

Extended Linear Dynamic range with a new electron multiplier system on Single Quadrupole GC-MS

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ABSTRACT

In this work a new electron multiplier detector system is compared with the previous generation electron multiplier detection system on a Thermo Scientific™ GC-MS. Experiments included running extended calibration curves on both detectors to assess linearity and spectral fidelity. The two main advantages of the new detector system are the greater linear dynamic range and extended lifetime compared to the previous generation. These improvements have been made possible because of complete redesign of the electron multiplier system, better material technology of the multiplier dynode, and improved an electrometer that can manage the increased current output from the multiplier.

The GC-MS system was run using the previous electron multiplier detection system to perform analysis of an octafluoronaphthalene (OFN) with 2 standard calibration curve between 4.3 fg to 43 ng on-column using selected ion monitoring (SIM) acquisition and OFN from 0.43 ng to 43 ng and the data acquired in full scan mode. The detection system was then replaced with the new detector on the GC-MS system and the experiment repeated. No other conditions were modified on the systems to ensure the comparison was being made on the detectors only. The analysis of the OFN calibration curve from 0.43 fg to 43 ng on both detectors showed clear improvements using the new detection system, achieving 7 orders of linear dynamic range. Utilizing the full scan data, the spectral quality of OFN was assessed at the highest concentration of 46 ng of OFN on column. On the previous electron multiplier detection system, the spectral fidelity of the acquired data is compromised due to saturation. In comparison, the data on the new detector gave an almost identical spectral match to the library spectrum.

INTRODUCTION

Analytical laboratories utilize GC-MS or GC-MS/MS for both targeted analysis and known unknowns analysis using commercially-available libraries such as NIST or Wiley. These laboratories face challenges with limited detector dynamic range when analyzing compounds at high and low concentrations in a single run, which can lead to the analysis being split into class or compound specific methods. Dynamic range limitations can impede sample screening. If a compound saturates the detection system due to high concentration, the mass spectral fidelity is affected, leading to poor library matches and potential misidentification of the compound of interest or even a false negative. An extended dynamic range detector can help overcome these analytical challenges.

MATERIALS AND METHODS

System configuration used-

A Thermo Scientific™ ISQ™ 7610 system coupled to a Thermo Scientific™ TRACE™ 1610 autosampler with Thermo Scientific™ AI/AS 1610 autosampler. The experiments were initially run with the previous generation electron multiplier + electrometer detector system and then same experiments were repeated with the new generation electron multiplier + electrometer detector system, also known as Thermo Scientific™ XLXR™ detector system. Figure 1, shows the visual differences between the two electron multipliers.

Figure 1. Visual comparison of the previous generation electron multiplier (left) and the XLXR™ electron multiplier (right).



Sample used-

OFN solution in iso-octane with concentrations ranging from 4.3 fg/μL to 43 ng/μL

Method Conditions

AS 1610	
Syringe	10 μL, 25 gauge, 50 mm length, cone tip (P/N 36500525)
Injection volume	1 μL
Pre-injection solvent and cycles	None
Sample rinses	3
Post-injection solvent and cycles	None

TRACE 1610	
Column	Thermo Scientific™ TraceGOLD™ TG-SQC, 15 m × 0.25 mm × 0.25 μm
Liner	Splitless Liner single taper with wool, 4 mm ID, 78.5 mm length (P/N 453A0924)
SSL mode	Splitless
Inlet temperature	220 ° C
Split flow	50 mL/min
Splitless time	0.8 min
Septum Purge Flow	Constant flow of 5.0 mL/min
Carrier flow	Constant He flow of 1.2 mL/min
Oven Program	40° C (1.0 min), 30° C/min to 250° C (2 min)

ISQ 7610	
MS transfer line temperature	250 ° C
Ion source temperature	200 ° C
Source Type	ExtractaBrite
Ionization mode, Electron energy	EI, 70eV
Emission current	50 μA
Scan range (Da)	SIM m/z 272
Dwell time	0.2 s

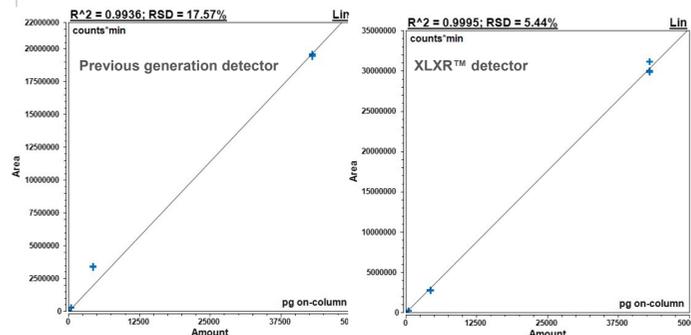
For experiments conducted to assess the mass spectral fragmentation and spectral fidelity comparisons a TraceGOLD™ TG-5ms, 30 m × 0.25 mm × 1 μm was used with full scan range of m/z 50-300 Da.

RESULTS

Linear Dynamic Range of the XLXR™ detector system

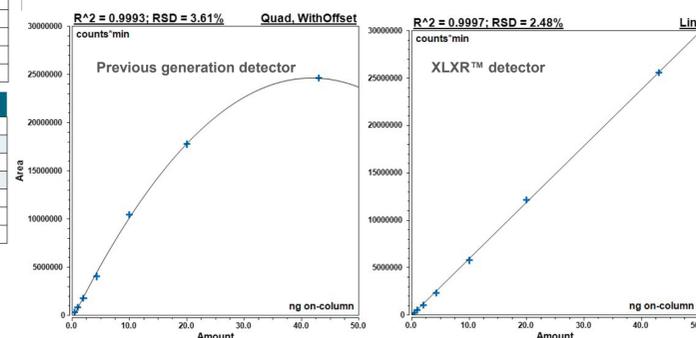
To assess the dynamic range of the detector system a calibration curve was run from 4.3 fg to 43 ng on-column in selected ion monitoring (SIM) mode. The lowest standard is near the system LOD while the highest level is near the expected detector saturation. Figure 2 shows a comparison of the calibration curve between the previous generation detector system and the XLXR™ system, the linearity on the previous electron multiplier detection system gives a reasonable R² value of 0.994. However, the % RSD of the residual values is 17.9, and it is clear that the data at 4.3 ng does not fit on the linear curve. If this curve were used to quantify samples, the results would be inaccurate. With the XLXR detector, the linearity is improved with an R² value of 0.9995 and a % RSD of the residual values is 5.4. This curve would allow accurate quantification over the whole range. The data shows that XLXR™ detector system has a linear dynamic range of at least 7 orders.

Figure 2. Comparison of the previous electron multiplier detection system and the XLXR™ detector on the ISQ 7610 GC-MS using OFN over a range of 4.3 fg to 43 ng on-column.



The benefits of the XLXR detector for linearity over a large dynamic range are even clearer when reviewing the data for the second set of experiments conducted at higher concentration range between 0.43 ng and 43 ng on-column. Using the previous electron multiplier detection system, it is impossible to use a linear regression on the curve and a quadratic curve must be used. This is due to the calibration points of 20 ng and 43 ng saturating the detector. If a sample at high concentration was run on this detector, it would not be accurately quantified and therefore requiring a reanalysis. In comparison, the calibration curve on the ISQ 7610 GC-MS equipped with the XLXR detector gives a linear regression with an R² value of 0.9997 and a percentage RSD of 2.5%. Figure 3 shows the comparison of the linearity on the ISQ 7610 GC-MS using each detector. This extended dynamic range allows for methods to be consolidated and accurate quantification of trace and high-level compounds to be performed in a single run.

Figure 3. Comparison of the previous generation electron multiplier detector system and the XLXR™ detector system on the ISQ 7610 GC-MS using OFN over a range of 0.43 ng to 43 ng on-column.



Spectral Fidelity comparisons at the highest level

Utilizing the full scan data from the ISQ 7610 GC-MS, the spectral quality of OFN was assessed at the highest concentration of 43 ng of OFN on column. On the previous electron multiplier detection system, the spectral fidelity of the acquired data is compromised due to saturation. The increased abundance of m/z 222, 241, and 273 gives a relatively poor spectral match to the library spectrum. In comparison the data on the ISQ 7610 GC-MS equipped with the XLXR™ detector gives an almost identical ion abundances to the library spectrum. This spectral quality aids in the determination of the presence of compounds in samples and gives confidence in data analysis. The higher dynamic range also allows for better confirmation of targeted compounds that use ion ratio as confirming criteria. Figure 4 shows the comparison of acquired spectrum versus the library spectrum at 43 ng on-column level on the previous generation detector system and Figure 5 shows the same for the XLXR™ detector system.

Figure 4. Spectral comparison of acquired versus library spectrum of OFN at 43 ng on-column using the previous generation detector.

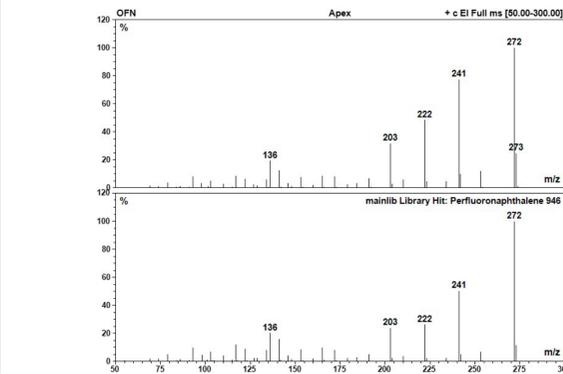


Figure 5. Spectral comparison of acquired versus library spectrum of OFN at 43 ng on-column using the XLXR™ detector system.

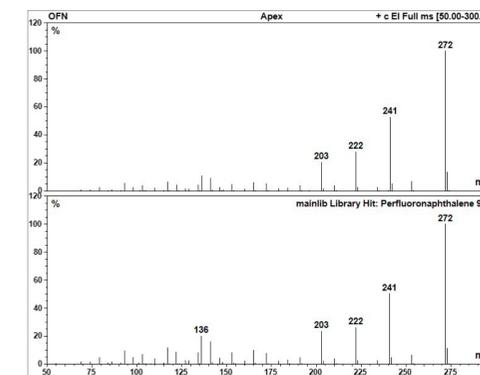
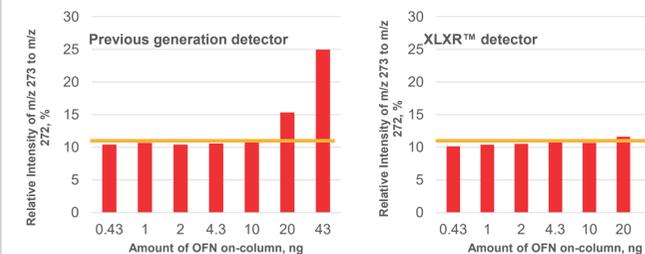


Figure 6 compares the isotopic fidelity of OFN by comparing the relative intensity of m/z 273 to m/z 272 at various on-column concentrations. One can clearly observe that for the previous electron multiplier detection system, the relative intensity deviates significantly from the theoretically predicted isotopic ratio of 10.82% at 20 ng and 43 ng on-column concentration, while the XLXR™ detector system deviates slightly, about 2.6 percentage points, at 43 ng on-column. Based on this and aforementioned results, the XLXR detector system is expected to have about two to four times higher dynamic range than the previous electron multiplier detection system.

Figure 6. Chart comparing the relative intensity of m/z 273 to m/z 272 for various OFN on-column amounts for the previous electron multiplier detection system and the XLXR™ detector system. The theoretically predicted relative intensity is 10.82% and is indicated by the orange horizontal line in the chart.



Reasons for superior performance of the XLXR™ detector system

The following primary reasons for the superior performance of the XLXR™ detector system over the previous generations-

- Material changes to the material of the discrete dynodes (even emissive properties)
- Ceramic shielding to better protect the dynode surface from water and other contaminants
- Design changes
- Better electronics
- Electrometer change in order to handle the high current that the new EM is able to produce

CONCLUSIONS

The XLXR detector has been shown to have increased dynamic range over the previous-generation detector systems. This addresses the challenges faced by analytical testing laboratories and offers several advantages:

- Ability to consolidate methods and quantify low and high concentrations in a single method
- Reduction of the need to rerun high concentration samples to make them fit into the dynamic range of the system
- Utilization of linear regression for data analysis without the need to use quadratic fit
- Increase in spectral fidelity at high concentration, producing quality spectral matches with accurate isotopic patterns

These advantages, coupled with the extended lifetime of the XLXR™ detector, allow the ISQ 7610 GC-MS and TSQ 9610 GC-MS help analytical laboratories to maximize instrument utilization and increase sample throughput.

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TRADEMARKS/LICENSING

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