Screening and Quantitation of 250 Pesticides in Fruit Juices with Positive/Negative Switching LC/MS/MS

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Introduction

Liquid chromatography coupled with tandem mass spectrometry operated in multiple reaction monitoring (MRM) mode with electrospray ionization (ESI) is widely used for polar, semi-volatile, and thermally labile pesticides in food testing. Many contract labs currently perform multi-residue analysis of pesticides using separate positive and negative methods due to instrument limitations especially for methods with hundreds of MRM transitions. This requires twice the sample and twice the analysis time. Recently, the Bruker EVOQ Elite LC-triple quadrupole system has been introduced to the market; thereby providing fast positive/negative switching allowing for simultaneous determination of positive and negative co-eluting compounds numbering in the hundreds.

A study using the EVOQ analyzed 250 pesticides in apple juice, cranberry juice, grape juice, orange juice and vegetable juice using only one method with positive negative switching for over 500 MRM transitions. The measurements were conducted by dilute-and-shoot without sample enrichment. The fruit juices were diluted 10-fold and filtered by filter vial prior to injection. An YMC-Pack ODS-AQ, 3 µm, 150 mm x 3 mm (I.D.) column with mobile phases (A) 5 mM ammonium fluoride in water, and (B) methanol were used. The total run time was 18 minutes including re-equilibration.

Fig. 1 EVOQ Elite triple quadrupole mass spectrometer coupled to a Bruker UHPLC and CTC Autosampler

Methods

Instruments:

EVOQ Elite triple quadrupole mass spectrometer coupled to a Bruker UHPLC and CTC Autosampler (see Fig. 1)

LC Parameters:

Column: YMC-Pack ODS-AQ 3 µm, 150mm x 3mm (I.D.)
Column Temperature: 40 °C
Injection Volume: 30 µL
Mobile Phase A: 5 mM ammonium Fluoride in water
Mobile Phase B: Methanol
Gradient:

Time	%A	%B	Flow (µL/min)
0.00	90	10	400
0.20	90	10	400
2.00	30	70	400
10.0	0	100	400
15.0	0	100	400
15.1	90	10	500
17.5	90	10	500
18.0	90	10	400

MS Parameters:

Source: HESI
Spray Voltage (Positive):4000V
Spray Voltage (Negative):4000V
Cone Gas Flow:20-unit
Cone Temperature:250° C
Heated Probe Gas Flow:40-unit
Heated Probe Temperature:400°C
Nebulizer Gas Flow:60-unit
Exhaust Gas:On

Results & Discussion

The compound based scanning (CBS) can automatically compute and assign the scan (dwell) time for each MRM (Fig. 2) for timed MRM, based on peak width and data points required.

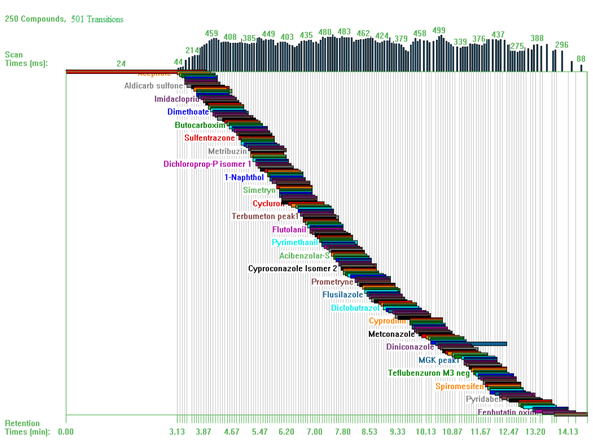

Fig. 2. Timed MRM windows for 250 pesticides

Fruit Juice=>	Apple Juice	Orange Juice	Cranberry Juice	White Grape Juice	Vegetable Juice
Pesticide	µg/L (ppb)				
Azoxystrobin	ND	ND	0.32	ND	0.48
Boscalid	ND	ND	0.16	ND	ND
Carbaryl	ND	0.39	1.47	ND	ND
Carbofuran	ND	0.14	ND	ND	ND
Dimethoate	ND	0.30	ND	ND	ND
Imidacloprid	ND	ND	0.60	ND	0.20
Mandipropamid	ND	ND	0.59	ND	ND
Metalaxyl	ND	ND	0.21	ND	ND
Methoxyfenozide	ND	ND	ND	ND	0.84
Tebuconazole	ND	ND	0.32	ND	ND
Thiabendazole	1.8	ND	ND	ND	ND

Table 1. Test result (ND= not detected or <0.1ppb)

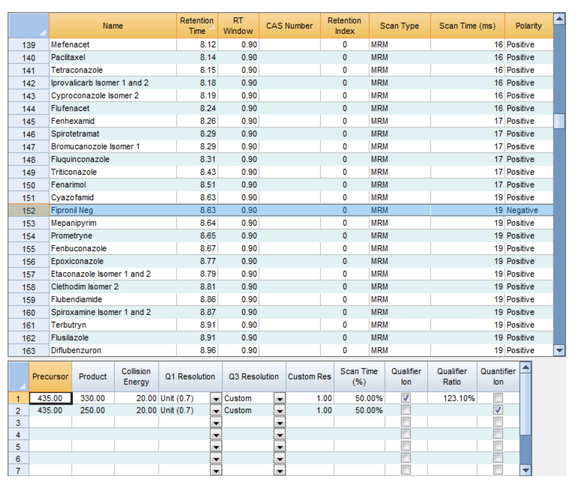

Fig. 3. MRM method for pesticides

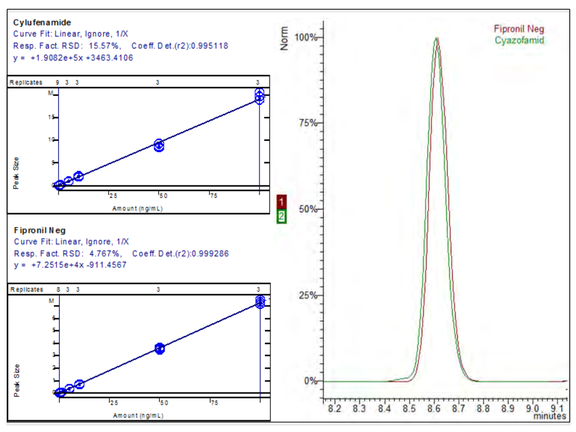

Fig. 4. Calibration curve of negative pesticide Fipronil (left top) and positive pesticide Cyazofamid (left bottom), and their co-eluting plots (right).

Compound No. 151 (positive Cyazofamid) and No. 152 (negative Fipronil) have same retention time and assigned same scan time (Fig 3).

Single injection of standard calibration solutions were injected before juice samples and duplicate injections of standard calibration solutions were performed after the sample.

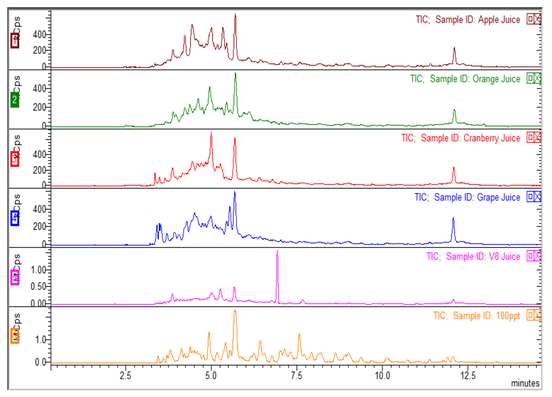

Fig. 5. Total Ion Chromatograms of (top to bottom): Apple juice, orange juice, cranberry juice, grape juice and vegetable juice.

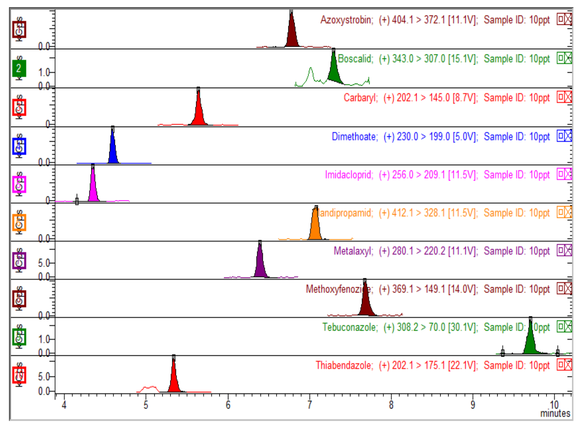

Fig. 6. Chromatograms of standard solution of the compounds listed in table 1 at 0.01 ppb (equivalent to 0.1ppb in juice).

The calibration on triplicate injections showed excellent linearity and response factor RSD over 3 orders range (Fig 4.).

- Three orders Linear range:0.01ppb to 10ppb (equivalent to 0.1 ppb to 100 ppb in fruit juice).
- R2 0.999 for both pesticides.
- Response factor RSD<5%

- A total of twelve pesticides were detected in apple juice, orange juice, cranberry juice or vegetable juice (table 1.).
- There were no pesticides detected in white grape juice using the screening method (table 1.).
- The multiple pesticides detected in orange juice, cranberry juice and juice may suggest that juice comes from multiple sources of raw materials or pooled juices.

Conclusions

- Good linearity, sensitivity and response factor RSD for positive and negative co-eluting pesticides.
- Bruker EVOQ Elite LC/MS/MS is a system of choice for simultaneous determination of positive and negative compounds numbering in the hundreds.