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An Optimization Tool for MS Signal Acquisition in GC Triple Quadrupole Mass Spectrometry

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Introduction

Development of GC/MS/MS MRM transitions is a challenging and time-consuming multi-step process, which may be further complicated by analyte co-elution and matrix interferences.

A new modular optimization tool allows for fully automated end-to-end MRM development. Alternatively, each of the modules, i.e., MRM development steps, can be completed individually. These steps include:

- ✓ Precursor ion identification
- ✓ Product ion scan at various collision energies
- ✓ Selection of product ions
- ✓ Collision energy optimization

The optimization tool uses spectral deconvolution to reliably identify precursor ions, even in the presence of chromatographic interferences such as column bleed or co-eluting peaks. The tool significantly reduces the need for user intervention and generates the complete GC/MS/MS data acquisition method, containing the optimized MRM transitions.

Experimental

GC coupled to a triple quadrupole MS was used for MRM development. The tool is fully integrated with GC/MS data acquisition software.

It enables:

- ✓ Identification of the analytes using library search of deconvoluted spectra
- ✓ Selection of precursor ions
- ✓ For each selected product ion, a product ion scan at various collision energies
- ✓ Selection of the best product ions
- ✓ Collision energy optimization
- ✓ Generation of time-segment MRM or dynamic MRM acquisition methods

The tool allows the user to perform only those selected steps that are necessary, depending on the information already available. For example, precursor ions can be imported from an existing GC/MS SIM acquisition method.

The software is capable of generating the sequences necessary for gathering all the data required for optimization. All generated data files, methods, and log files are stored within a Project folder, and may be re-opened at a later date for further optimization.

Experimental

Optimizer for GC Triple Quad

Installed automatically with MassHunter GC/MS Data Acquisition Version 10.0. Supported for use with Agilent 7000 series and 7010 series TQ GC/MS.

Who will benefit from using the Optimizer?

- New TQ users
  - ✓Convert existing SQ SIM or scan methods to MRM
- Existing TQ users
  - ✓Re-optimize collision energies for current MRM method
  - ✓Create MRMs for new targets using scan data
  - ✓Update retention times for a new column configuration or oven program

Workflows Available for the Optimizer for GC Triple Quad

User provides source method
- Source method may be scan, SIM, or MRM
- The GC method, MS solvent delay, gain, and tune file used by the Optimizer need to be supplied with the source method

MRM or dMRM method

SIM method

Scan method

Retention time (RT) determination
- With SIM or MRM workflow, the source method needs to have RTs
- With scan workflow, to determine RTs, a library search of the deconvoluted mass spectra against the library can be performed

Select precursor ions (for scan method)
- Can be automated by Optimizer, or manual selection by user
- Only the ions from the deconvoluted mass spectrum are considered – to avoid accidental optimization of interference ions
- Follows the rules for picking the best ions (abundance, m/z, ion clusters)

Product ion scan experiments
- Determine product ion masses and roughly estimate the collision energy out of up to 4 collision energy values

Select product ions
- Can be automated by Optimizer, or manual selection by user

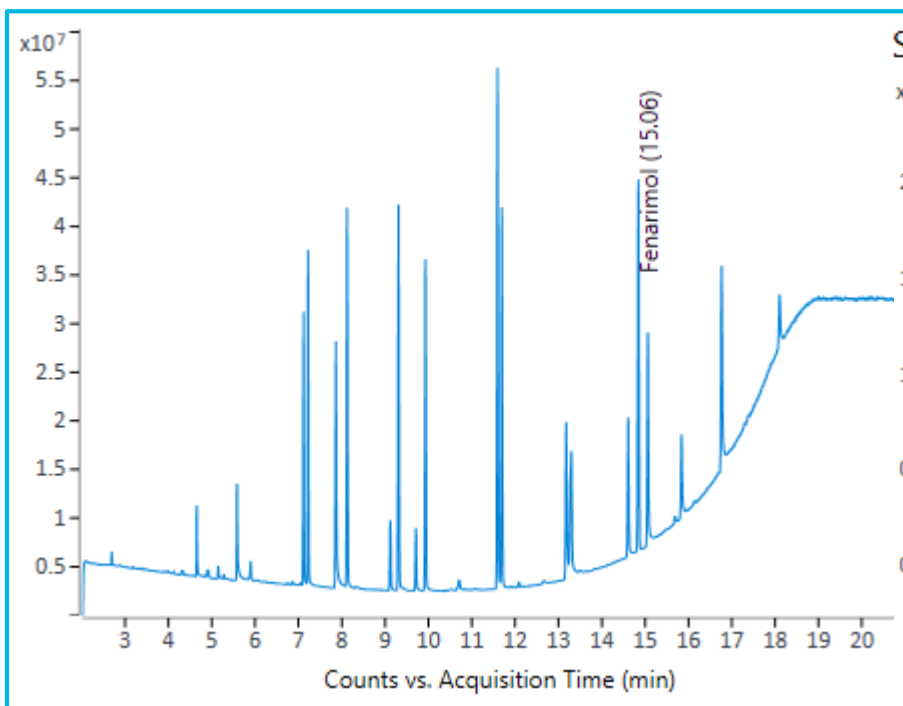
Collision energy optimization
- Determine optimal collision energy for each MRM
- MRM or dMRM based method, >10 collision energies evaluated per injection

Save the optimized method
- Method may be saved in MRM or dynamic MRM (dMRM) format
- Results can be saved as a comma separated values file (*.csv)

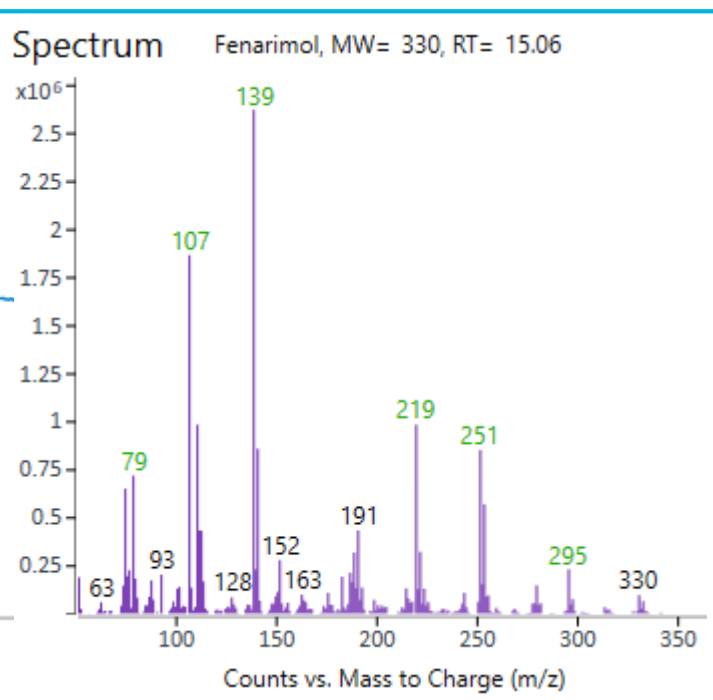
The type of method (Scan, SIM, or MRM) supplied during setup will determine the optimization steps and the options available during setup. The Optimization Tool can automate portions of the optimization procedure, or the user may choose to manually review the results of each optimization step and optimize only the ions of interest.

MRM Optimization for an Environmental Contaminant: Fenarimol

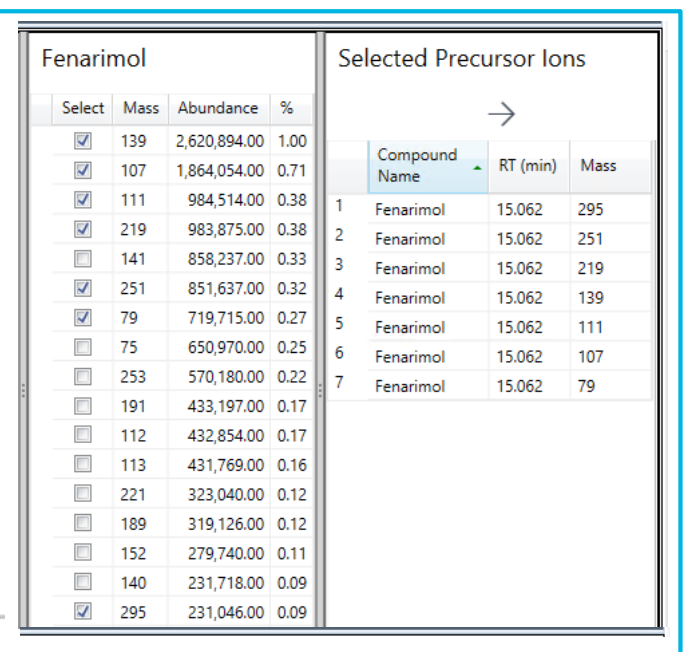
Retention Time Determination and Precursor Ion Selection



Scan TIC of a pesticide mixture.



Deconvoluted mass spectrum of fenarimol.


Fenarimol

Select	Mass	Abundance	%
☑	139	2,620,894.00	1.00
☑	107	1,864,054.00	0.71
☑	111	984,514.00	0.38
☑	219	983,875.00	0.38
☐	141	858,237.00	0.33
☑	251	851,637.00	0.32
☑	79	719,715.00	0.27
☐	75	650,970.00	0.25
☐	253	570,180.00	0.22
☐	191	433,197.00	0.17
☐	112	432,854.00	0.17
☐	113	431,769.00	0.16
☐	221	323,040.00	0.12
☐	189	319,126.00	0.12
☐	152	279,740.00	0.11
☐	140	231,718.00	0.09
☑	295	231,046.00	0.09

Selected Precursor Ions

	Compound Name	RT (min)	Mass
1	Fenarimol	15.062	295
2	Fenarimol	15.062	251
3	Fenarimol	15.062	219
4	Fenarimol	15.062	139
5	Fenarimol	15.062	111
6	Fenarimol	15.062	107
7	Fenarimol	15.062	79

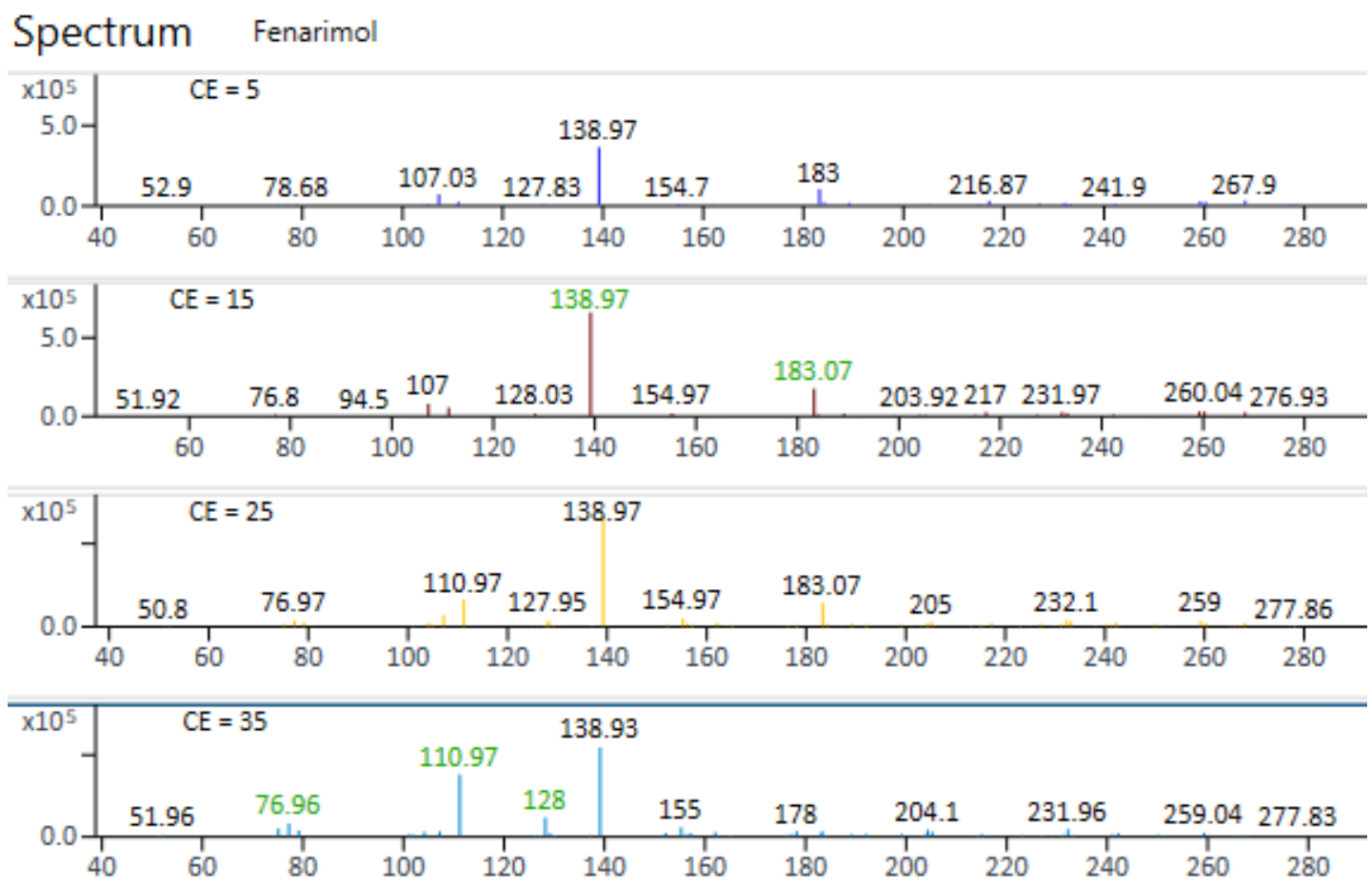
Available and selected precursor ions.

MRM Optimization for an Environmental Contaminant: Fenarimol, cont.

Product Ion Selection

In a product ion scan experiment, a maximum of four collision energies may be used. In this experiment, the collision energies used were 5, 15, 25, and 35 eV.

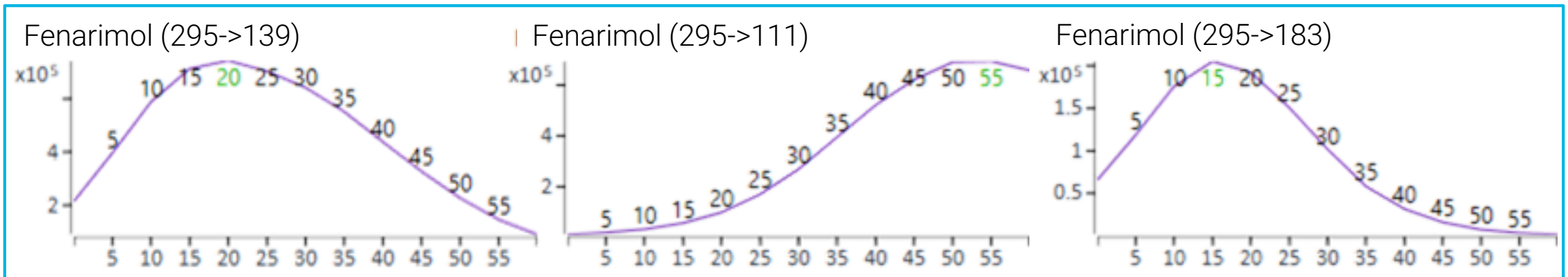
Fragment	CE	Abundance	Rel. Abund.
139	15	659,116	1
111	35	379,559	0.58
183	15	179,339	0.27
128	35	116,770	0.18
107	15	84,469	0.13
77	35	81,016	0.12
155	35	57,080	0.09
75	35	50,044	0.08
232	35	46,093	0.07
204	35	41,693	0.06
77	25	38,707	0.06
79	35	38,524	0.06
259	25	36,323	0.06
260	15	35,121	0.05
178	35	33,152	0.05
217	15	30,861	0.05
233	25	30,208	0.05



Product ion scan results for precursor mass 295.

Collision Energy Optimization

Once the MRM transitions are selected, the next step is to determine the optimal collision energy. The optimization can be performed over the defined range or within several steps around the optimal collision energy from the previous step.



Breakdown plots for precursor mass 295.

Conclusions

- A highly-automated optimization tool for MS signal acquisition allowed for efficient development of method-ready MRM transitions.
- The Optimizer may be used as either a complete workflow with automation, or the user may review the results of each optimization step before continuing.
- The optimized results can be saved as MRM or dMRM method.

This information is subject to change without notice.

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