Fast SRM Transition Speeds for High Sensitivity, High Capacity and Selective Multi-Residue Pesticide GC-MS/MS Analysis

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Overview

Purpose: Explore fast collision cell technology to build capacity in pesticide methods

Methods: QuEChERS coupled with GC-MS/MS (Thermo Scientific™ TSQ™ 8000 Evo)

Results: Fast transition speeds possible to measure pesticide at concentrations below EU level of interest.

Introduction

Pesticides residue analysis is applied to a wide range of food commodities. Rice, is one of the top ten food commodities in the world, with 470 million tones traded in 2013. Production of rice is heavily weighted towards Asian countries with India and China two of the biggest exporters. Pesticide residue control in such a commodity leads to a high volume of analysis taking place in laboratories across the globe.[1] There are more than 450 pesticide residues that have specified maximum residue levels (MRLs) in rice as described European Union regulations [2] and EU databases [3].

Measuring a high number of pesticides in an efficient way requires targeting as many residues as possible in a single test method. The consolidation of multiple pesticide residues in a single analytical method is an approach that has become more common with the development of generic sample preparation techniques, such as QuEChERS as well as selective separation and measurement technologies such as GC-MS/MS.

However, these high capacity methodologies often lead to a compromise in instrument sensitivity due to lower dwell times for individual selected reaction monitorings (SRMs). Many users compensate for this by decreasing quadrupole resolution, an approach which increases the risk of interference, especially in more complex matrices.

Recent development of GC Triple Quadrupole MS technology has not only been focused on hardware, indeed the software used to drive the instrumentation and deal with complex data outputs is absolutely crucial in making multi-residue pesticide workflows possible in the high throughput environment.

This work addresses the need for high sensitivity, selectivity and method capacity focussing on large multi-residue methods using a GC-MS/MS system with a novel, faster collision cell technology, uniquely combined with smart software tools.

Methods

Sample Preparation

1 g/mL matrix extracts of rice were prepared using the QuEChERS technique. Final extracts were exchanged into cyclohexane/ethyl acetate (50: 50 v/v).

Gas Chromatography

Thermo Scientific™ TRACE™ 1310 Gas Chromatographwas used for compound separation. The system was configured with an iC-PTV injector. The injector conditions are given in Table 1 and oven program in Table 2. The analytical column was a Thermo Scientific™ TraceGOLD TG-5SILMS 30m x 0.25mm x 0.25µm.

TABLE 1. TRACE 1310 Injector Parameters

Carrier Gas, (mL/min):	He, 1.2
Injection Volume (µL):	1
Inlet Module and Mode:	iC-PTV
Initial Temp (°C):	75
Splitless Time (min)	1
Transfer Rate (°C/s)	2.5 (to 300°C)
Transfer Time (min)	3
Cleaning Rate (°C/s)	14.5 (to 330°C)

TABLE 2. TRACE 1310 Oven Parameters

	Rate	Temp.	Hold Time
Initial	°C/min.	°C	min.
1	25	40	1.5
2	25	90	1.5
3	5	180	0
4	10	280	0
Final		300	5

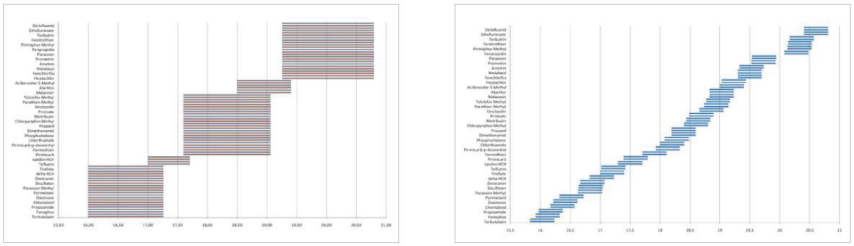
Mass Spectrometry

TSQ 8000 Evo instrument was operated in MS/MS mode using electron ionization (EI+). This instrument is fitted with a novel enhanced velocity optics collision cell (EvoCell) which allows much higher SRM transition speeds. For data acquisition, typically 2-3 SRM transitions per compound were chosen unless otherwise stated. Data was acquired using timed-SRM (Figure 1) with a minimum of 12 points/chromatographic peak. Selected SRM transitions and their collision energies were taken from the Thermo Scientific™ TraceFinder™ Compound Database.

TABLE 3. Triple quadrupole mass spectrometer parameters

TSQ 8000 Evo Mass Spectrometer Parameters	
Transfer line (°C):	280
Ionization type:	EI
Ion source(°C):	300
Electron energy (eV):	70
Acquisition Mode:	Timed-SRM
Q2 Gas Pressure(argon)(psi):	60
Q1 Peak Width (Da):	0.7
Q3 Peak Width (Da):	0.7

FIGURE 1. Comparison of segmented SRM (left) and timed-SRM (right) acquisition schedules. Timed-SRM allows a much more efficient use of dwell time by avoiding acquiring for unnecessary transitions which can occur in a segmented method.



Traditional Segmented SRM

TSQ 8000 Evo GC-MS/MS Timed-SRM

Data processing was performed with Thermo Scientific TraceFinder Software. All processed LOD data is calculated using uncorrected peak area precision at 99% confidence (Student's t).

Results

Effect of transition speed

The TSQ 8000 Evo instrument offers the possibility to use transition speeds up to 800 SRM/s with the development of an enhanced velocity optics collision cell.

This allows for the possibility to:

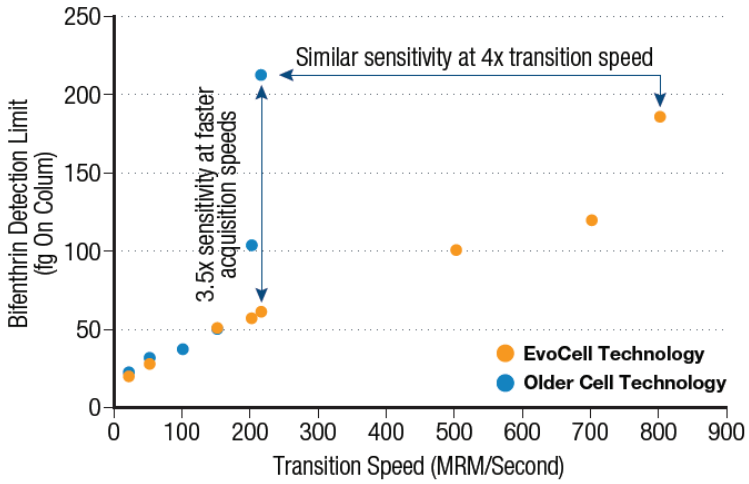
- Utilize fast chromatography
- Increase the number of transitions per compound
- Increase the number of compounds in a method
- Use fast GC or fast GC oven ramps

One risk with increasing the speed of the MS acquisition is the possibility that analytical performance is compromised to a level which renders the methodology unsuitable for the analytical task. In the case of multi-residue pesticide methods, the requirement is to measure a large number of compounds (100-350) within a single run. This often needs to be achieved down to levels of 10 ppb and below.

The Limit of Detection (LOD) of the pesticide bifenthrin was determined at differing transition speeds in order to observe the effect of increasing transition speeds (up to 800 SRM/s) on the ability to precisely detect a compound at low levels. This experiment was also repeated using older collision cell technology.

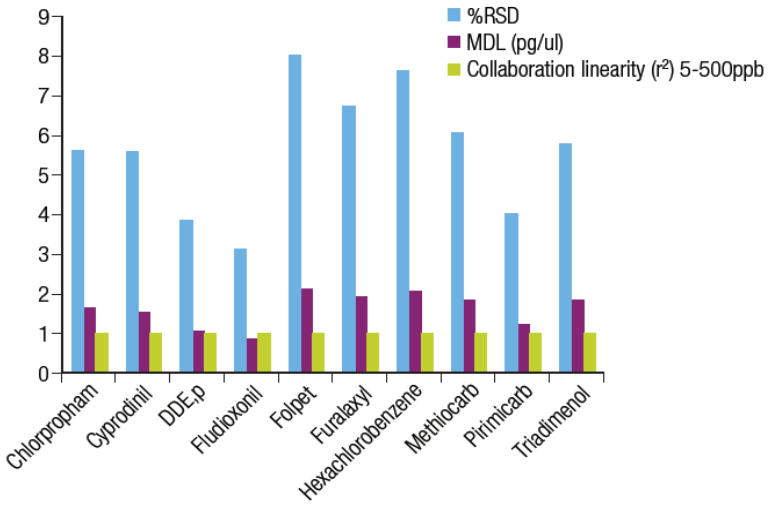
Figure 2 shows the data obtained with these experiments. The data shows an expected increase in the detection limit as the transition speeds increase for both the old collision cell technology (unable to measure faster than just over 200 SRM/s) and EvoCell. However, when comparing with older collision cell technology the EvoCell allows for a similar level of sensitivity at 4x the transition speed as well as 3.5x the sensitivity at transition speeds of around 200 SRM/s.

FIGURE 2. LOD of bifenthrin vs transition speed for both old collision cell technology and EvoCell.



This experiment was expanded to a wider group of pesticides in a real matrix sample (rice) but this time focusing on analytical performance at the limit of EvoCell transition speeds. In order to do this a method with more than 666 pesticides and other contaminants was created and a selection of pesticides was recorded with dwell times at 500µs. The quantitative data obtained is presented in Figure 3.

FIGURE 3. Analytical performance of a selection of pesticides measured at 500 µs dwell times in rice matrix.



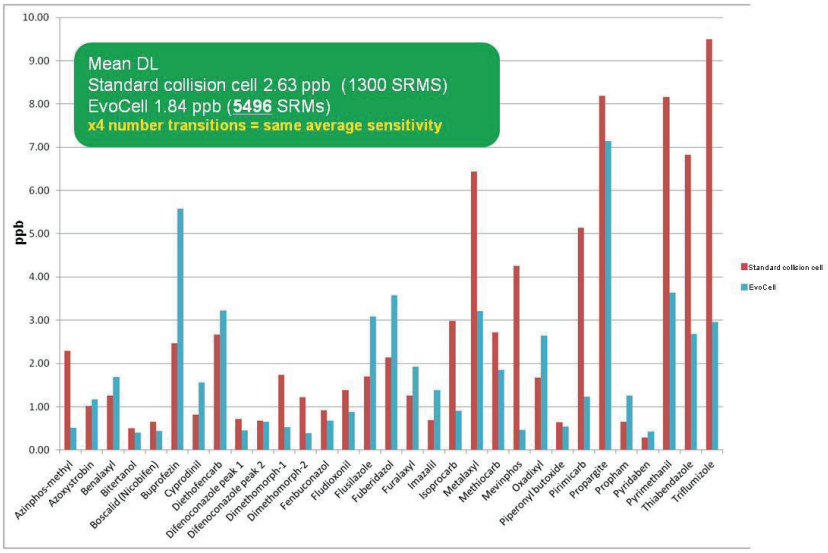
Despite the extreme acquisition environment, the pesticides measured were on average below 2 ppb which is lower than the typical 10 ppb limit as stipulated in EU regulations. In addition, the vast majority of compounds showed linearity of response (uncorrected) >0.99 in the range of 5-500 ppb with matrix matched calibration curves.

Increasing the number of transitions

Running 666 pesticides in a single run is not practical in terms of general method procedures, GC performance and data processing. Many labs limit their GC-MS/MS pesticide methods in the range of 100-350 compounds with the majority monitoring around 100-200 residues. Extremely fast transition speeds to 800 SRM/s (especially when using timed-SRM) is not usually necessary when running under standard method conditions.

One way to take advantage of faster transition speeds is to add more transitions to your method for your current compound list. This can be advantageous in a number of ways. Firstly, the more transitions you have available for each compound the higher the confidence in any positive confirmation of a detected residue. Another advantage is the increased resistance to matrix interference in your method as the probability of a direct SRM interference is reduced as the number of transitions is increased. This means a method can be applied confidently to a wide range of sample types.

FIGURE 4. Comparison of older standard collision cell technology and EvoCell when considering LODs for pesticide residues in a method targeting 262 residues with a different number of transitions.



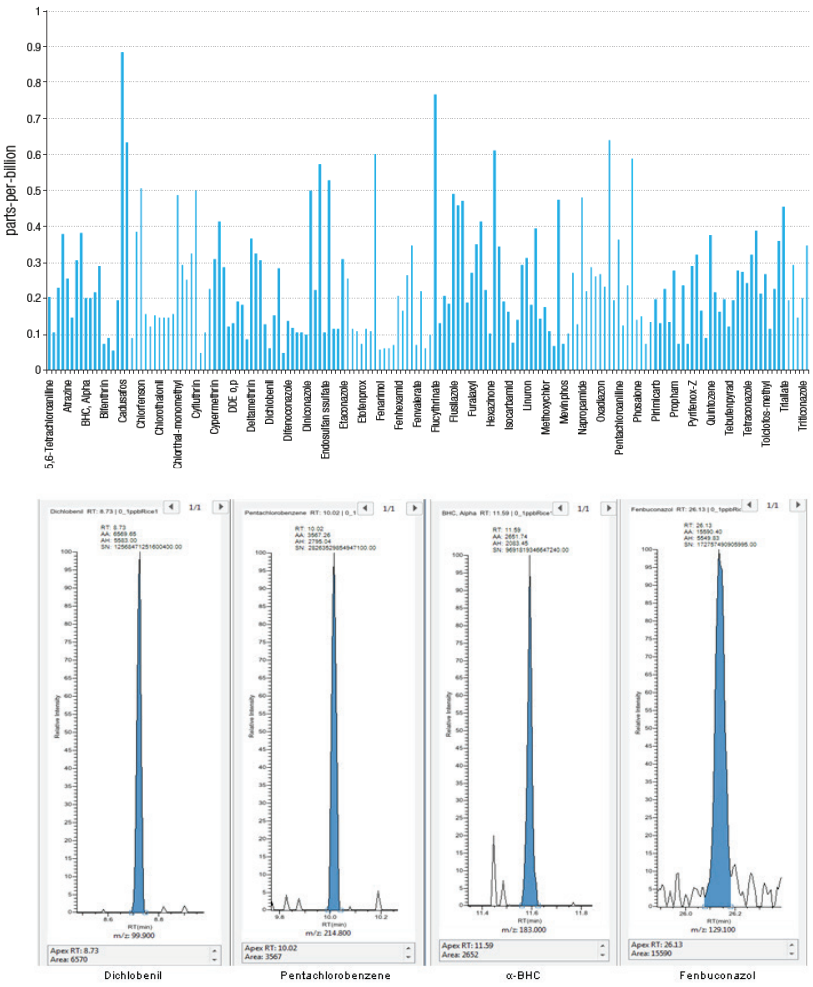
Using EvoCell technology allowed 4x the number of SRM transitions, with 5496 SRMs being run (Figure 4). The LOD obtained (on average) for all 262 compounds using EvoCell (1.84 ppb) was below that obtained with older collision cell technology (2.63 ppb) which only acquired 1300 SRM transitions. This demonstrates that increased capacity in the method is possible with fast SRM transition speeds when considering the levels of interest for these types of compounds

System performance at moderate transition speeds

Experiments were also performed to determine the quantitative performance of the TSQ 8000 Evo system in a more usual acquisition environment when considering multi-residue methods.

In total, 262 pesticide residues were targeted in rice matrix when monitoring for either 2 or 3 SRM transitions per compound. A high proportion of the target compounds could be quantified well below the 1 ppb level in matrix with a good level of selectivity. (Figure 5).

FIGURE 5. LOD (ppb) of pesticides with LODs below 1 ppb in rice matrix (top) and four pesticides spiked at their respective LOD concentrations in rice matrix (bottom).



Conclusion

- TSQ 8000 Evo GC-MS/MS utilizes fast collision cell technology (EvoCell) which provides the ability to build extremely high capacity analytical methods for multi-residue pesticides determination.
- High SRM transition speeds can be used at (and below) the level of interest for pesticides opening additional possibilities in methods such as more transitions or faster chromatography.
- Increased number of transitions could be further explored as an application of increased acquisition capacity in order to allow methods to be resistant to changing sample matrices.
- Future work will focus on applying faster acquisition speeds to faster GC separations on short columns to increase method efficiency.

References

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