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

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Anja Grüning[1], Susanne Kräher[1], Ichiro Hirano[2], Yuka Fujito[3], Kiyomi Arakawa[2], Yusuke Inohana[2]
[1]Shimadzu Europa GmbH, Albert-Hahn-Straße 6-10, Germany
[2]Shimadzu Corporation, 1, Nishinokyo-Kuwabaracho, Nakagyo-ku, Japan
[3]Shimadzu Analytical & Measuring Center Inc., 1,Shimoaicho, Nishinokyo, Nakagyo-ku, Japan

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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

- Sample: 5 g
  - ← Addition of 20 mL of water and then left to stand for 15 min.
  - ← Addition of 50 mL of acetonitrile
- Homogenize
- Extraction ← Preparation of 100 mL solution of supernatant with acetonitlie.
- Suction Filtration ← Partitioned 20 mL of extracted solution (equivalent to 1 g of sample)
- Salting-out ← Addition of 10 g of NaCl and 20 mL of 0.5 mol/L phosphate buffer (pH 7.0)
  Shaking for 10 min after adding adequate amount of anhydrous sodium sulfate.
- Dehydration
  - ← Filtration
- Concentration ← Residue dissolved in 2 mL of 25% toluene / acetonitrile
- Purification by ENVI-Carb/LC-NH2 column
  - ← Conditioned with 10 mL of 25% toluene / acetonitrile
  - ← Elution with 20 mL of 25% toluene / acetonitrile
- Concentration
- Analyte ← 4 mL of solution was prepared by dissolving in methanol
- LC/MS analysis (Method reported by Japan's Ministry of Health, Labour and Welfare)

Analytical Conditions

HPLC : Nexera UHPLC system

Column	: Shim-pack XR-ODSII (75 mm x 2 mmI.D., 2.2 um)
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

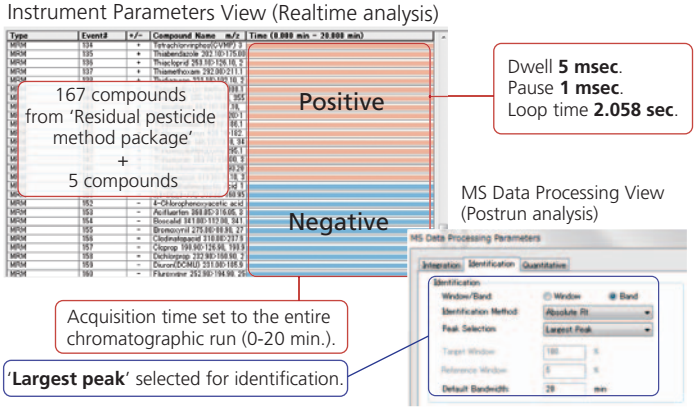
- **5 times** higher sensitivity compared to LCMS-8030
- An ultra fast scan speed of **15000 u / sec**.
- An ultra fast polarity switching of **15 msec**.
- An ultra fast MRM transition speed of **555 ch./ sec**.

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.

Instrument Parameters View (Realtime analysis)



Results

Screening of 10 pesticides in food matrices

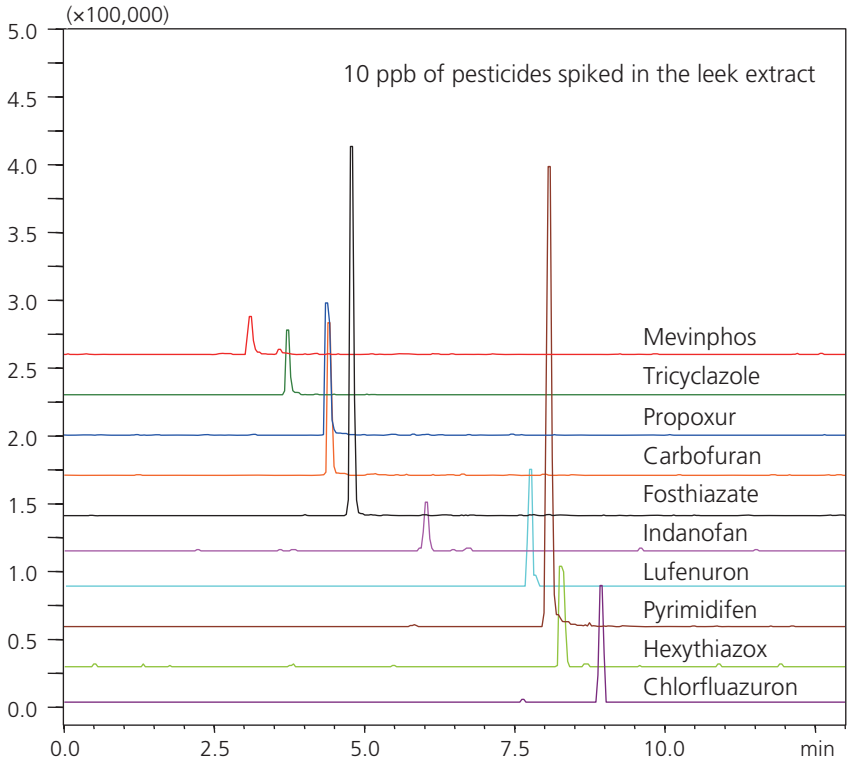


Fig. 2 MRM chromatogram of 10 pesticides

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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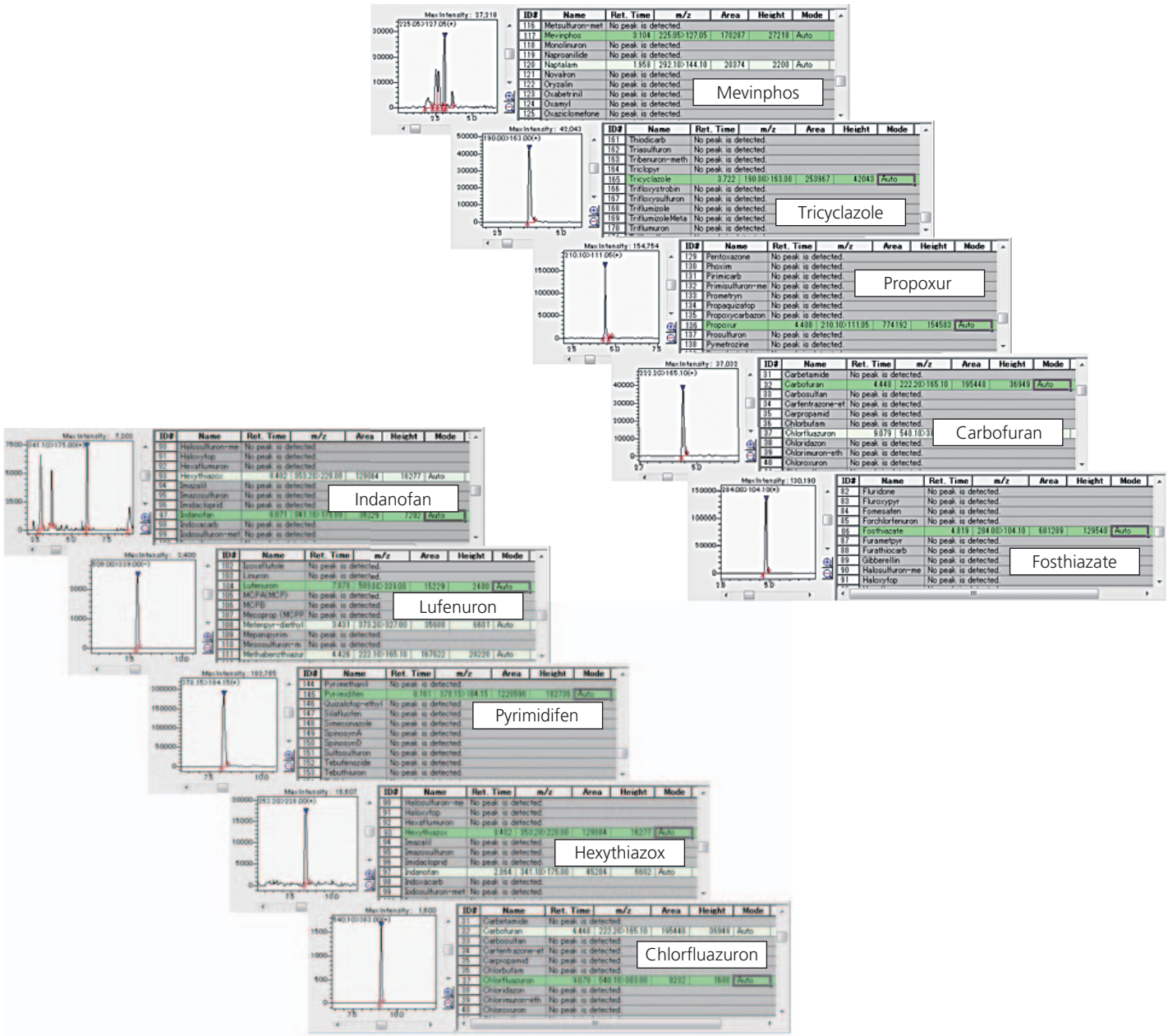

Fig. 3 Result of automatic identification (10 ppb spiked in the green tea leaves)

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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