Characterization of a detection system with high sensitivity and range for a novel HRAM mass spectrometer

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Introduction

Efficient detection is key to a mass spectrometer’s sensitivity, and linearity of response typically dominates the dynamic range of the instrument. Detection systems in Q-ToF or QqQ mass spectrometers are usually based on ion-to-electron conversion and subsequent electron multiplication.

For the novel high-resolution and accurate-mass Thermo Scientific™ Orbitrap™ Axiom™ analyser, we have developed a detection system to maximize sensitivity, linear dynamic range, and detection lifetime which also allows for high resolution. The system is comprised of a post-acceleration electrode stack, El-MuL MTOF ion detector, and a preamplifier (see figure 1 and 2). The electrode stack accelerates ions with an attractive potential of several kilovolts on the conversion dynode of the detector to increase the number of released secondary electrons and thereby the detection efficiency. The secondary electrons are accelerated onto the surface of a multiplier, releasing photoelectrons which are further guided on a photomultiplier tube with a gain of ca. 10⁹. The signal from the last dynode of the photomultiplier tube is fed into the dual channel preamplifier with a gain ratio of 1:10 to maximize the dynamic range. Both output signals are led to an 14-bit analog-to-digital converter for further processing.

Figure 1 a) shows a schematic drawing of the Axiom analyzer and the primary ion trajectory through the analyzer. Trapped ions are extracted into the Axiom analyzer and travel along the drift direction back and forth between the two ion mirrors until they reach inflection point and are released. At the end of their return path, they traverse the post-acceleration and arrive at the detector (shown in b). Panel c) shows a detailed view on the components of the primary ion delivery to the detector. The detector exhibits a time response of ca. 1.7ns to allow for high resolution measurements.

Experimental

Experiments were obtained on a prototype system comprising an Axiom analyzer coupled to a Thermo Scientific™ Orbitrap™ Explore™ 480 mass spectrometer. Electropositive ions from Thermo Scientific™ Pierce™ FlexMix™ calibration solution and ammonium hexafluorophosphate (AHFP) were used to characterize the detection system over a wide m/z range.

To exclude effects from multi-ion peaks and variations of the signal intensities coming from the electron source, single ion measurements were performed to investigate most of the characteristics of the detection system. The mirror system of the Axiom analyzer was hereby utilized by setting the high voltages at the mirror electrodes in a deconvoluting mode to effectively deflect and remove multi-ion events. The separation between single ion events and electrical noise peaks was guaranteed by high detection thresholds at the ADC and sufficiently high gain on the detector level.

Results

Sensitivity

Figure 2 shows the single ion detection efficiency as function of the PMT voltage (left panel) and the mass-to-charge ratio (right panel). Single ion intensities of m/z 524 were measured by deconvoluting the mirror system of the Axiom analyzer under varying PMT voltages. Around 150% is needed to reach a detection efficiency of 80% without compromising the linear dynamic range of the detection system, the correct setting of the PMT voltage is therefore a trade-off between high detection efficiency and achievable dynamic range. The mass-to-charge ratio dependency was determined using FlexMix and AHFP and shows a high detection efficiency over the mass range, dropping down to 80% at m/z 5000 as electron yield at the conversion dynode has a higher probability for zero electrons being released.

Experimental

Figure 3 shows a FlexMix™ mass spectrum acquired in a single shot for a m/z range of 150-750 with two abundant peaks at m/z 85-106. The most intense peak, doubly charged MPPA at m/z 262, contains several thousand charges while the detection system is still able to detect single ions like m/z 446/225 with an intensity of 0.04%, showing a linear dynamic range much higher than 1:1000.

Linear Dynamic Range

Figure 4 shows the signal intensity of single ions of m/z 524 measured over 30 hours with an automatic detector calibration routine while continuously delivering FlexMix onto the detection unit. The single ion area and therefore the detector response is highly stable allowing an accurate quantification of the number of ions released over time. The detector gain is also linear after staving and baking the system due to the capacitated PMT.

Figure 5 shows the detector lifetime measurements in a dedicated test stand delivering ions up to m/z 614 from PTFEIA vapor. The single ion pulse height distribution width is representative of the detector lifetime and reaches a linear dynamic range of 150-300 with a gain of 100-1000 for any ion species. The average pulse height decreases by about 1% over the detector lifetime of several years of the ion-to-photons detector due to the capacitated PMT.

Discussion

The authors are grateful to acknowledge the enormous contributions of fellow scientists, engineers, and technicians at the Thermo Scientific HRAM product team. The detector is a dedicated system to provide high sensitivity and range for the Orbitrap-Axiom™ mass spectrometer.

CONCLUSION

The detection system of the new Axiom mass analyzer has been fully characterized concerning its sensitivity, dynamic range, detector gain stability, detector lifetime and the mass-to-charge ratio dependent response. The high sensitivity and linear dynamic range of the detection system allow the detection of single ions and multi-ion peaks with several thousand charge state and therefore a broad spectrum of application.

REFERENCES


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