

Improving Negative Ion Detection for Tandem Quadrupole Mass Spectrometry

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INTRODUCTION

Quantitative analysis using tandem quadrupole mass spectrometry is required for the food safety, environmental, pharmaceutical, and clinical application areas. There is an increasing need for lower limits of quantitation in order to meet many challenges such as new regulatory requirements for food safety, quantifying low levels of toxic contaminants in the environment, performing studies on new drug candidates, and detecting highly potent drugs at sub-therapeutic levels. Therefore the performance of the mass spectrometer for reliable and sensitive ion detection is critical for many laboratories.

CHALLENGES DETECTING NEGATIVE IONS

Detecting positive ions in mass spectrometers is relatively simple and very efficient. The positive ions are typically impacted onto a dynode held at a high negative potential to create secondary electrons, and then use either an electron multiplier or phosphor/photomultiplier tube (PMT) combination held at a relatively low positive potential to create a measurable signal (Figure 1).

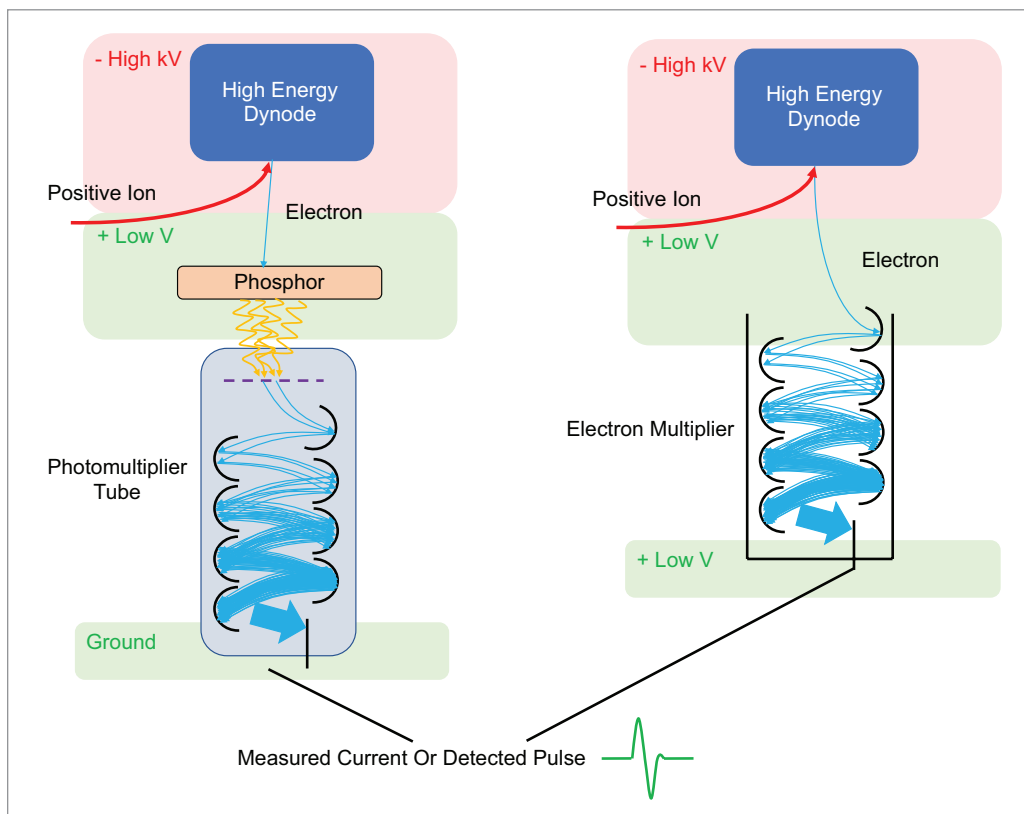


Figure 1. Positive ion detection using electron multiplier and phosphor/photomultiplier tubes

However, the detection of negative ions introduces complications because an electron is the same polarity as the incoming ion. When a negative ion impacts on a surface with high energy it results in the generation of secondary electrons and/or secondary positive ions. There are, therefore, several options available as shown in Figures 2a, 2b, and 2c.

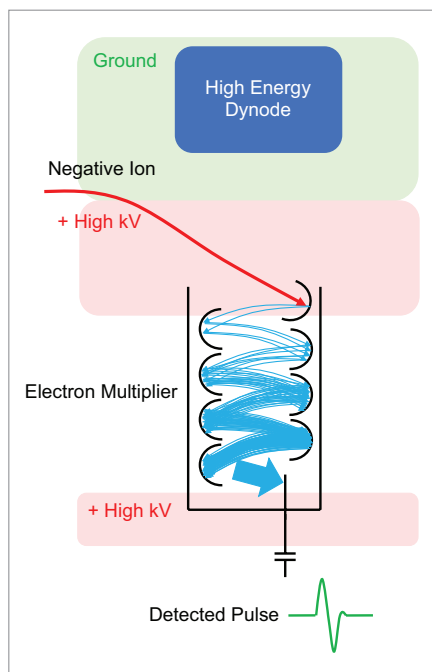


Figure 2a. Ions striking the electron multiplier directly.

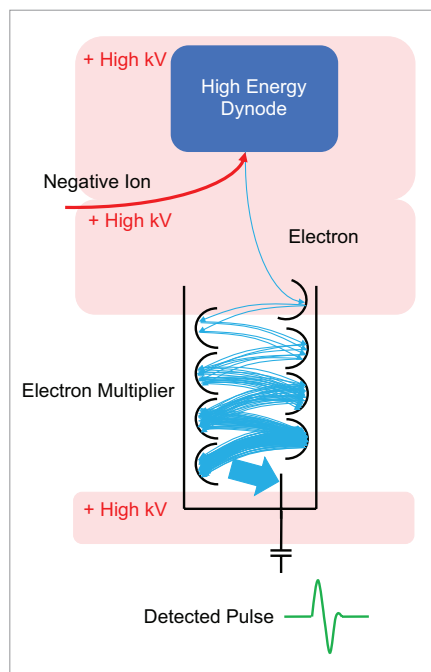


Figure 2b. Using secondary electrons from a high energy dynode.

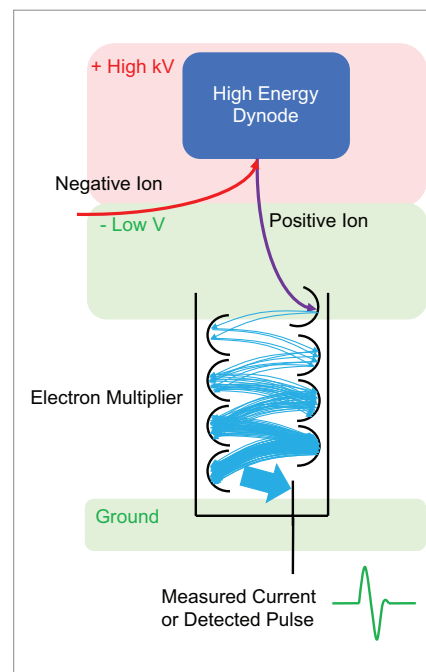


Figure 2c. Using secondary positive ions.

The negative ions can be impacted on the electron multiplier directly (Figure 2a) – but in order to obtain an efficient conversion of the ion into electrons from the initial strike, the electron multiplier must be set to very high positive potential. Alternatively, the negative ions can be impacted on a dynode held at high positive potential to generate secondary electrons (Figure 2b). The electron multiplier must then be held at an even higher positive potential to attract the electrons into it. Since electron multipliers require a positive potential gradient to be present down it, in both of these cases the final section of the electron multiplier which is connected to the detection electronics would need to be held at a yet higher potential. The whole detection electronics would therefore then need to be either floated to a very high potential or, more commonly, capacitively decoupled from the end of the electron multiplier. Detectors which are capacitively decoupled rely on the detection of the pulse resulting from a single ion striking the detector rather than measuring the actual current. This introduces limitations on the dynamic range of the detector as the incoming ion current increases and the pulses overlap.

Another solution is to rely on the generation of secondary positive ions (Figure 2c). In this case, the dynode is held at a high positive potential and the electron multiplier is held at a low negative potential. This allows the control electronics to be held at low voltage and the current to be measured rather than relying on pulse counting. However, it is known that the efficiency of the conversion of negative ion species to secondary positive ions is extremely poor for low mass ions.¹

Instead of these approaches, Waters™ instruments use a phosphor and PMT as this electrically decouples the electron creation to the electron multiplication process. The PMT can then be held at a relatively low voltage and therefore does not rely on pulse counting. These detectors are configured as a conversion dynode followed by a phosphor, followed by a PMT (Figure 1). The PMT is configured as a (typically bialkali) glass vacuum tube containing a photocathode followed by an electron multiplier. For these detectors, the ions strike the conversion dynode at high energy to generate secondary electrons. These electrons are accelerated into a phosphor. The phosphor generates photons (light) which enter the PMT and strike a photocathode. The photons are converted to electrons by the photocathode and these electrons are then multiplied to generate a current.

The glass tube allows photons to enter the PMT whilst keeping the active surfaces of the electron multiplier section permanently protected and under vacuum. Because of this, the lifetime of PMT-based detectors is generally much longer than the lifetime of the instrument. Unlike electron multiplier-based detectors, these detectors do not need regular gain adjustment or replacement.

Secondary electrons and/or secondary positive ions are both created whenever a negatively charged organic ion strikes a surface with high energy, but there are differences in the way the quantum efficiency varies with mass for each conversion type.

It is therefore possible to have the following situation:

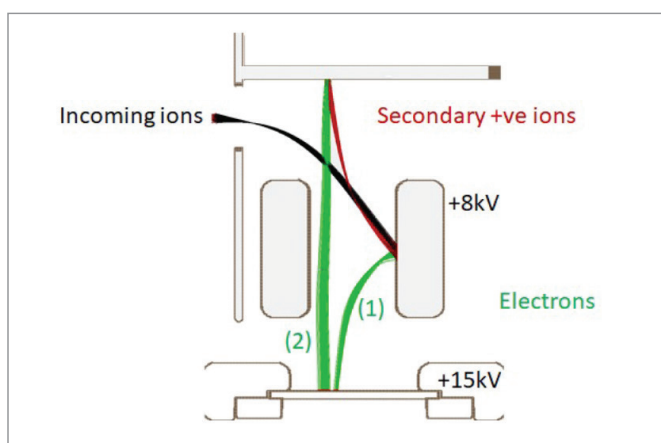
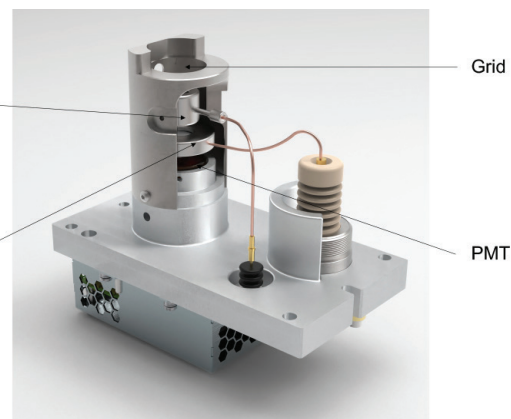


Figure 3. Secondary electron and secondary positive ion creation.

In the above example, the electrons generated from a strike on the dynode (1) hit the phosphor with an energy of 7keV whereas the electrons generated from the secondary positive ion strike on the earth plate (2) strike the phosphor with 15keV. Because the quantum efficiency of the creation of secondary positive ions varies with mass, at some masses the incoming ion will only generate secondary positive ions some of the time. The result of that is a wide variation in the possible height of a single ion hitting the detector. If not handled effectively, this can cause a reduction in the instrument sensitivity due to a broadening of the potential signal seen from a single ion strike and therefore more ions being required to obtain a reproducible measurement. It is therefore preferable for only the secondary electrons to be used to generate the signal seen from negative ions.



XEVO™ TQ ABSOLUTE DETECTOR

The Xevo TQ Absolute Detector utilizes an off-axis high energy dynode and highly efficient P47 phosphor combined with an extremely long lifetime photomultiplier tube which maximizes the sensitivity in negative ion mode without needing adjustment over the instrument lifetime. It utilizes the XDR detection system which enables the Xevo TQ Absolute instrument to achieve up to 6 orders of linear dynamic range enabling the quantification of a diverse range of analytes at varying concentration levels in a single chromatographic run.

The use of a grid (rather than a grounded plate) allows a suitable field to be formed to direct ions into the dynode, but also allows any secondary positive ions to pass through and therefore not contribute to the signal (Figure 4).

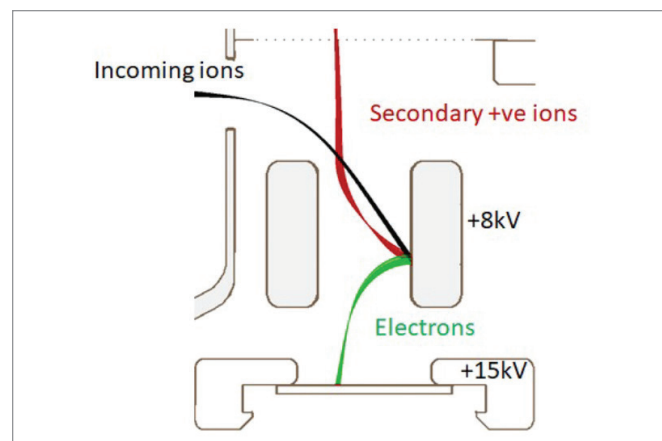


Figure 4. Secondary positive ions pass through a grid.

As can be seen, the secondary positive ions pass through the grid and do not generate electrons.

Table 1. Comparing to other detection types.

Who	Initial Conversion	Secondary Particle	Signal Amplification	Counting Type	Lifetime	Linearity	Sensitivity*
Competitors	High Energy Dynode	Electron	Electron Multiplier	Pulse Counting	✗	✗	✓
Competitors	High Energy Dynode	Positive Ion	Electron Multiplier	Analogue	✗	✓	✗
Xevo TQ Absolute	High Energy Dynode	Electron	Phosphor and PMT	Analogue	✓	✓	✓

* Specifically low mass negative ion species.

A good example of the practical aspects of this improvement in sensitivity can be shown with the analysis of anionic polar pesticides. These compounds ionize in negative mode and create product ions with low m/z which makes them difficult to sensitively detect using the traditional detectors. However, with the new Xevo TQ Absolute Detector there are significant improvements in sensitivity as shown in Figure 5.

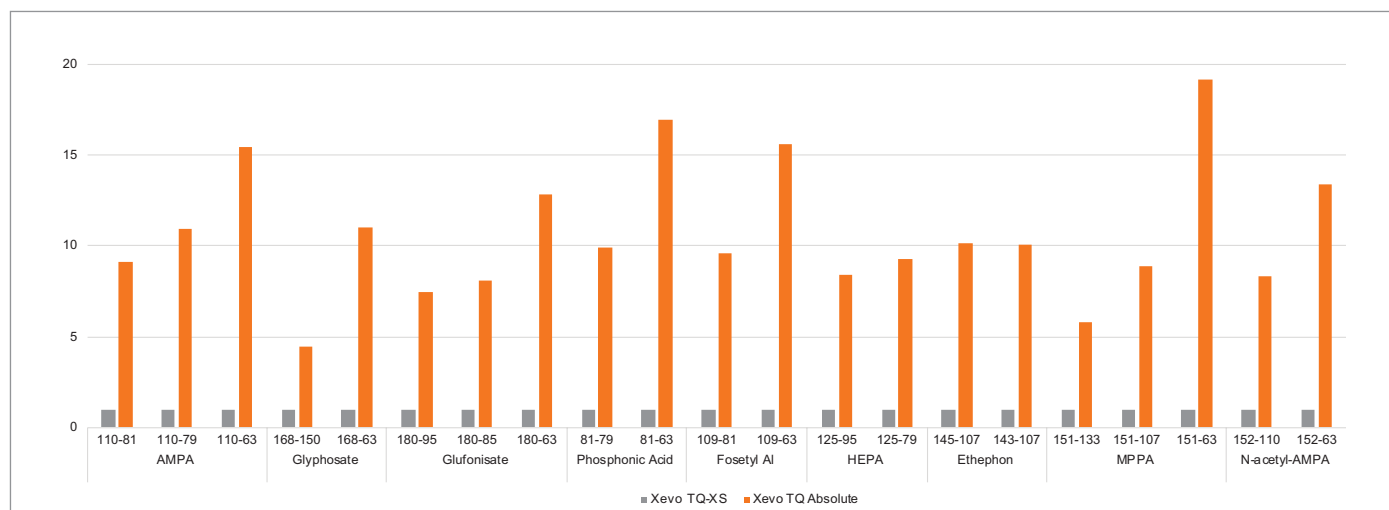


Figure 5. Comparison of Xevo TQ Absolute detection of anionic polar pesticides to the Xevo TQ-XS.

CONCLUSION

In summary the new Xevo TQ Absolute now enables very sensitive detection of both positive and negative ionizing compounds whilst maintaining the advantages afforded by the photomultiplier detection system which does not require regular gain adjustments or typically require replacement during the lifetime of the instrument.

References

1. G.C. Stafford, Instrumental Aspects of Positive and Negative Ion Chemical Ionization Mass Spectrometry, *Environmental Health Perspectives*, 36, p. 85–88, 1980.

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