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Multi-class pesticides analysis in challenging vegetable matrices using fast 5 msec MRM with 15 msec polarity switching

ASMS 2012 WP27-575

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Introduction

Many regulatory authorities have established multi-class residual pesticides methods for the analysis of vegetables, fruits and other food stuffs. There is, however no global agreement on the provision of a target list of pesticides and this presents a risk with products moving between different regulatory requirements. In order to eliminate this risk, food safety laboratories need to ideally screen as many compounds as possible in a single run which may reach maximum residual limits (MRL); typically 10 ppb in food matrices.

In this study, we report the application of ultra-fast 5 msec MRM with 15 msec polarity switching for the analysis of 138 pesticides in vegetable matrices (72 and 66 compounds measured by LC-QqQ and GC-QqQ in the European Union Reference Laboratory (EURL) method) .

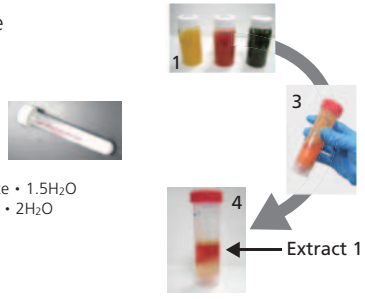
Materials and Methods

Sample Preparation (QuEChERS EU method)

Food sample	
Vegetables	Origin
Paprika (Sweet pepper)	New Zealand
Leek (Garlic chives)	Japan

Step 1 : Sample Extraction

1. Homoginize vegetables with food processor and homoginizer
2. Weigh 10 g homoginized sample
   - Add 10 mL acetonitrile
   - Add Salt-mixture*1
     - 4 g $MgSO_4$
     - 1 g NaCl
     - 0.5 g Na_2H citrate • $1.5H_2O$
     - 1 g Na_3 citrate • $2H_2O$

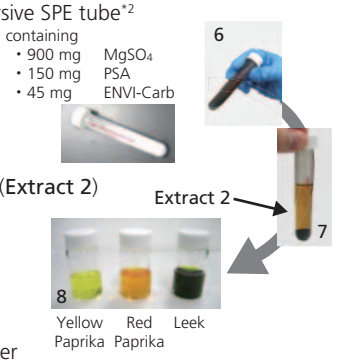


3. Shake vigorously by hand 1 min.
4. Centrifuge for 5 min. at 4000 rpm (**Extract 1**)

*1 : Citrate Extraction Tube (SIGMA ALDRICH)

Step 2 : Sample Clean up

5. Transfer 6 mL **Extract 1** into Dispersive SPE tube*2 containing
   - 900 mg $MgSO_4$
   - 150 mg PSA
   - 45 mg ENVI-Carb
6. Shake vigorously by hand 2 min.
7. Centrifuge for 5 min. at 3000 rpm (**Extract 2**)
8. Transfer 1 mL **Extract 2** into a vial
   - Add 200 uL acetonitrile
9. Vortex sample to mix it
10. Filtrate sample with disposable filter



*2 : PSA/ENVI-Carb SPE Clean Up Tube 2 (SIGMA ALDRICH)

LC/MS/MS analysis

Analytical Conditions

HPLC : Nexera UHPLC system

Column	: Shim-pack XR-ODSII (75 mm x 2 mmI.D., 2.2 um)
Mobile phase	: A ; 2 mM ammonium formate containing 0.1% formic acid – water B ; Methanol
Gradient program	: 5% B (0-2.5 min.)→55% B (2.51-6 min.)→80% B (6.01-12 min.) →100% (12-15 min.)→5% (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	: 276 MRM transitions (2 MRMs / compound) Dwell time 5 msec. / Pause time 1 msec.

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

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Results

MRM of pesticide standards

Table 1 LOQs of 138 pesticides in the EURL method by LCMS-8040

Technique (on the EURL method)	LOQs < 10 ppb	LOQs > 10 ppb	Not Ionization
by LC-QqQ	72 (100%)	0 (0%)	0 (0%)
by GC-QqQ	47 (71%)	6 (9%)	13 (20%)

• 71 % of pesticides measured by GC-QqQ in the EURL method could achieved excellent LOQs (0.08-10 ppb) .

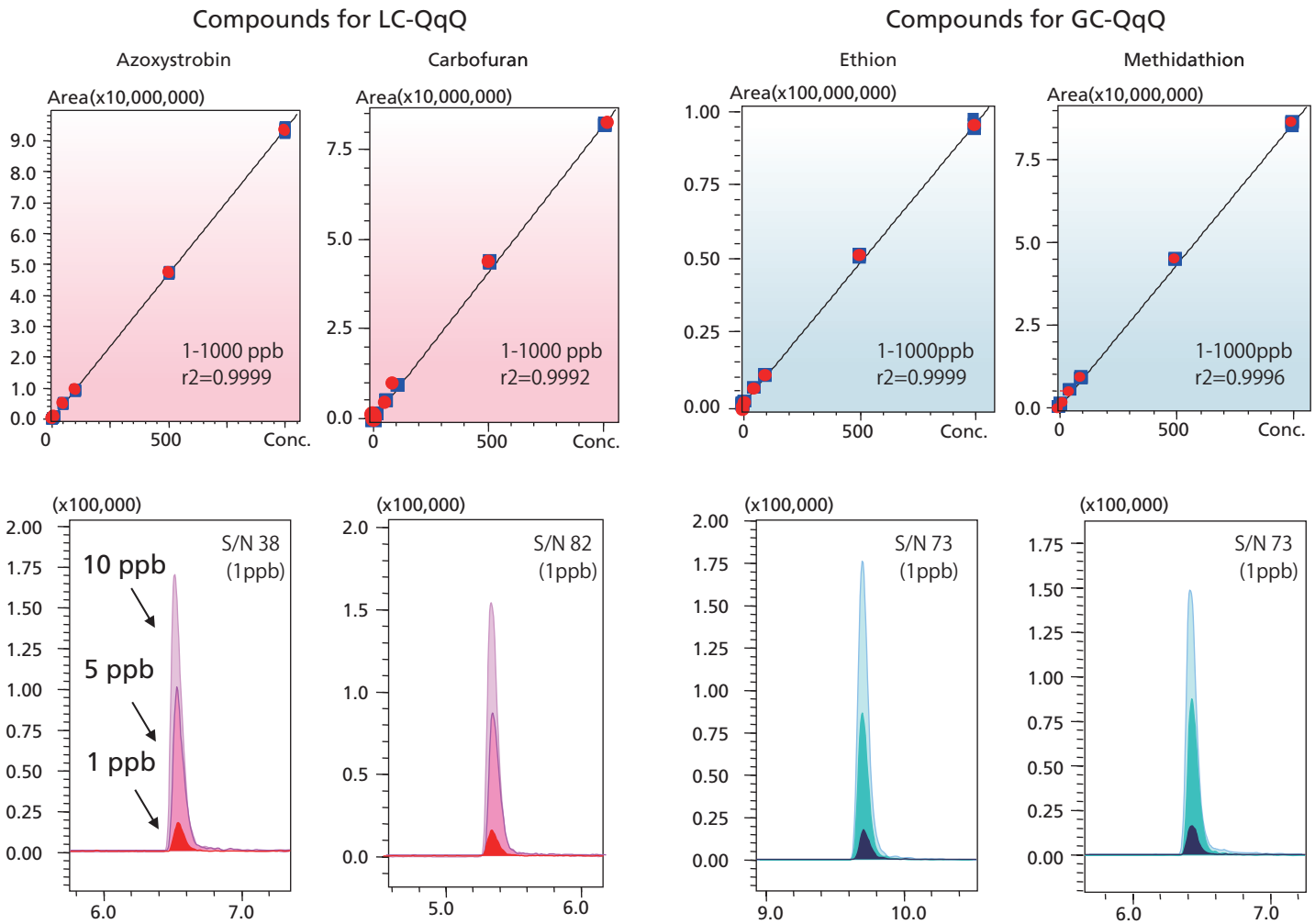

Fig. 2 Calibration curves and MRM chromatograms of typical pesticides

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Recovery of pesticides in vegetable matrices

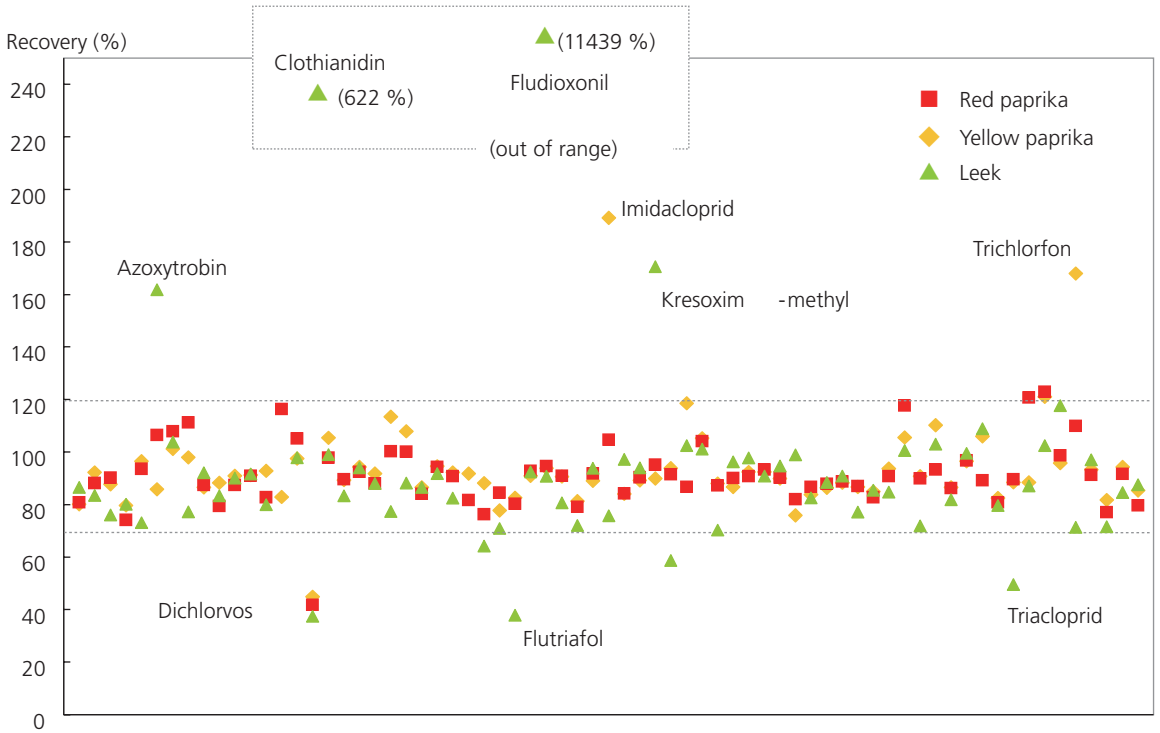
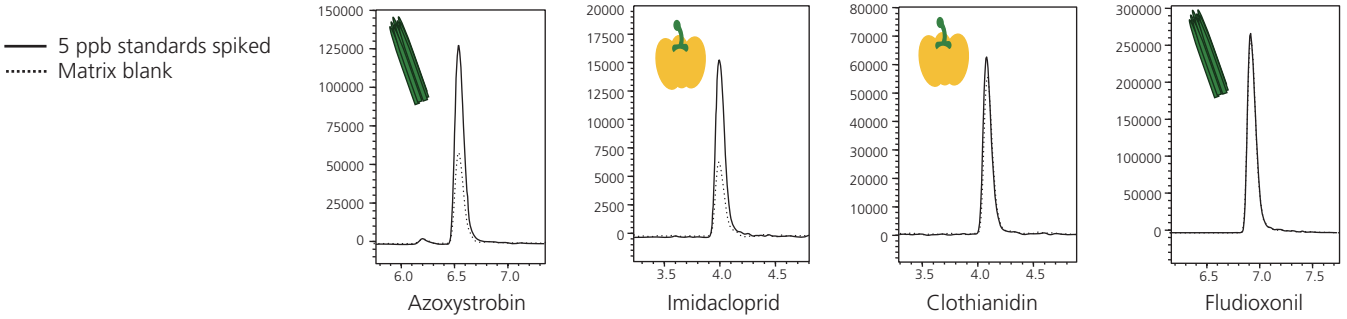


Fig. 3 Recovery of pesticides in the vegetable matrices (5 ppb spiked)

- Approximately 90% of pesticides represented good recoveries in the range of 70-120% in all studied matrices.
- Some pesticides indicating up to 120% of recovery were also detected in the matrix blank (Fig. 4).



	Azoxystrobin	Imidacloprid	Clothianidin	Fludioxonil
5ppb standards spiked	8.19 ppb	8.99 ppb	21.39 ppb	556.58 ppb
Matrix blank	3.77 ppb	3.19 ppb	25.78 ppb	550.92 ppb
MRL (Japan)	5 ppm	3 ppm	15 ppm	10 ppm

Fig. 4 MRM Chromatograms and quantitative results of 4 pesticides

Conclusion

- MRL of pesticide in vegetable matrices pre-treatment by QuEChERS method could be measured successfully using fast 5 msec MRM with 15 msec polarity switching.
- Majority of pesticides being suggested to GC-QqQ technology on the EURL method was successfully covered by LC-QqQ.

First Edition: May, 2012

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