

Pesticide Residue Screening in Surface Water by Orbitrap™ HRAMS

PRESENTED BY

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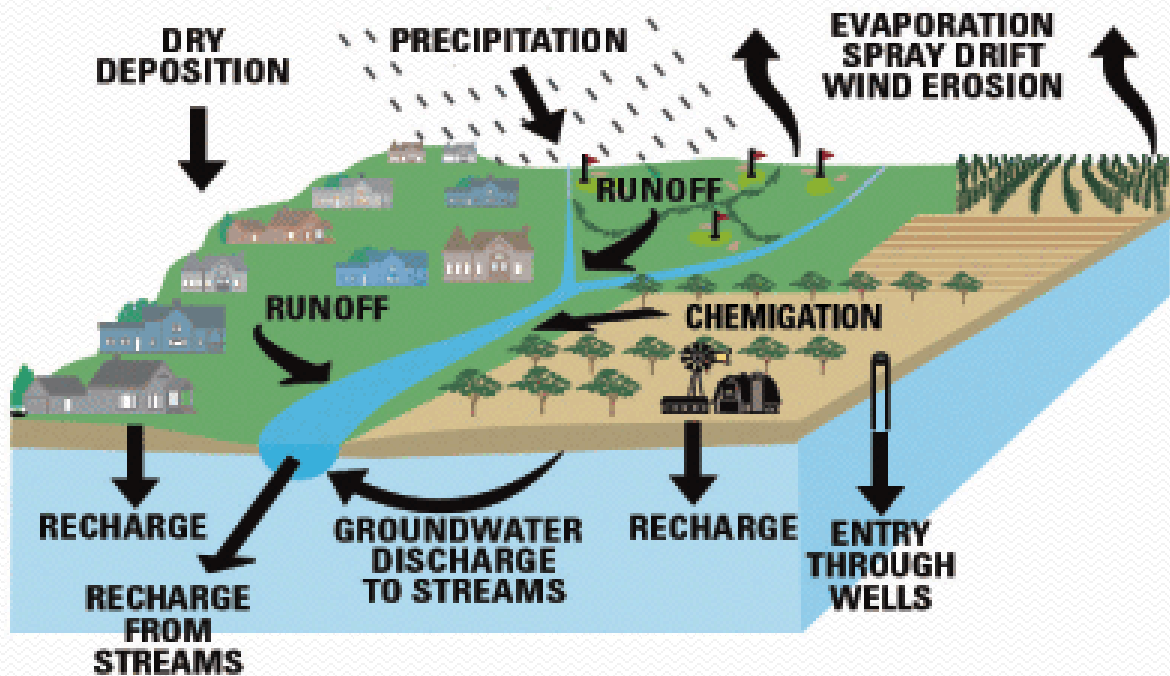
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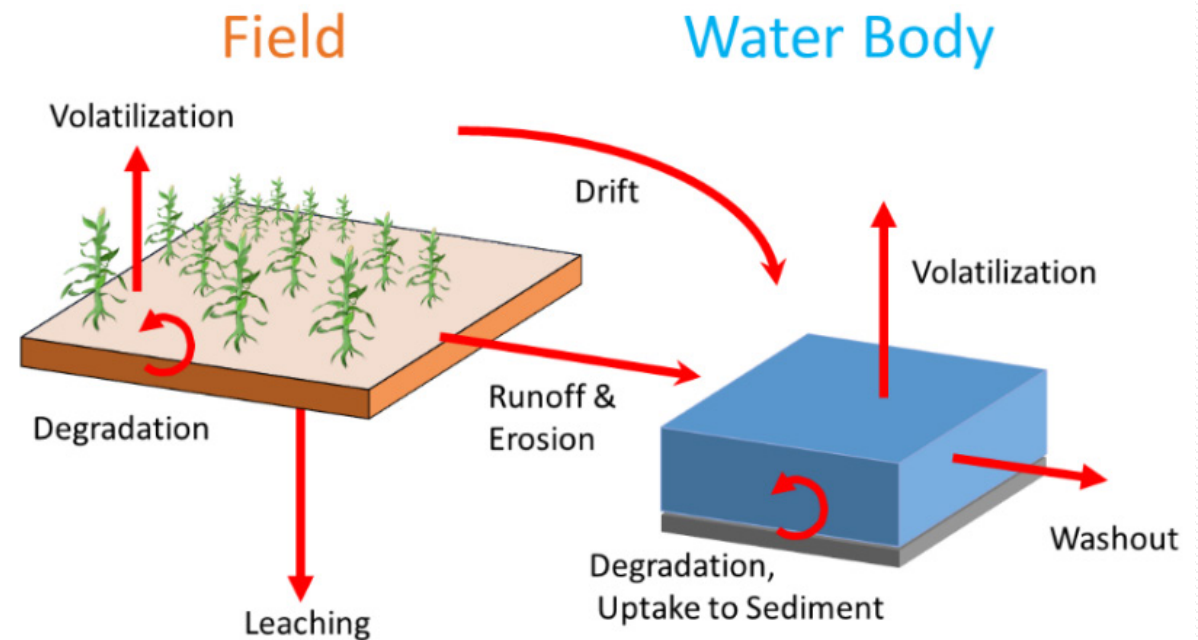


Pesticide in Surface Water



Schematic diagram illustrating routes of pesticides into streams and groundwater.
(Modified from Gilliom and others, 2006.)

Framework for Conducting Pesticide Drinking Water Assessments for Surface Water



The EPA Conceptual Model for Pesticide Fate and Transport to Surface Water



24.8.2013

EN

Official Journal of the European Union

L 226/1

I

(Legislative acts)

DIRECTIVES

**DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 12 August 2013**

**amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of
water policy**

(Text with EEA relevance)

Among 45 controlled substances there are several pesticides (maximum allowable concentration):

- alachlor ($0.7 \mu\text{g L}^{-1}$)
- aclonifen ($0.012 \mu\text{g L}^{-1}$)
- atrazine ($2 \mu\text{g L}^{-1}$)
- bifenox ($0.004 \mu\text{g L}^{-1}$)
- chlorfenvinphos ($0.3 \mu\text{g L}^{-1}$)
- chlorpyrifos ($0.1 \mu\text{g L}^{-1}$)
- cybutrine ($0.016 \mu\text{g L}^{-1}$)
- cypermethrin ($6 \times 10^{-5} \mu\text{g L}^{-1}$)
- dichlorvos ($7 \times 10^{-5} \mu\text{g L}^{-1}$)
- diuron ($1.8 \mu\text{g L}^{-1}$)
- endosulfan ($0.004 \mu\text{g L}^{-1}$)
- heptachlor ($3 \times 10^{-3} \mu\text{g L}^{-1}$)
- isoproturon ($1 \mu\text{g L}^{-1}$)
- quinoxifen ($0.54 \mu\text{g L}^{-1}$)
- simazine ($4 \mu\text{g L}^{-1}$)
- terbutryn ($0.034 \mu\text{g L}^{-1}$)

11th of Q1 Journal in Analytical Chemistry
on Scimago Journal & Country Ranking

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Multi-residue analysis of pesticides in surface water by liquid chromatography quadrupole-Orbitrap high resolution tandem mass spectrometry

J. Casado*, D. Santillo, P. Johnston

Greenpeace Research Laboratories, College of Life and Environmental Sciences, Innovation Centre Phase 2, University of Exeter, Exeter, United Kingdom



Anal. Chem. 2000, 72, 1156–1162

Electrostatic Axially Harmonic Orbital Trapping: A High-Performance Technique of Mass Analysis

Alexander Makarov*

HD Technologies Ltd., Atlas House, Simonsway, Manchester, M22 5PP, U.K.

This work describes a new type of mass analyzer which employs trapping in an electrostatic field. The potential distribution of the field can be represented as a combination of quadrupole and logarithmic potentials. In the absence of any magnetic or rf fields, ion stability is achieved only due to ions orbiting around an axial electrode. Orbiting ions also perform harmonic oscillations along the electrode with frequency proportional to $(m/z)^{-1/2}$. These oscillations are detected using image current detection and are transformed into mass spectra using fast FT, similarly to FT ICR. Practical aspects of the trap design are presented. High-mass resolution up to 150 000 for ions produced by laser ablation has been demonstrated, along with high-energy acceptance and wide mass range.

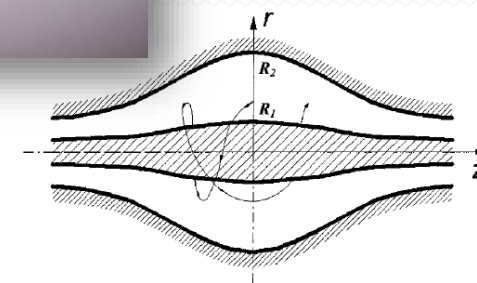
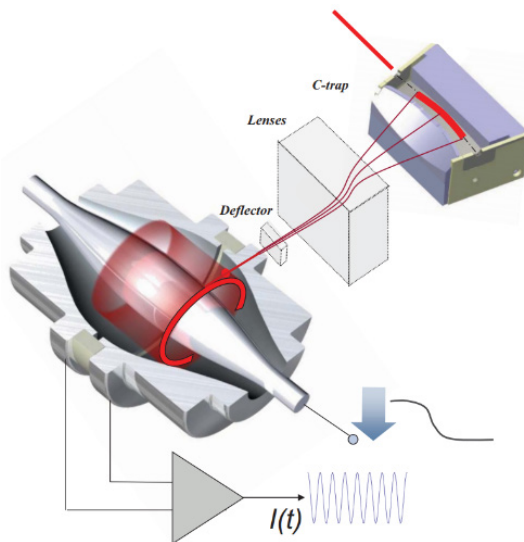


Figure 1. Equipotentials of the quadro-logarithmic field and an example of a stable ion trajectory

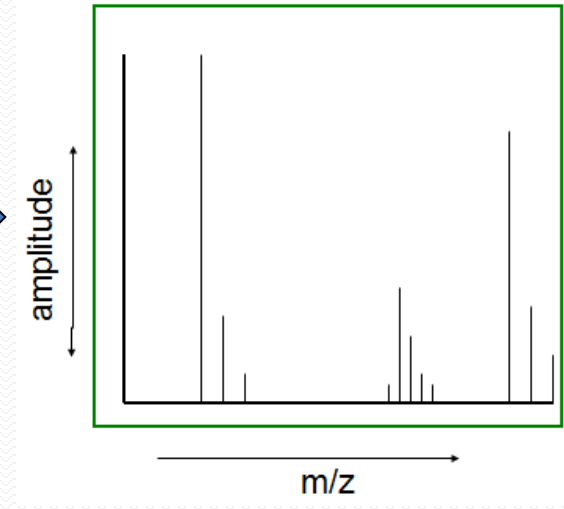
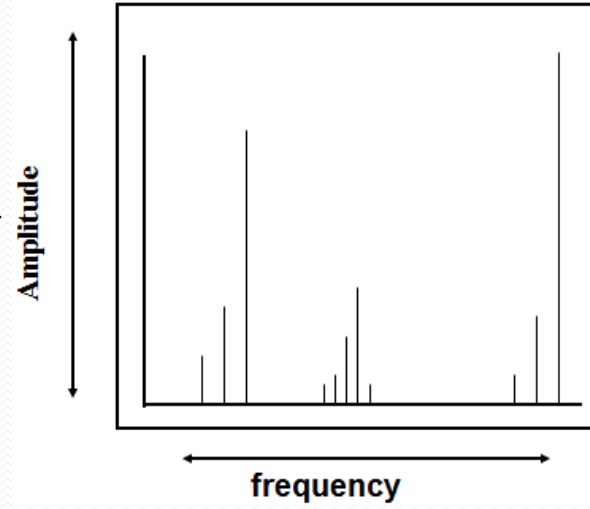
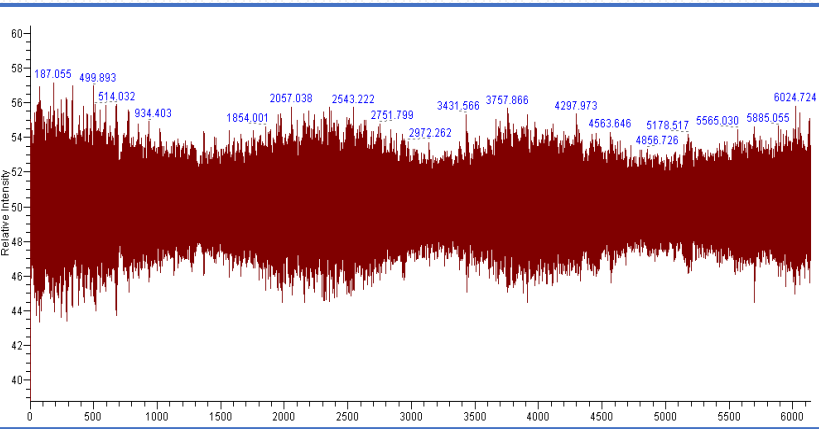
Mass Analyzer : Orbitrap™ Technology

Image Current

Frequency Domain

Mass Spectrum

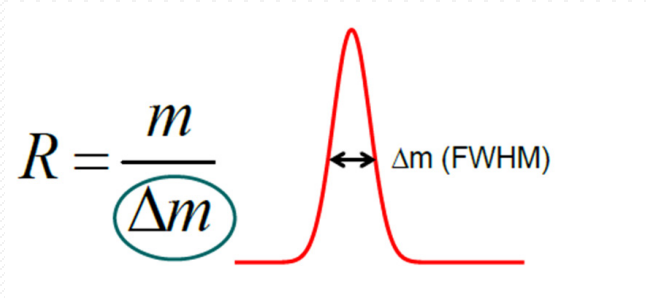
Fourier Transform



$$\omega_z = \sqrt{\frac{k}{m/q}}$$

Mass Resolution

- Ability of a mass spectrometer to distinguish between ions of nearly equal m/z ratios.



m - measured mass

Δm - peak width measured at 50% peak intensity (Full Width Half Maximum)

C = 12.0000

H = 1.0078

N = 14.0031

O = 15.9949

S = 31.9721

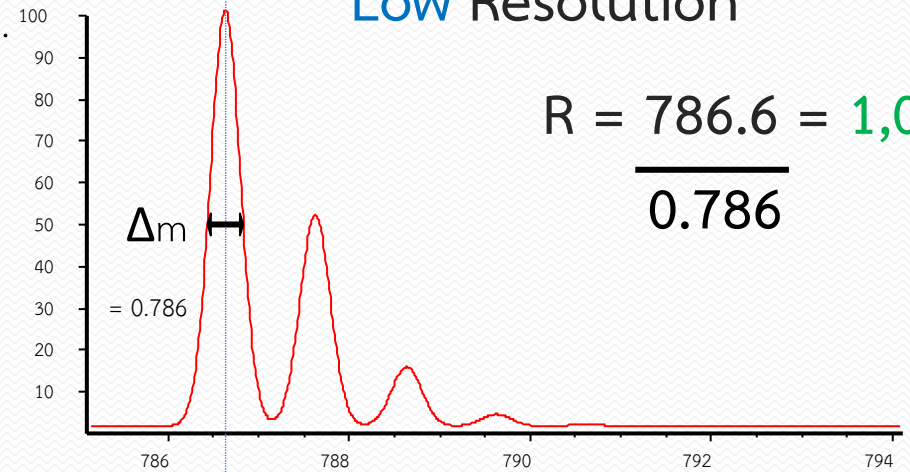
CO = 27.9949

N₂ = 28.0061

C₂H₄ = 28.0313

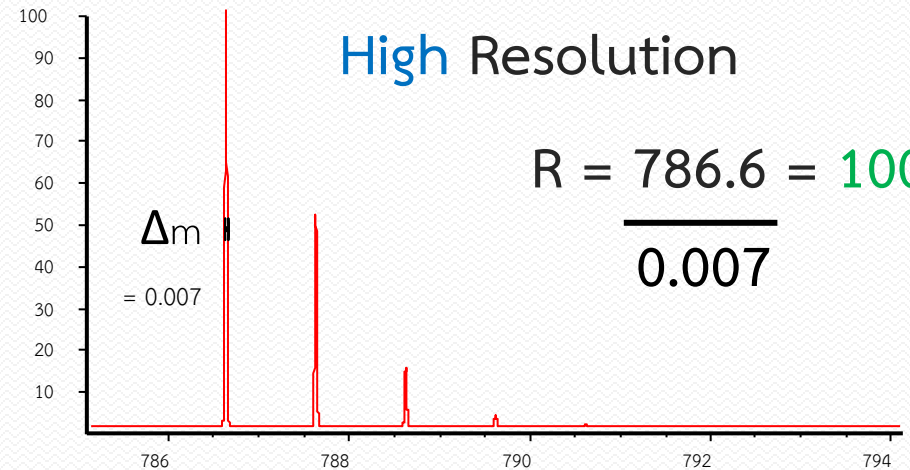
- It is possible to have combinations of atoms which have the same nominal mass but different accurate mass
- Nominal mass measurements cannot distinguish these compounds
- These elemental combinations have the same nominal mass but different accurate mass
- If such compounds can be mass measured with sufficient accuracy it is possible to determine elemental composition

Low Resolution



$$R = \frac{786.6}{0.786} = 1,000$$

High Resolution



$$R = \frac{786.6}{0.007} = 100,000$$

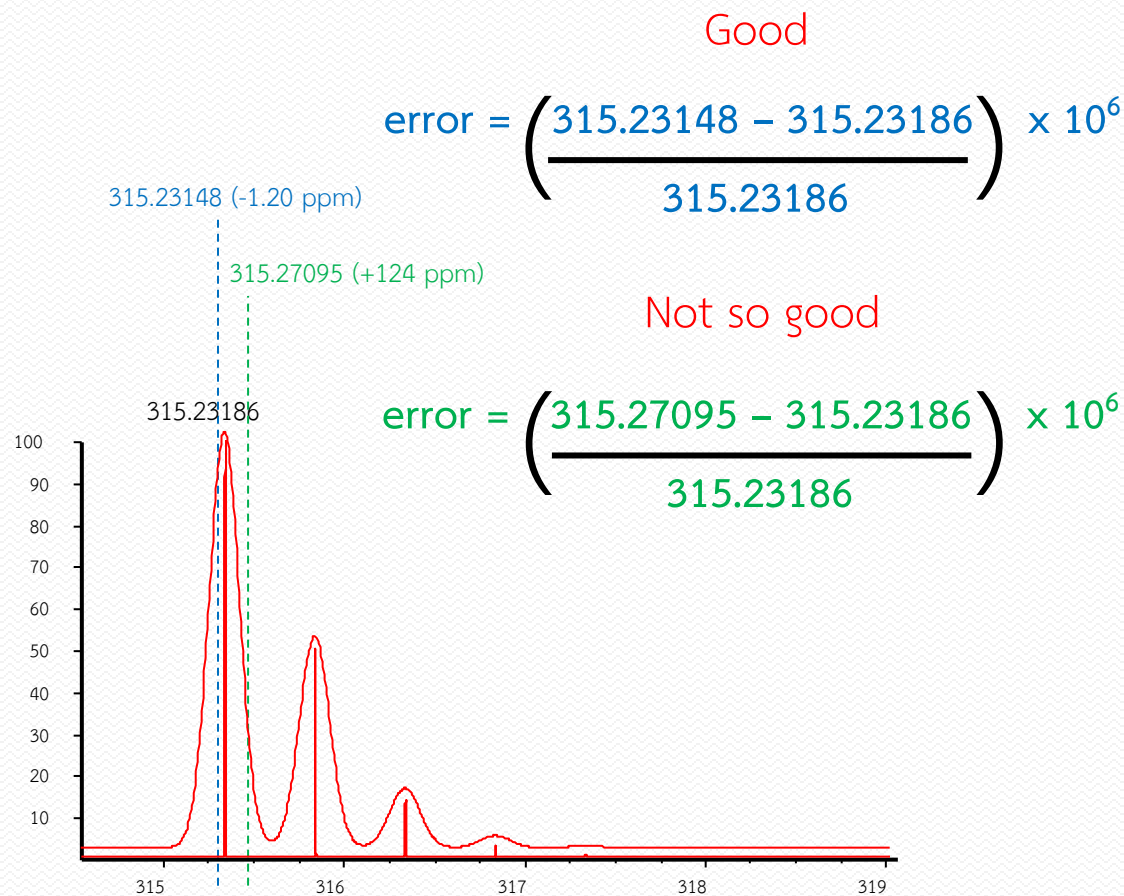
Mass Accuracy

- Mass Accuracy is the precision of which the mass is measured by MS.
- Typical way of reporting mass error in ppm (relative measure).
- Increases confidence in identification.

$$\text{Mass error} = \left(\frac{\text{Measured} - \text{Theoretical}}{\text{Theoretical}} \right) \times 10^6 = \text{ppm}$$

[M+H]⁺ = 315.23148

Mass Error	Number of Hits
± 200 ppm	265
± 100 ppm	133
± 30 ppm	39
± 10 ppm	14
± 5 ppm	5
± 3 ppm	4
± 1 ppm	1



Mass Resolution & Accuracy

Measured Mass	Mass Error (Da)	Possible Formula	Exact Mass
32.0	± 0.2	O ₂	31.9898
		CH ₃ OH	32.0261
		N ₂ H ₄	32.0374
		S	31.9721
32.02	± 0.02	CH ₃ OH	32.0261
		N ₂ H ₄	32.0374
32.0257	± 0.002	CH₃OH	32.0261

C = 12.0000

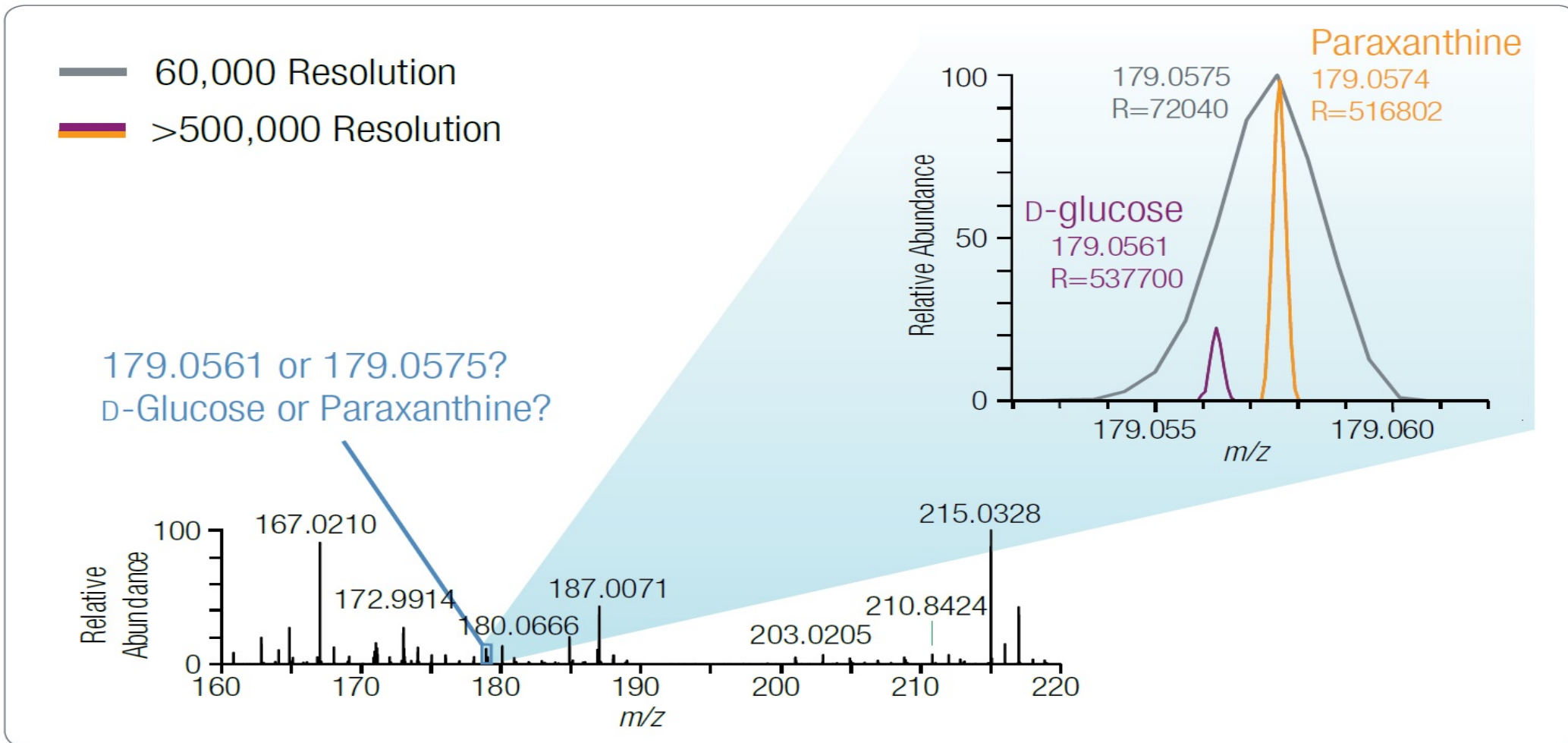
O = 15.9949
S = 31.9721

H = 1.0078
N = 14.0031

- **Main advantage:** the possibility to determine the elemental composition of individual molecular or fragment ions, a powerful tool for the structural elucidation or confirmation.

Mass Resolution & Accuracy

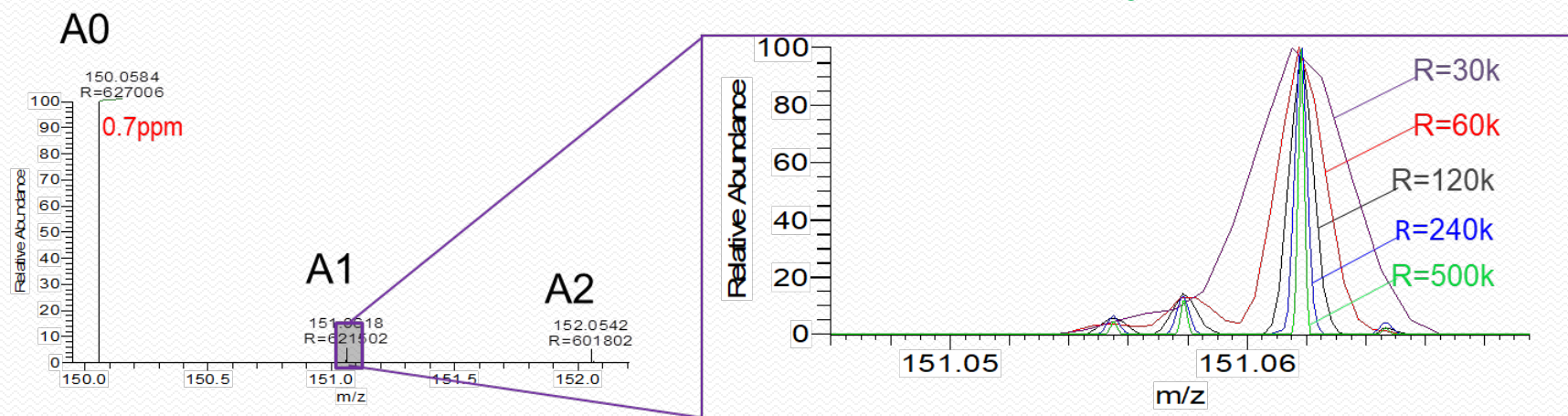
- Isobaric compounds separation



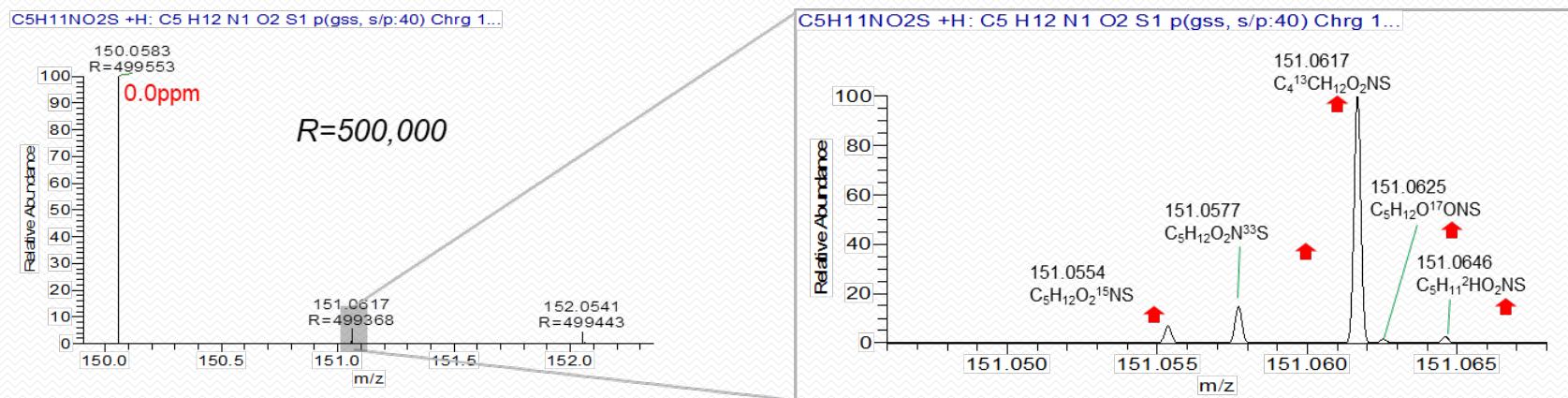
Mass Resolution & Accuracy

- Fine Isotopic Pattern

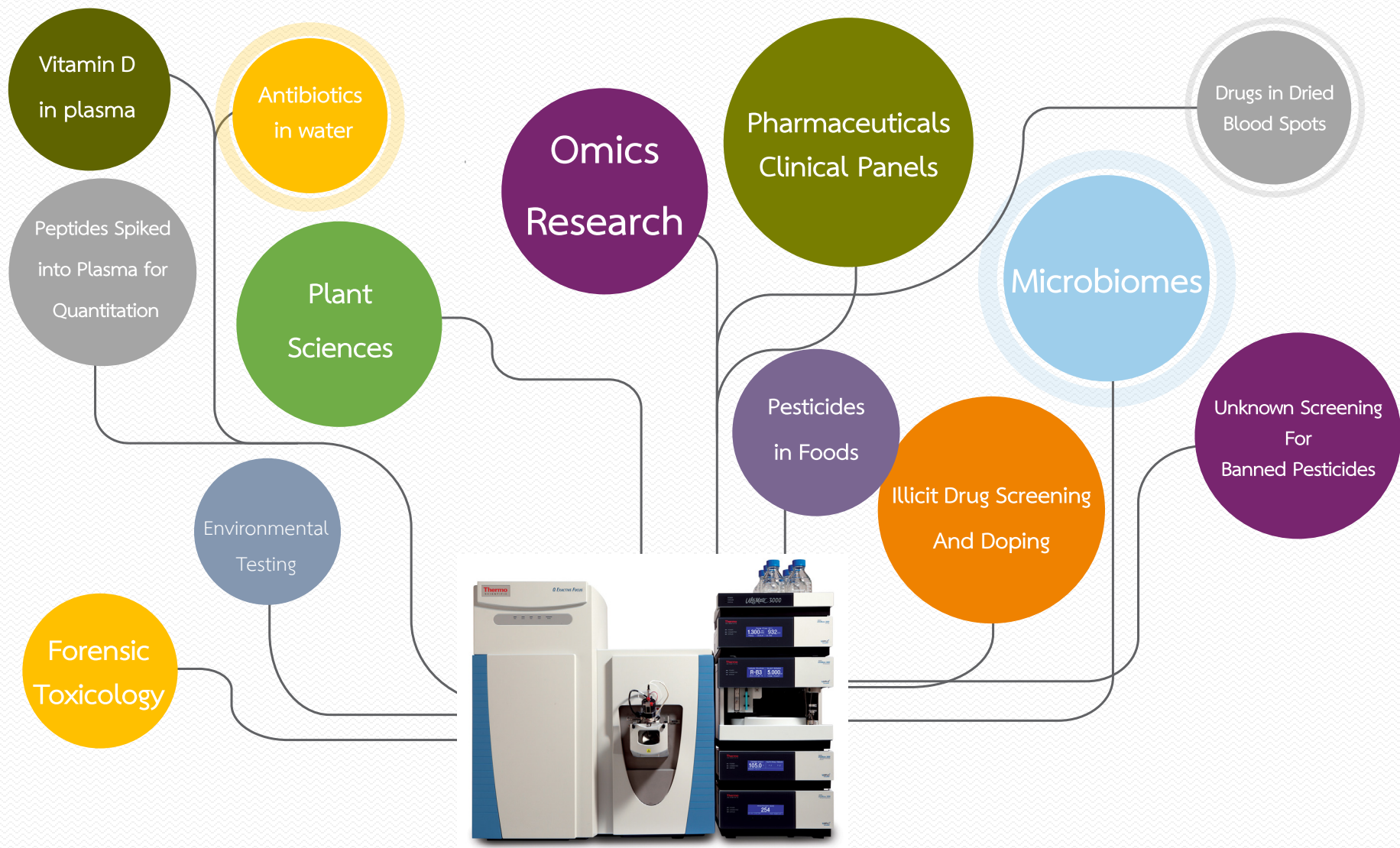
Observed



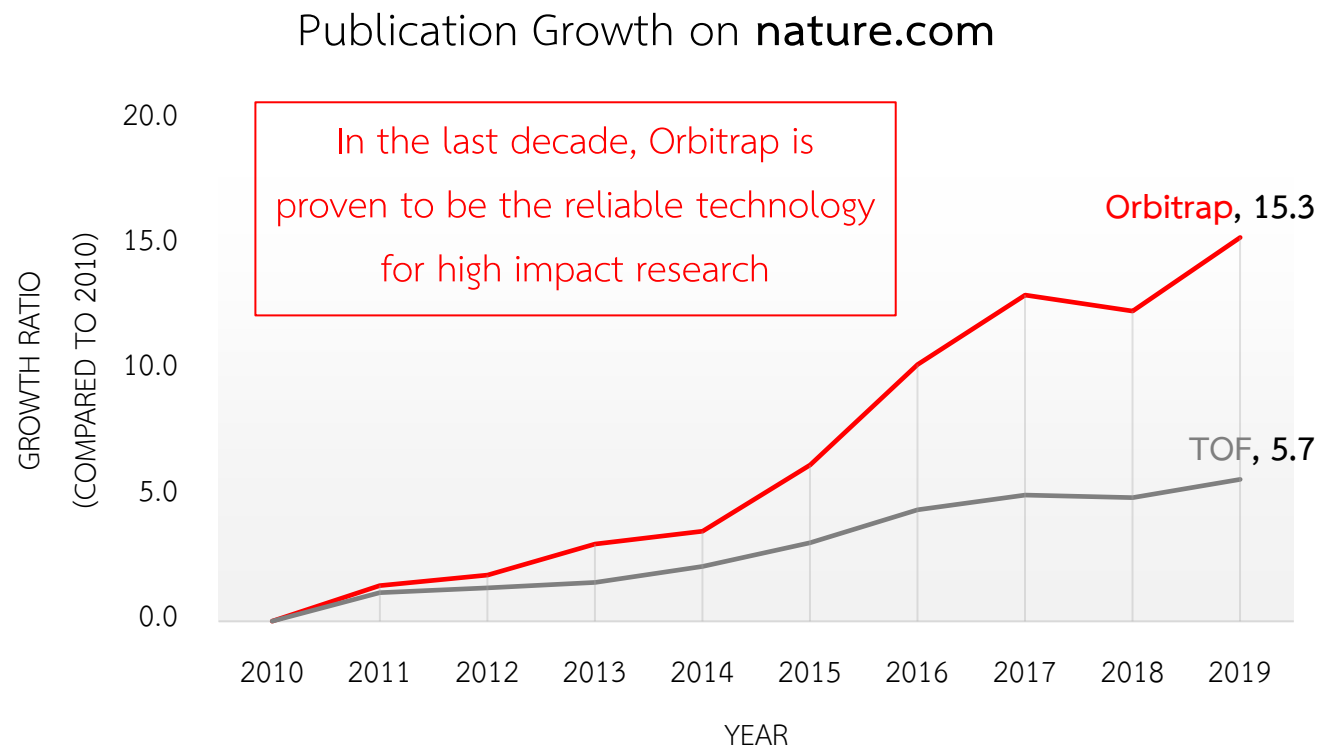
Simulated



Orbitrap Applications Universe



Year	Orbitrap	TOF
2010	61	165
2011	87	189
2012	112	219
2013	188	255
2014	219	361
2015	380	516
2016	625	734
2017	794	830
2018	755	813
2019	934	934
<i>Total</i>	<i>4,155</i>	<i>5,016</i>



- In 2019, the publications of Orbitrap technology and TOF on nature.com was equally at 934 publications
- However, when compared year 2019 to year 2010, the publication ratio of Orbitrap technology was exclusively at 15.3 whereas the ratio of TOF was just at 5.7

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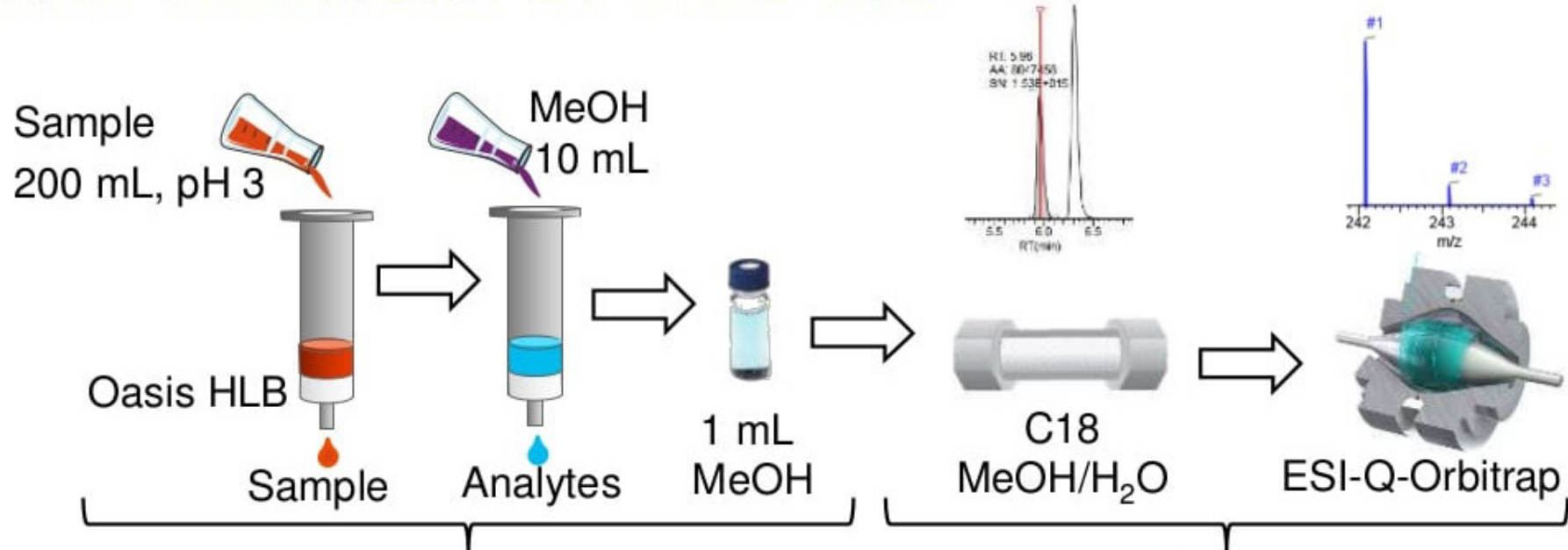
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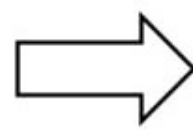
Pesticide Analysis: Why is Orbitrap HRAMS better than Triple Quadrupole (QqQ) MS?

- The major advantage is the possibility of acquiring **full-scan spectra at high resolution**, whereas QqQ techniques only register SRM or MRM data defined by the user before the analysis.
- LC-HRAMS is possible to identify every substance that ionizes in the source, to make the **retrospective analysis** of other substances, and even to **qualitatively screen the compounds** without reference standards.
- Another important advantage of the HRAMS over QqQ instruments is the **reduction of a false positive** identification, especially when dealing with complex matrices.

Sample Preparation



Thermo AutoTrace SPE



Thermo Q Exactive Focus LC-MS

Reference: GREENPEACE RESEARCH LABORATORIES (2019)

Targeted Screening – Pesticide Explorer Workflow

HPLC parameters

Column temperature	30 °C
Flow rate	300 µL/min
Total run time	15 min
Injection volume	1 µL
Column	Accucore aQ, 100 × 2.1 mm, 2.6 µm
Mobile phases	A: Water with 5 mM ammonium formate, 0.1% formic acid B: Methanol with 5 mM ammonium formate, 0.1% formic acid
Gradient	Table 1

Table 1. HPLC gradient run program

Time [min]	Flow rate [mL/min]	A%	B%	Curve
0.0	0.300	98	2	5
1.0	0.300	98	2	5
2.0	0.300	50	50	5
9.0	0.300	2	98	5
12.0	0.300	2	98	5
12.1	0.300	98	2	5
15.0	0.300	98	2	5

HRAMS parameters

Ion source	H-ESI
Polarity	Positive or Negative
Acquisition mode	Full MS and dd-MS ² (discovery) <ul style="list-style-type: none"> - Full MS @ resolution 70,000 - dd-MS² @ resolution 17,500
Mass tolerance	5 ppm



Compliant with regulatory methodology (FDA, USDA, SANCO)

Quantitation method: 250 pesticides

Screening method: 550 pesticides

Targeted Screening – HRAM MS/MS Database

TraceFinder Software: Library search parameters are easily activated by checking the box. The capability to search multiple localized mzCloud curated spectral libraries gives you the confidence of the exact match.

Search Options

Search Types

Database Search

Library Search

Elemental Composition

ChemSpider Search

Highest Point Analysis

Exhaustive Search Simple Search

Number of top matches

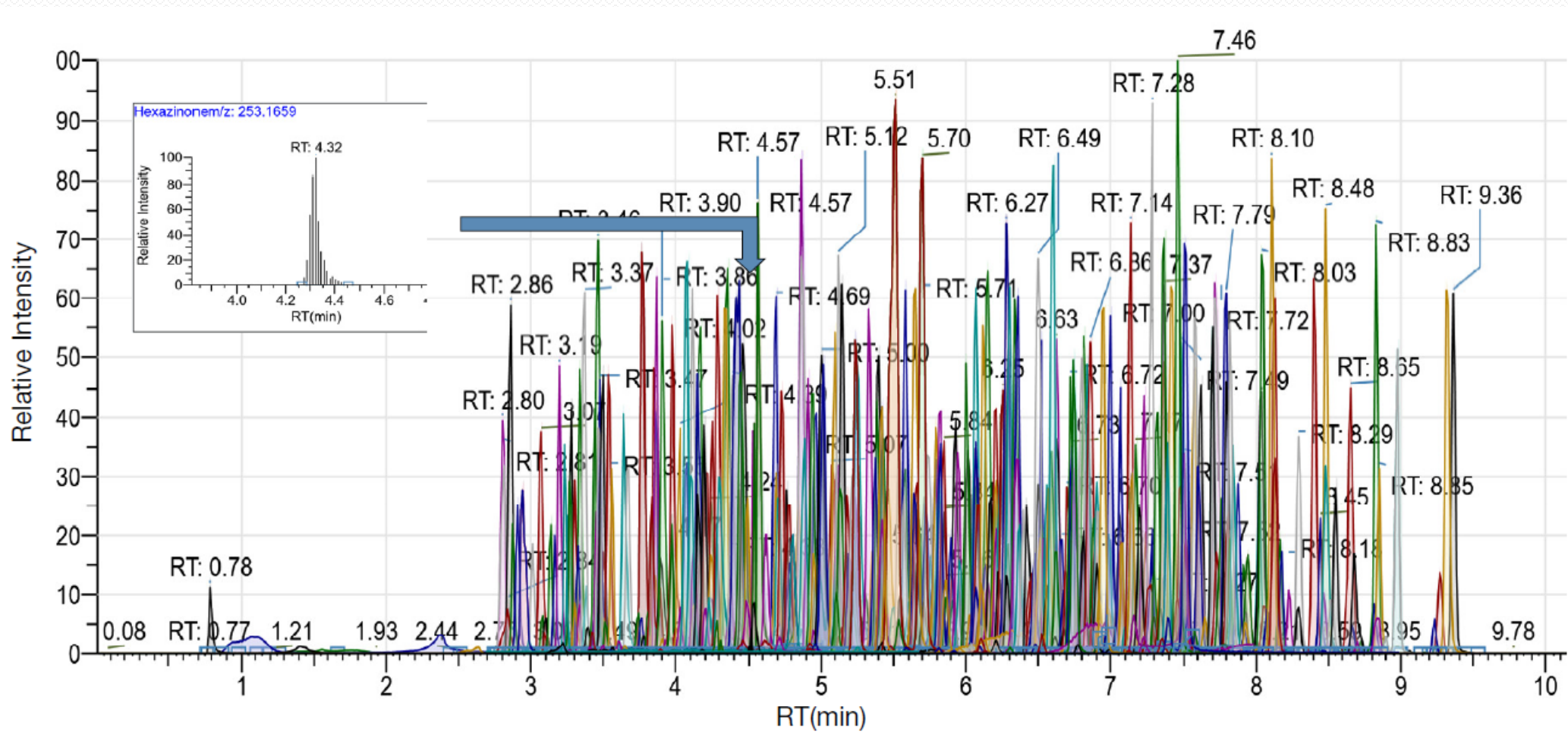
Library Settings			
Library Selection			
	Enabled	Library Name	Library Type
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2	<input checked="" type="checkbox"/>	EFS_HRAM_Spectra_Library.db	mzVault
3	<input type="checkbox"/>	mzCloud Offline for mzVault 2.3_Pest-Herb_2020A.db	mzVault
4	<input type="checkbox"/>	EFS_Library.db	mzVault
5	<input type="checkbox"/>	LibraryManager_Toxicology_combined_v1.db	mzVault
6	<input checked="" type="checkbox"/>	mzCloud Offline for mzVault 2.3_2020A.db	mzVault

Compound Groupings	Unique Entries	Total Spectra
Environmental and Food Safety	1,634	8,906
Clinical Research and Forensic Toxicology	926	4,630

COMPOUND CLASS	
Food Safety and Environmental	Forensic Toxicology
Emerging Environmental Contaminants	Drugs of Abuse
Pesticides	Natural and Industrial Toxins
Veterinary Drugs	Prescription Drugs
Mycotoxins	Performance Enhancing Drugs
Perfluorinated Compounds (PFCs)	Other Drug Monitoring Research

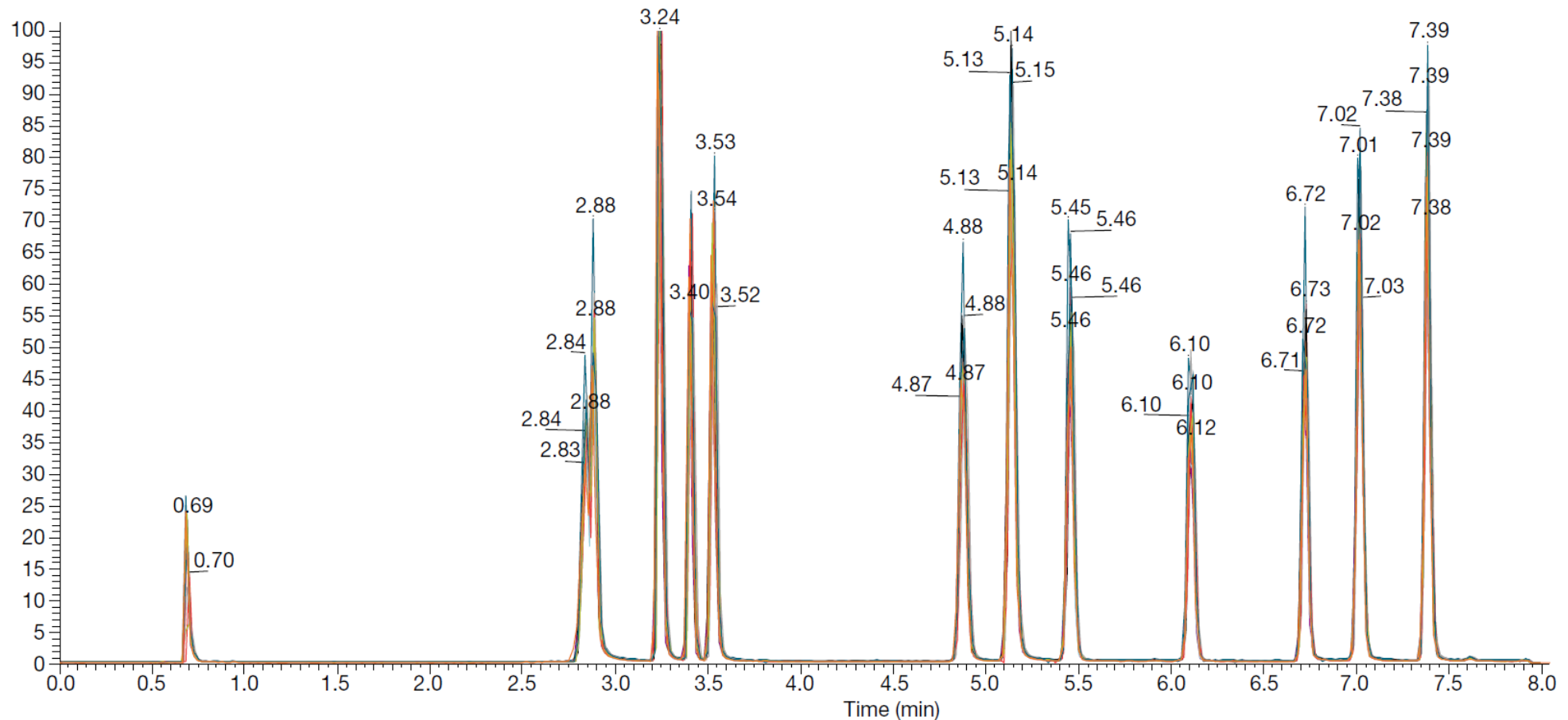
Targeted Screening – Pesticides Chromatogram

Chromatogram of over 500 pesticides in 15 min in the matrix spiked at 10 ppb. The peak highlighted at 4.32 min is hexazinone showing over 11 scans across the Full Scan quantitation ion used for the analysis.



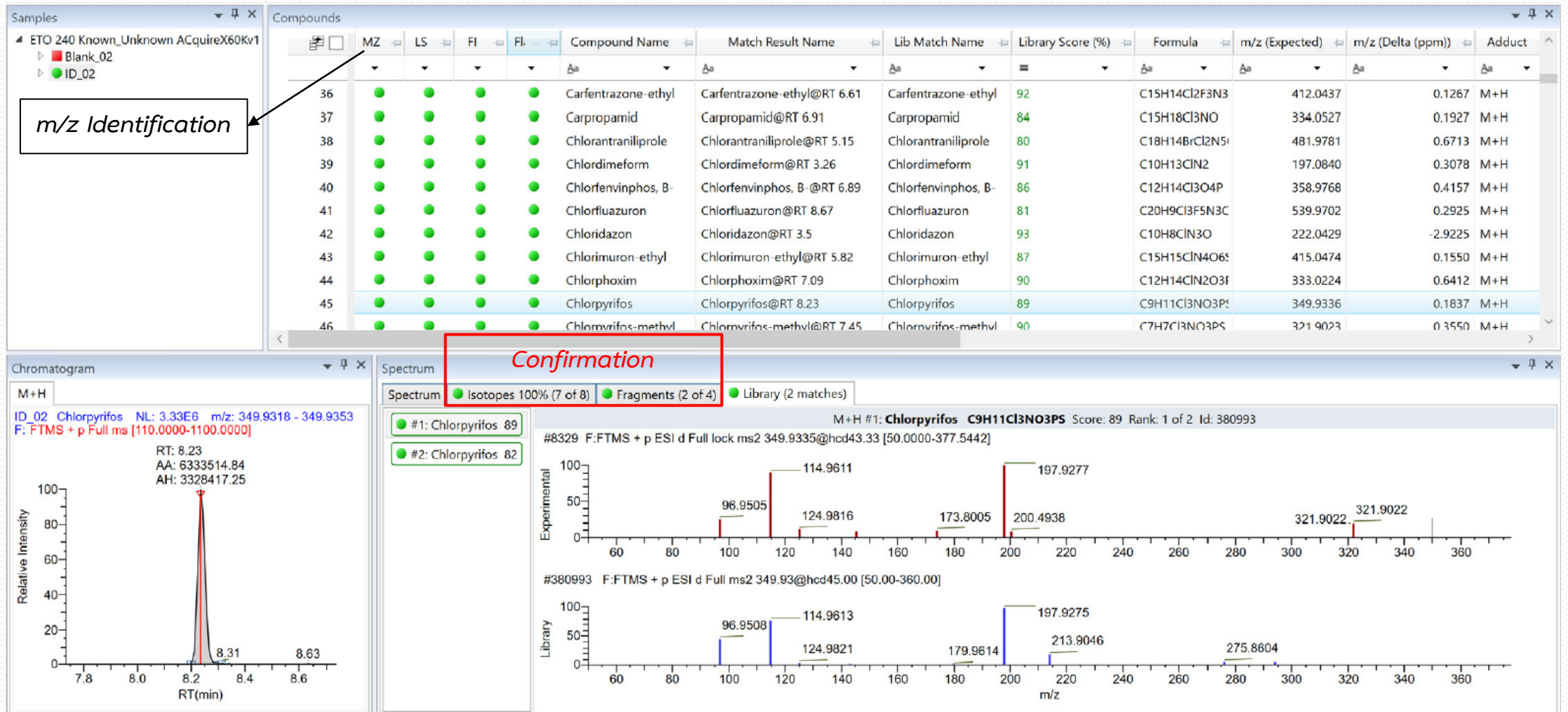
Targeted Screening – Reproducibility

Robust LC-MS reproducibility of pesticides spiked in the matrix, selected pesticides (overlay of injections 1 to 250) with extracted mass tolerance of 3 ppm



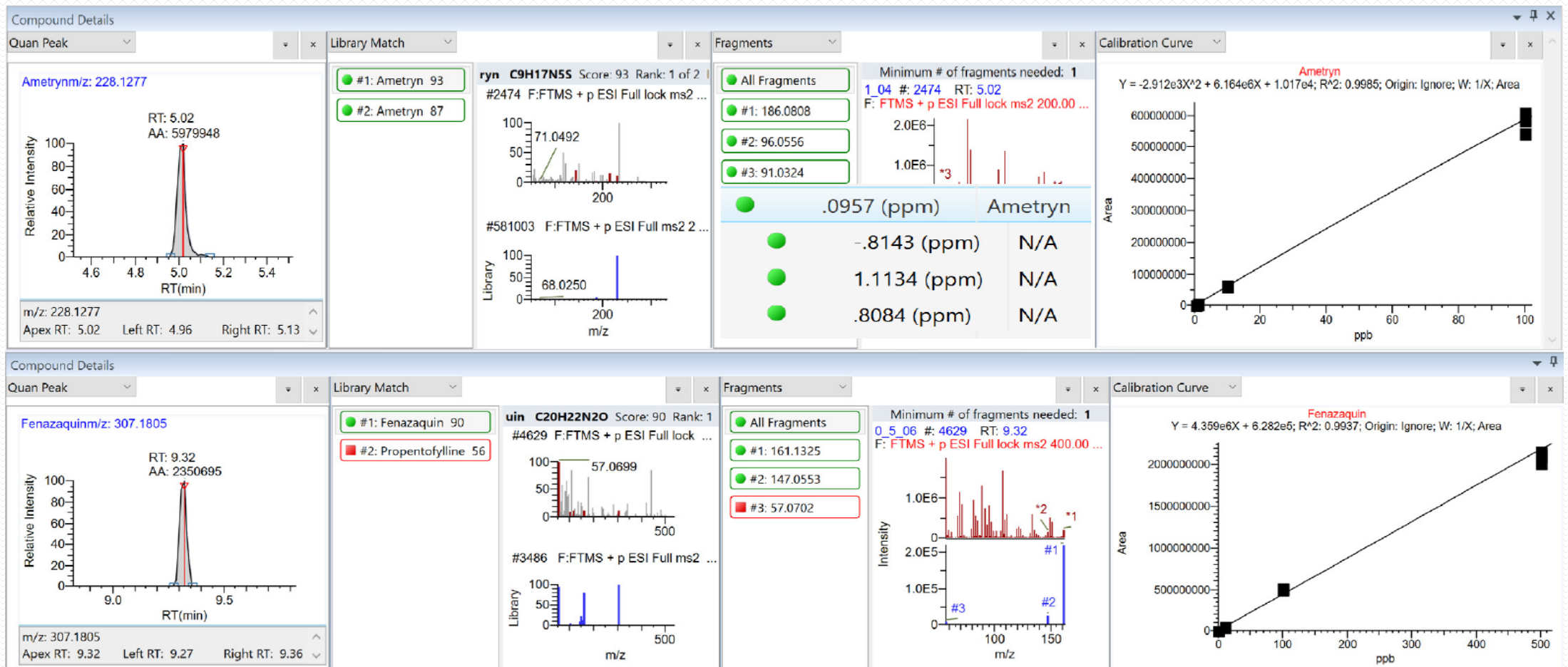
Targeted Screening – Compound Library Matching

Overview of targeted compound detection for chlorpyrifos with library scoring of 89% and Δ ppm of 0.1837



Targeted Quantitation – Residue Level Detection

Quantitation ions and confirming ion in the sample, along with calibration range from 0.5 to 100 (500) ppb for ametryn at 1 ppb and fenazquin at 0.5 ppb, which shows excellent R^2 . The technique allows for confident quantitation and screening with confirmation well below the MRL concentration.



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Highlights

- LC-Q-Orbitrap-MS method fully optimized and validated for a **total of 252 pesticides** in surface water.
- **Target quantification** of pesticides and broader **qualitative screening** in **one** single injection.
- Limits of quantification **below 5 ng/L** for most of the pesticides.
- Application of the method to the analysis of river water samples from England.





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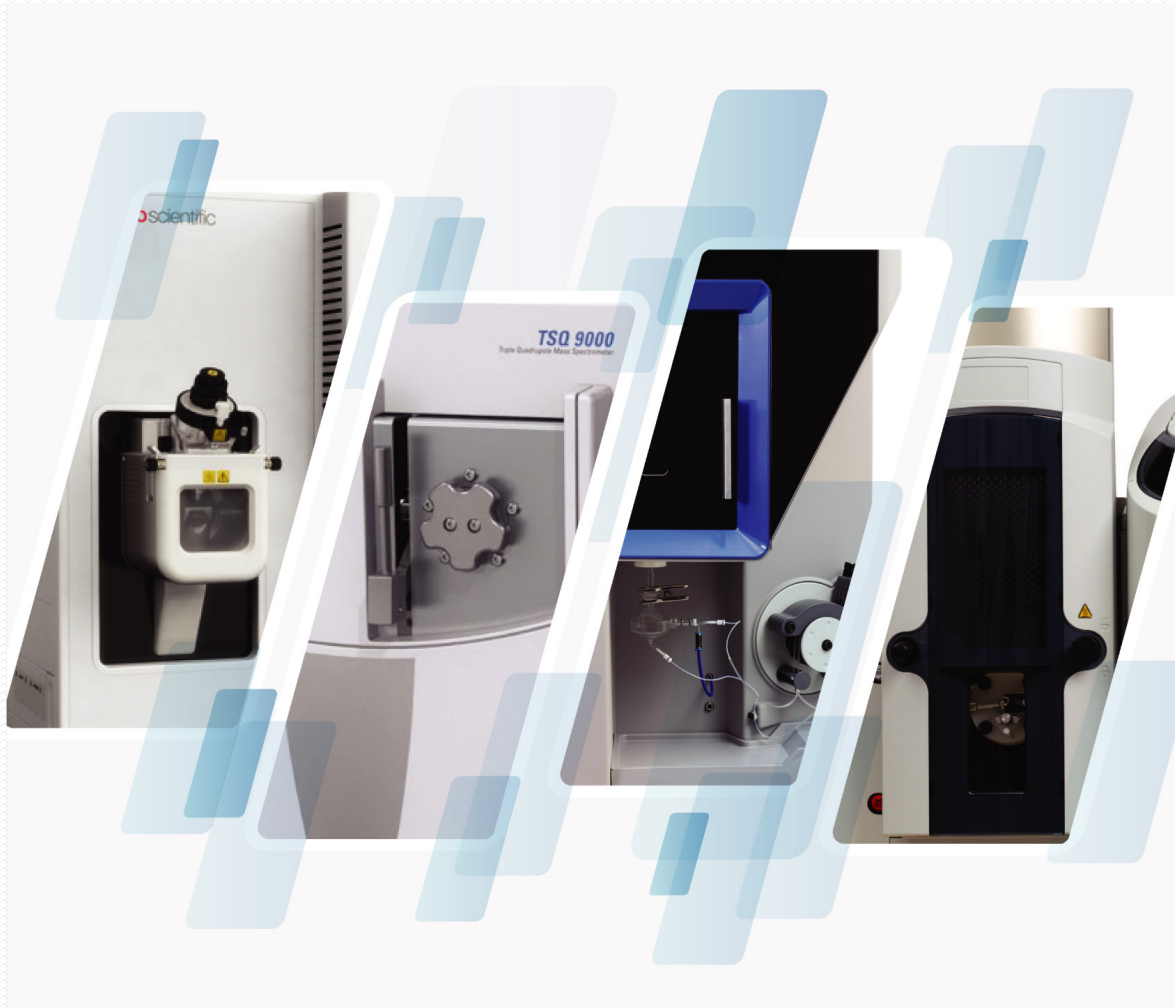
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