

Exploring the application of a universal method for pesticide screening in foods using a high data acquisition speed MS/MS

IMSC 2012 PTh-175

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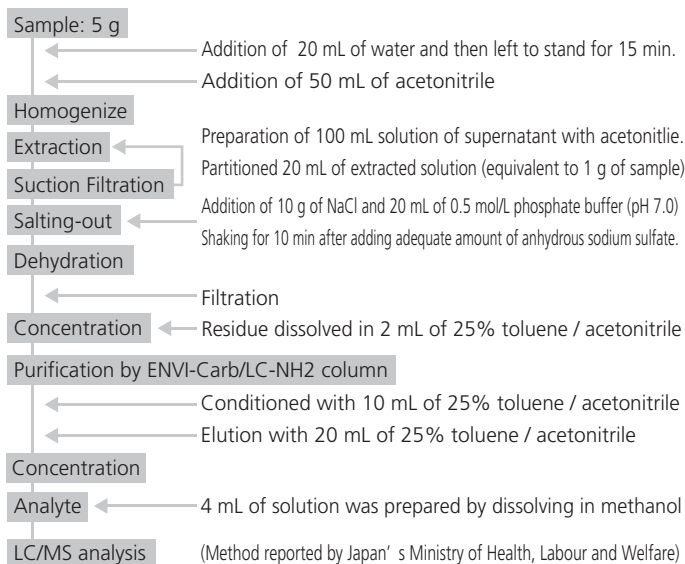
Introduction

Effective management, use, and disposal of agrochemicals, particularly pesticides, is an increasingly important health and environment issue in developing countries where economies may be heavily reliant on agriculture. The conventional approach to monitor these pesticides is to develop highly optimized triple quadrupole MRM methods to achieve the required levels of sensitivity, selectivity and

speed of analysis whilst still providing confidence in pesticide identification. In this study LCMS technology, developed for ultra-fast scanning MRM analysis, allows the possibility of a single generic 'universal' method. High speed MRM analysis and a generic parameters were used for screening 172 pesticides (344 MRM transitions) with 5 msec dwell and 1 msec pause times in food matrices.

Materials and Methods

Sample Preparation



Analytical Conditions

HPLC : Nexera UHPLC system

Column : Shim-pack XR-ODSII (75 mm × 2 mmI.D., 2.2 μm)
 Mobile phase : A ; 5 mM ammonium acetate – water
 B ; 5 mM ammonium acetate – methanol
 Gradient program : 30% B (0 min.) → 80% B (4 min.) → 95% B (10-15 min.) → 30% B (15.01-20 min.)
 Flow rate : 0.2 mL / min.
 Column temperature : 40°C

MS : LCMS-8040 Triple quadrupole mass spectrometer

Ionization : ESI (Positive / Negative)
 Ion spray voltage : +4.5 kV / -3.5 kV
 MRM : 344 MRM transitions (2 MRMs / compound)

Features of LCMS-8040

- **5 times** higher sensitivity compared to LCMS-8030
- An ultra fast scan speed of **15000 u / sec.**
- An ultra fast polarity switching of **15 msec.**
- An ultra fast MRM transition speed of **555 ch./ sec.**



Fig. 1 LCMS-8040 Triple Quadrupole Mass Spectrometer

Setting of MRM analysis & integration parameter

- In this study, no scheduling of MRM transitions was applied; thereby creating a universal generic method.

FiltrInstrument Parameters View (Realtime analysis)

Type	Event#	+/−	Compound Name	m/z	Time (0.000 min - 20.000 min)
MRM	118	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	285.0	0.000
MRM	119	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	287.0	0.000
MRM	120	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	289.0	0.000
MRM	121	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	291.0	0.000
MRM	122	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	293.0	0.000
MRM	123	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	295.0	0.000
MRM	124	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	297.0	0.000
MRM	125	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	299.0	0.000
MRM	126	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	301.0	0.000
MRM	127	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	303.0	0.000
MRM	128	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	305.0	0.000
MRM	129	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	307.0	0.000
MRM	130	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	309.0	0.000
MRM	131	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	311.0	0.000
MRM	132	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	313.0	0.000
MRM	133	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	315.0	0.000
MRM	134	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	317.0	0.000
MRM	135	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	319.0	0.000
MRM	136	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	321.0	0.000
MRM	137	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	323.0	0.000
MRM	138	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	325.0	0.000
MRM	139	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	327.0	0.000
MRM	140	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	329.0	0.000
MRM	141	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	331.0	0.000
MRM	142	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	333.0	0.000
MRM	143	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	335.0	0.000
MRM	144	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	337.0	0.000
MRM	145	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	339.0	0.000
MRM	146	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	341.0	0.000
MRM	147	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	343.0	0.000
MRM	148	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	345.0	0.000
MRM	149	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	347.0	0.000
MRM	150	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	349.0	0.000
MRM	151	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	351.0	0.000
MRM	152	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	353.0	0.000
MRM	153	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	355.0	0.000
MRM	154	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	357.0	0.000
MRM	155	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	359.0	0.000
MRM	156	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	361.0	0.000
MRM	157	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	363.0	0.000
MRM	158	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	365.0	0.000
MRM	159	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	367.0	0.000
MRM	160	+	1,1-Dichloro-2,2-bis(4-chlorophenyl)ethane	369.0	0.000

MS Data Processing View (Postrun analysis)

Integration Identification Quantitation

Window/Band: [Window] [Band]

Identification Method: Absolute [X]

Peak Selection: Largest Peak

Default Bandwidth: 20 min

Acquisition time set to the entire chromatographic run (0-20 min.).

'Largest peak' selected for identification.

Dwell 5 msec. Pause 1 msec. Loop time 2.058 sec.

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Results

Screening of 10 pesticides in food matrices

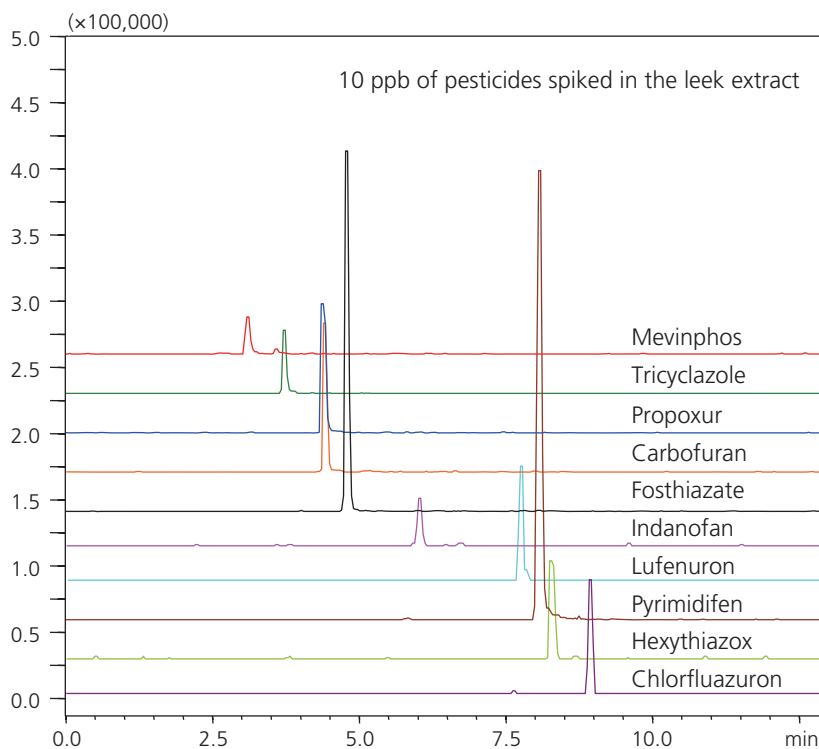


Fig. 2 MRM chromatogram of 10 pesticides

Table 2 Result of 10 pesticides screening (10 ppb spiked in each matrices)

Compounds	LeeK	Paprika	Green tea leaves
Carbofuran	✓	✓	✓
Chlorfluazuron	✓	✓	✓
Fosthiazate	✓	✓	✓
Hexythiazox	✓	✓	✓
Indanofan	✓	✓	✓
Lufenuron	✓	✓	✓
Mevinphos	✓	✓	✓
Propoxur	✓	✓	✓
Pyrimidifen	✓	✓	✓
Tricyclazole	✓	✓	✓
False positives*	8	7	10

• All peaks were automatically selected as the target compound to permit automatic identification of target analytes without retention time information. (*Number of false positives out of 172 screened pesticides.)

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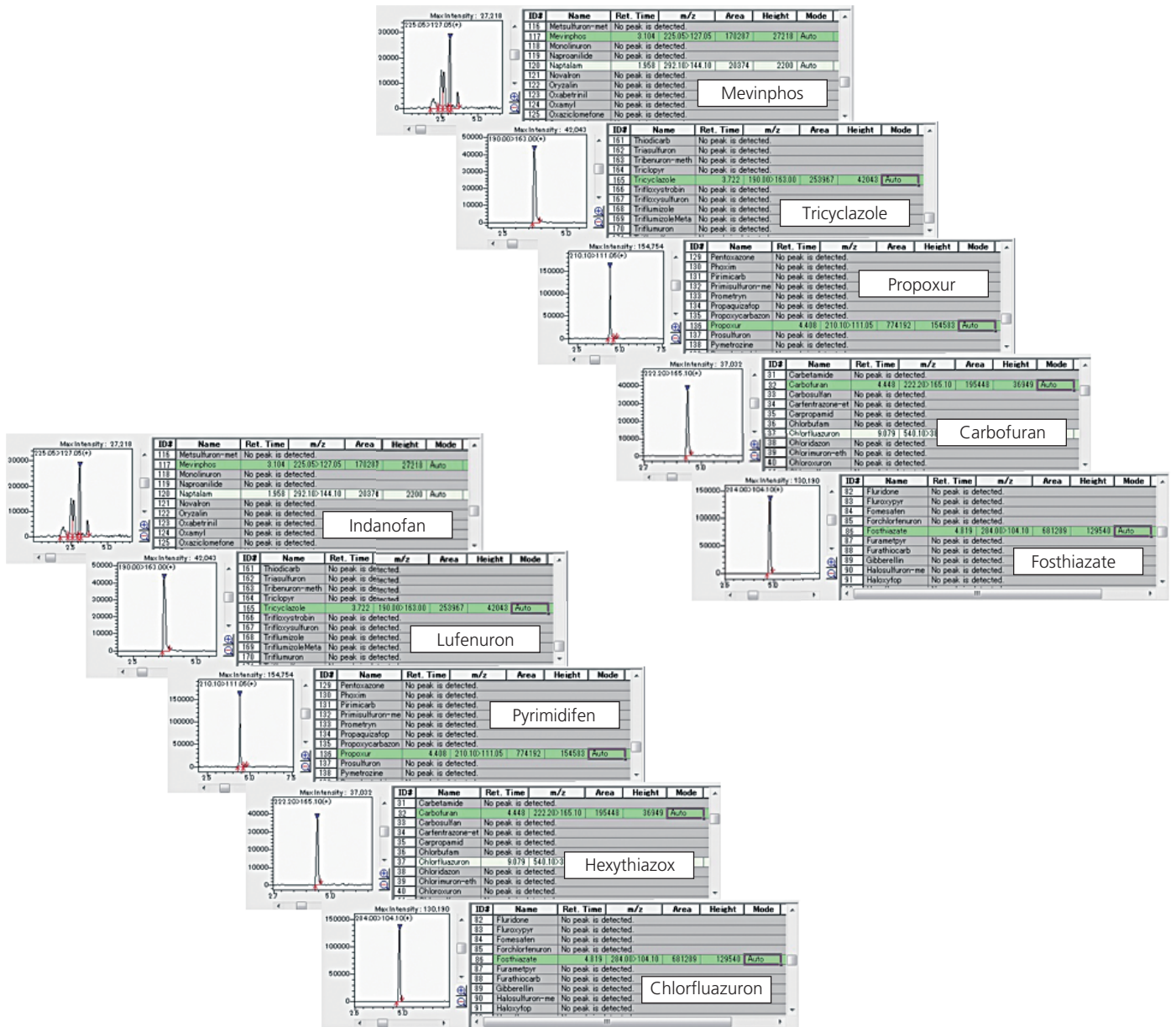


Fig. 3 Result of automatic identification (10 ppb spiked in the green tea leaves)

Conclusion

- Pesticides spiked in all matrices at 10 ppb (10 compounds) could be automatically detected using fast 5 msec MRM with 15 msec polarity switching without retention time information.



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