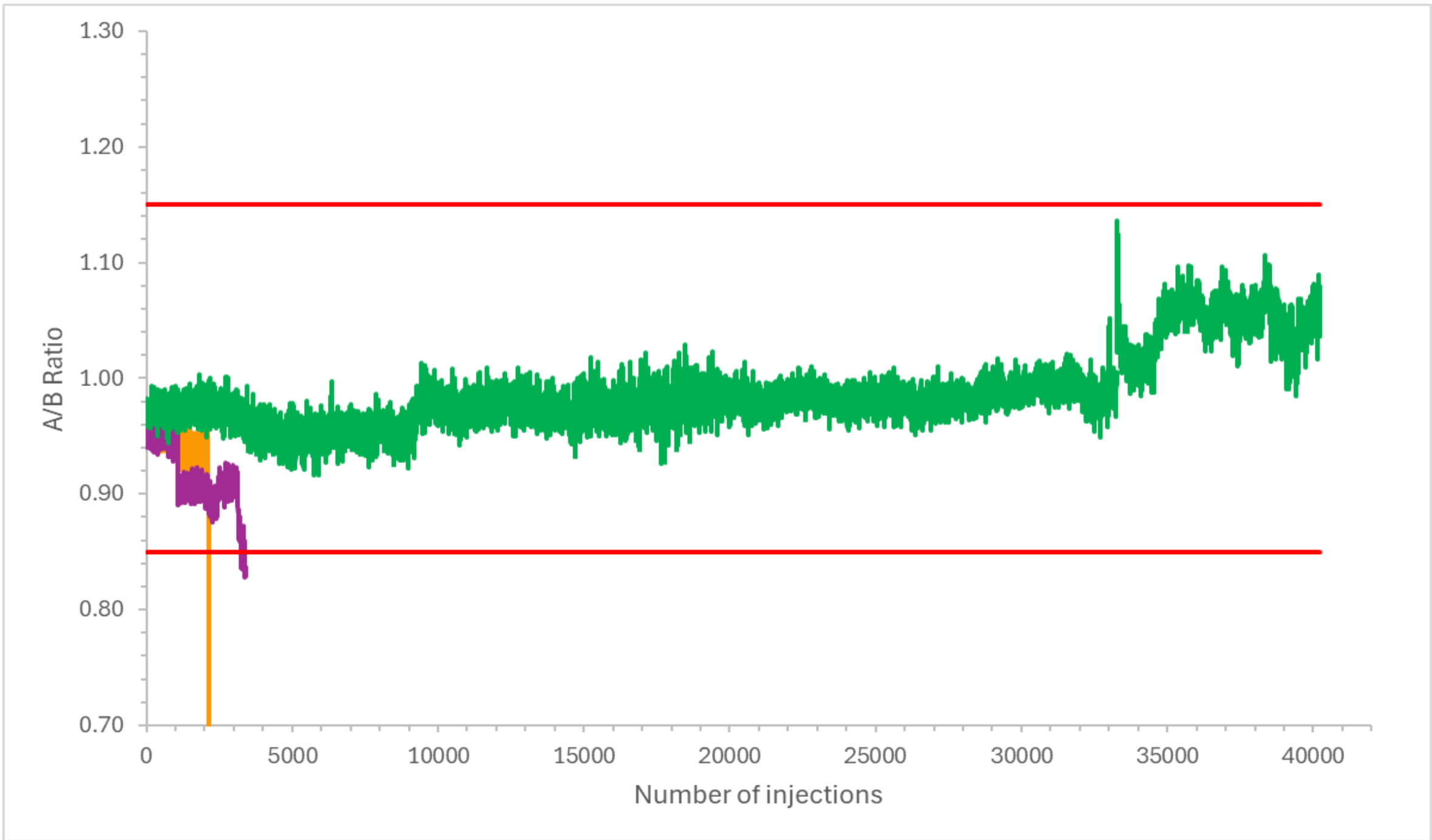


Figure 4. Ratio of A/B vs number of injections performed on two standard ion guides and a slotted bandpass segmented quadrupole ion guide.

MS Method

A polarity switching method was created, monitoring each of the compounds listed above. The negative ion chloramphenicol peak (m/z 321 → 152) was monitored in 10ms segments. The chromatographic peak area of the first 10ms segment was compared with the peak area obtained from the a measurement 80ms later. The setup is illustrated in Figure 3, where the first segment is labelled A and the final segment labelled B.

A ratio of A/B can be used to indicate whether quadrupole charging symptoms are present.

The system was considered to be failing if the A/B ratio changed by >15% as this would correlate to a typical QC failure.

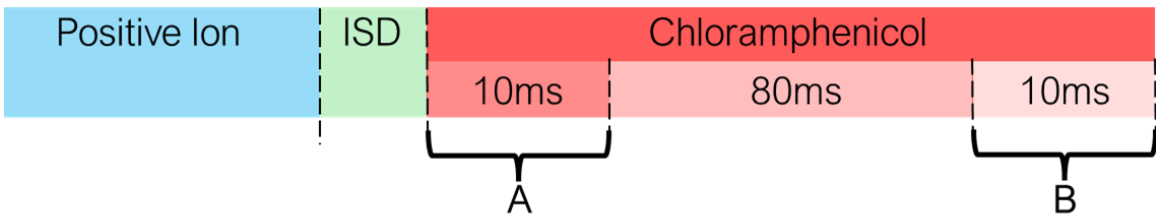


Figure 3. Illustration of the experimental setup to allow measurement of A and B

RESULTS

Figure 4 shows the A/B ratio vs the number of injections made on two standard ion guides and a slotted bandpass ion guide. The standard ion guides showed signs of quadrupole charging after approximately 2,100 and 3,400 injections. After each failure, the quadrupole was diagnosed to be the cause of the fault.

The slotted bandpass ion guide A/B ratio was still within 15% after > 40,000 injections. No quadrupole maintenance or changing of quadrupole parameters was required over this time. The quadrupole was examined and no ion burn was present.

CONCLUSION

This comparison study has demonstrated that a tandem quadrupole mass spectrometer fitted with a slotted bandpass segmented quadrupole ion guide can significantly increase the time before quadrupole maintenance is required for challenging matrices. The quantitative performance of the instrument has been retained after over 10x more injections that was possible using a standard ion guide.