Analysis of 200+ Pesticides at 500 SRMs/s using a Non-Timed SRM MS Method and a Short LC Method on TSQ Endura MS

Jia Wang, Charles Yang, Jonathan Beck, Jennifer Massi, Dipankar Ghosh and Mary Blackburn
Thermo Fisher Scientific, San Jose, CA, USA

Thermo SCIENTIFIC

Overview

Purpose: To demonstrate the 500 SRMs/sec data acquisition rate capability of the TSQ Endura triple quadrupole mass spectrometer

Methods: Thermo Scientific™ Dionex™ Ultimate™ 3000 RSLC system coupled with Thermo Scientific™ TSQ Endura™ triple stage quadrupole mass spectrometer was used for pesticides analysis.

Results: A multi-residue method was developed for the screening and quantitation of 224 pesticides with 500 SRMs in peach matrix using a non-Timed SRM (selective reaction monitoring) MS method and a short LC method (10 min). Due to the use of non-timed SRMs and the extreme fast scanning speed, method development was significantly simplified and productivity was improved.

Introduction

Increasing food safety concerns and the growing agricultural trade have resulted in stringent pesticide regulations globally. To comply with strict food safety standards, fast screening and quantitative methods for large numbers of pesticides are becoming important. Tandem quadrupole mass spectrometry offers highly specific and selective detection. However, it is also limited by intra-scan delays and dwell times required to get the maximum sensitivity and reproducibility. Therefore Timed-SRMs are needed for analyzing large numbers of analytes. This poster describes a method for rapid analysis of 200+ pesticides in food samples using a triple quadrupole mass spectrometer without the need for setting up a specific time window for each analyte.

Methods

Sample Preparation

Peach sample was extracted with acetonitrile using a QuEChERS method. The QuEChERS extract was diluted 2 times with water to optimize chromatographic peaks. Pesticides stock standards were spiked into the diluted QuEChERS extract. Then the appropriate amount of acetonitrile was added to adjust the organic composition of the final standard solution to 50:25:25%: water: matrix: acetonitrile. The concentration of the standards ranged from 0.1 to 100 ppb..

Liquid Chromatography

Chromatographic analysis was performed using the Ultimate 3000 RSLC system. The chromatographic conditions were as follows:

Column: Thermo Scientific™ Hypersil™ GOLD (150 x 3 mm, 3μm)
Column temperature: 40 ºC
LC run time: 10 min
Injection volume: 10 μL
Flow rate: 400 μL/min
Mobile Phase: A: 0.1% Formic Acid in water
B: 0.1% Formic acid in acetonitrile
Gradient:

Time (min)	%B
0.00	30
5.6	30
7.0	100
7.1	100
10.0	30

Mass Spectrometry

Samples were analyzed on the TSQ Endura triple stage quadrupole mass spectrometer with a heated electrospray ionization (HESI) source. 224 pesticides with 500 SRMs were monitored throughout the entire LC run in positive mode, non timed-SRM, 2 or 3 SRMs per compound.

The MS conditions were as follows:

Sheath Gas Flow Rate: 50 units
Aux Gas Flow Rate: 10 units
Spray Voltage: 3500 V
Capillary Temp: 300 °C
Heater Temp: 350 °C
Cycle Time: 1 s

Data Analysis

Method development, data acquisition, and data processing were performed with Thermo Scientific™ TraceFinder™ software. TraceFinder software is tailored for the environmental and food safety markets and simplifies method development, acquisition, data review and reporting. It provides a comprehensive system incorporating built-in methods for commonly found contaminants, processing methods, library searching capabilities, and data review with easily customizable reporting templates. TraceFinder software has a Compound Database (CDB) which includes transitions for several hundred pesticides, herbicides, personal care products, and pharmaceutical compounds.

Results

Multi-residue screening studies can generate very large SRM transition lists in a single experiment. A Timed-SRM (T-SRM) method is usually needed for qualitative and quantitative analyses of large number of analytes. In a T-SRM experiment, the method is set to look for specific transitions only during the expected retention-time window. This increases the number of SRM transitions that can be monitored effectively per experiment. But setting up a T-SRM MS method is very time consuming. The retention time of each analyte needs to be determined before the T-SRM MS method can be constructed. T-SRM MS methods also do not accommodate retention time shifts caused by matrix effects.

A mixture of 224 pesticides representing a broad spectrum of chemical classes was selected in this experiment. Either two or three SRMs were monitored for each compound. The first transition was used for quantitation and the 2nd/3rd transition were used for confirmation. There are 500 SRMs total in the method. Table 1 shows an extracted list of SRMs (first 14 analytes and last 7 analytes).

TABLE 1. Extracted SRM transition list

	Compound	Retention Time (min)	RT Time Window (min)	Polarity	Precursor (m/z)	Product (m/z)	Collision Energy (V)
1	Methamidophos	5	10	Positive	142	94.085	12
2	Methamidophos	5	10	Positive	142	125.11	11
3	Methomyl	5	10	Positive	163.1	88.098	10
4	Methomyl	5	10	Positive	163.1	106.078	11
5	Oxamyl Oxime	5	10	Positive	163.45	106.99	13
6	Oxamyl Oxime	5	10	Positive	163.45	135.312	10
7	Fenuron	5	10	Positive	165.1	72.107	14
8	Fenuron	5	10	Positive	165.1	120.081	18
9	Cyromazine	5	10	Positive	167.35	85.079	17
10	Cyromazine	5	10	Positive	167.35	125.248	17
11	Acephate	5	10	Positive	184	125.141	15
12	Acephate	5	10	Positive	184	143.056	8
13	Fuberidazole	5	10	Positive	185.07	156.216	29
14	Fuberidazole	5	10	Positive	185.07	157.118	22
15	Isocarbamid	5	10	Positive	186.1	87.12	15
16	Isocarbamid	5	10	Positive	186.1	112.91	16
17	Propamocarb HCl	5	10	Positive	189.35	74.103	20
18	Propamocarb HCl	5	10	Positive	189.35	144.145	9
19	Eptc	5	10	Positive	190.1	86.1	10
20	Eptc	5	10	Positive	190.1	128.462	7
21	Tricyclazole	5	10	Positive	190.11	109.086	37
22	Tricyclazole	5	10	Positive	190.11	136.184	29
23	Tricyclazole	5	10	Positive	190.11	163.121	23
24	Carbendazim	5	10	Positive	192.45	131.985	26
25	Carbendazim	5	10	Positive	192.45	160.17	16
26	Isoprocarb	5	10	Positive	194.1	95.111	14
27	Isoprocarb	5	10	Positive	194.1	137.361	8
28	Cycluron	5	10	Positive	199.2	72.247	20
29	Cycluron	5	10	Positive	199.2	89.202	13
487	Indoxacarb	5	10	Positive	528.1	150.153	17
488	Indoxacarb	5	10	Positive	528.1	203.028	34
489	Chlorfluazuron	5	10	Positive	540	158.1	17
490	Chlorfluazuron	5	10	Positive	540	383.043	17
491	Spinosad A	5	10	Positive	732.45	98.295	45
492	Spinosad A	5	10	Positive	732.45	142.273	28
493	Spinosad D	5	10	Positive	746.47	98.288	45
494	Spinosad D	5	10	Positive	746.47	142.297	30
495	Spinetoram J	5	10	Positive	748.49	98.321	47
496	Spinetoram J	5	10	Positive	748.49	142.29	30
497	Spinetoram L	5	10	Positive	760.48	98.319	45
498	Spinetoram L	5	10	Positive	760.48	142.289	31
499	Emamectin B1B	5	10	Positive	886.5	82.135	44
500	Emamectin B1B	5	10	Positive	886.5	158.239	31

In this experiment, 224 pesticides with 500 SRMs were monitored throughout the entire LC run. Without the need to set up a retention time for individual compounds. This significantly simplified method development. The total ion chromatogram is shown in Figure 1. All pesticides were eluted between 1.86 – 7.93 min.

FIGURE 1. Total ion chromatogram of 224 pesticides (10 ppb)

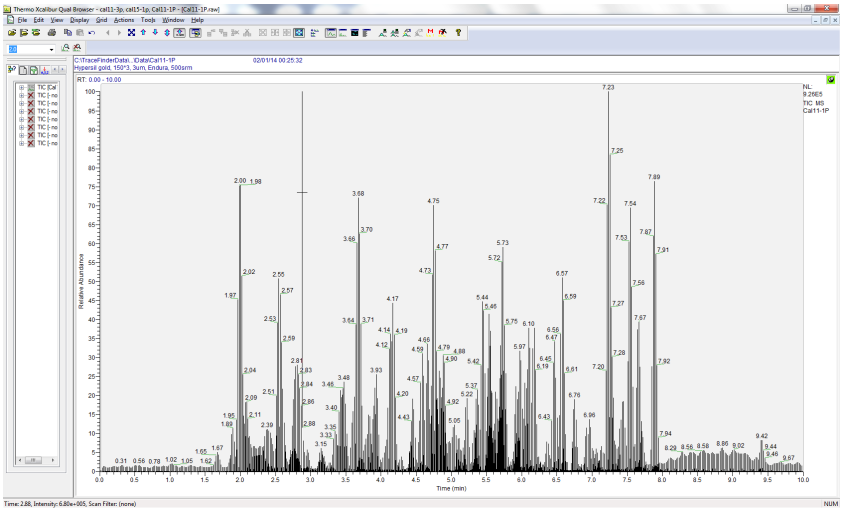
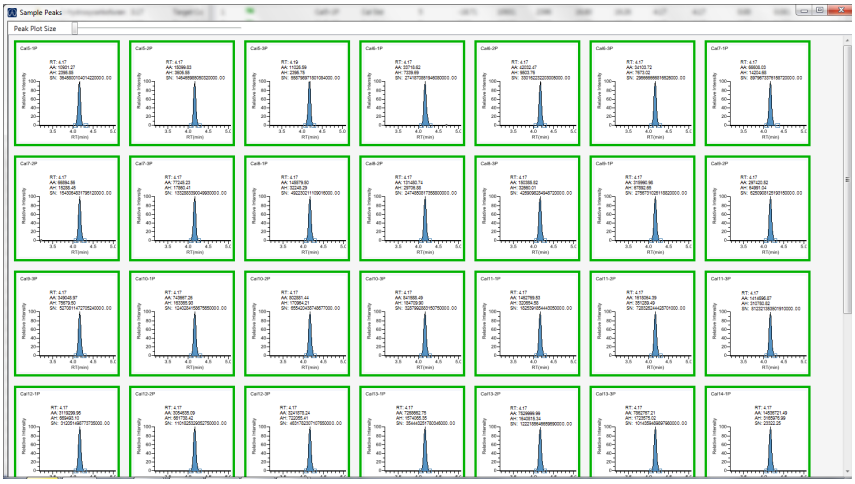


Figure 2 shows the extracted chromatogram of ametryn from 0.1 to 100 ppb (3 replicates at each level). Nice peak shape and stable retention time was observed. One advantage of using a non-timed SRM MS method is the ability to accommodate retention time shifts caused by matrix effects. So one method can be used for various matrices. Method development is also significantly simplified.

FIGURE 2. Example chromatograms: ametryn at all calibration levels (0.1-100ppb)



The experimental data was analyzed using the Data Review section of TraceFinder software. In this section, calibration lines, ion ratios, peak integration, and MS spectra can be monitored, and samples that meet certain user-set criteria can be flagged. In addition, user adjustments, such as peak re-integration, are permitted. The effects of the changes on the results are instantly updated in the results grid. The extracted ion chromatogram and calibration curve for example pesticides, prometon, buprofezin and schradan are shown in Figures 3, 4 and 5. Three replicates of each calibration standard were injected at each level. Excellent R^2 values were obtained for these analytes. This demonstrates that a Non-timed SRM MS method with a short 10 minute LC gradient is suitable for screening and quantitation of 224 pesticides with 500 SRMs using the TSQ Endura mass spectrometer.

FIGURE 3. TraceFinder software view of extracted ion chromatogram and standard calibration curve (prometon at 10 ppb, R^2 =0.9986, n=3)

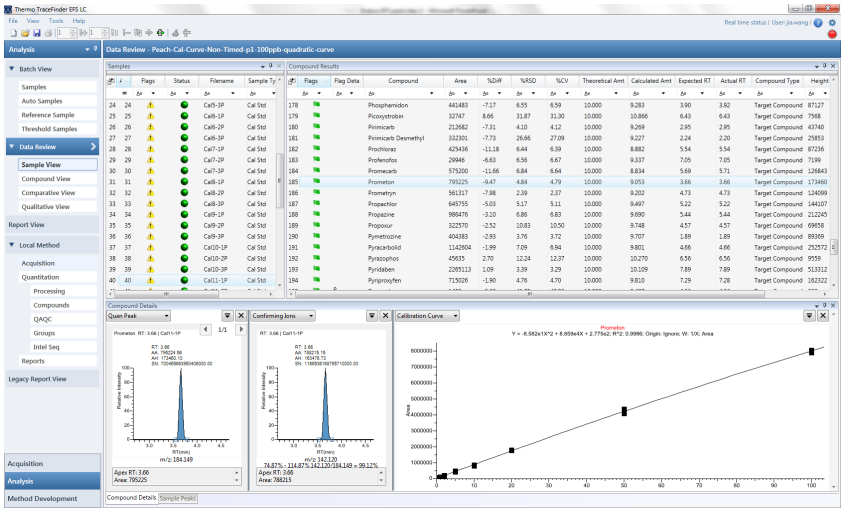


FIGURE 4. TraceFinder software view of extracted ion chromatogram and standard calibration curve (buprofezin at 10 ppb - R2 =0.9991, n=3)

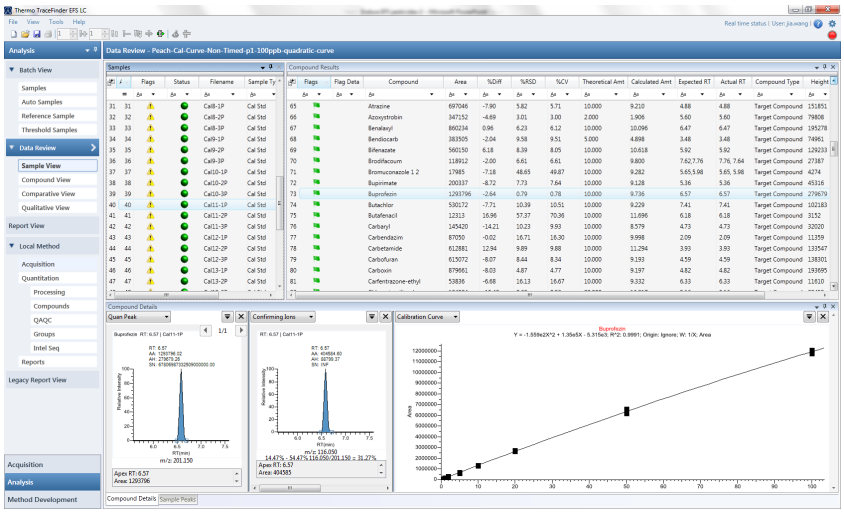
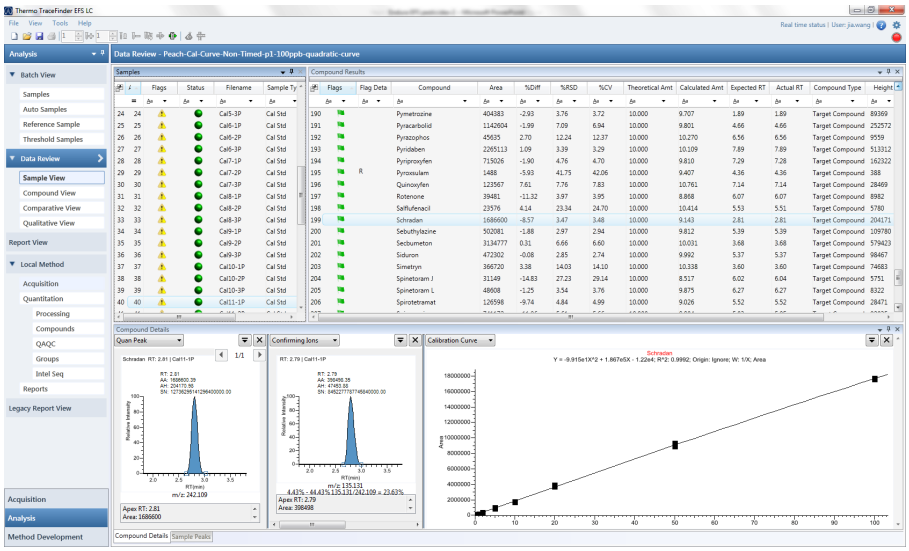


FIGURE 5. TraceFinder software view of extracted ion chromatogram and standard calibration curve (schradan at 10 ppb - R2 =0.9992, n=3)



Conclusion

- The TSQ Endura MS can perform screening and quantitation of 224 pesticides with 500 SRMs in peach matrix using a non-timed SRM MS method and a short LC run (<10 minutes)
- The ultra fast data acquisition rate of 500 SRM/s allowed us to improve productivity:
  - ✓ significantly simplified method development, especially for large compound lists
    - ➢ eliminate the need to set up a specific time windows for each compound
    - ➢ Accommodate shifting retention times in different matrices
  - ✓ shorten LC run time

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