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Multi-residue analysis of pesticides in crude food extracts using a simple extraction technique and LC/MS/MS

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Introduction

Analysis of pesticide residues in food is typically tedious and time-consuming due to the necessary extraction and clean up procedures. Furthermore, to deal with the ever-growing number of pesticides, the 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 illustrate the results utilizing an UF MRM capability (just 5 msec. MRM measurement includes dwell and pause time) with 5 msec. polarity switching (UF switching) for the analysis of 146 pesticides in crude food extracts by using easy and simple sample preparation technique.

Methods & Materials

Sample preparation

Food samples were purchased from a local grocery store in Japan. Each sample, with dry ice, was finely ground by milling until it became a powder and then extracted with acetonitrile. After filtration, the sample extracts were directly injected 1 µL to LC/MS/MS. This sample preparation technique is much easier and simpler than QuEChERS.

Sample	Origin
Soybeans	Japan
Brown rice	Japan
Spinach	Japan
Cucumber	Japan

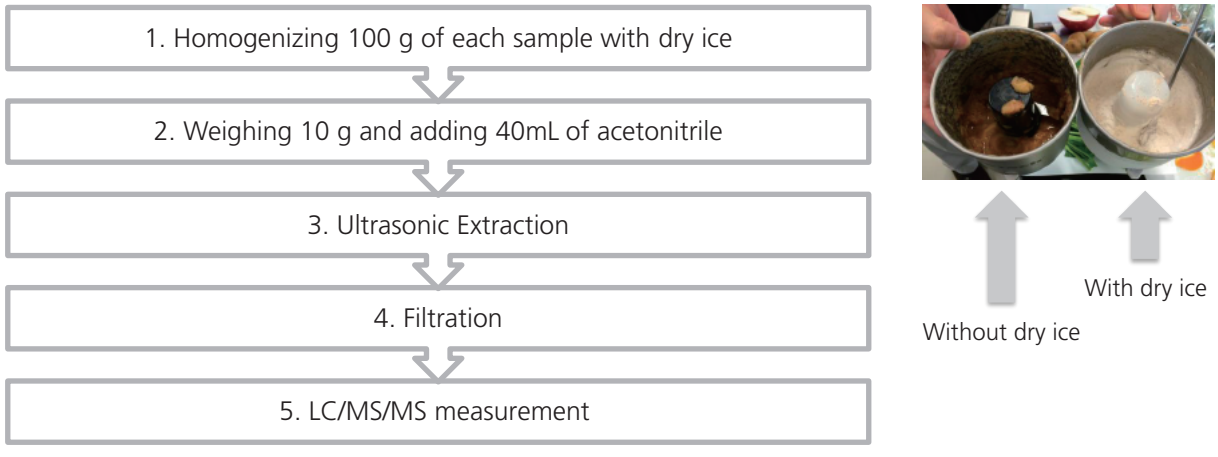

Figure 1 Protocol of sample preparation

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High Speed Mass Spectrometer
Ultra Fast Scanning
- 30,000 u / sec.
Ultra Fast Polarity Switching
- 5 msec.
Ultra Fast MRM
- Max. 555 transitions /sec

Figure 2 LCMS-8050 triple quadrupole mass spectrometer

LC/MS/MS analysis

HPLC conditions (Nexera UHPLC system)	
Column	: Shim-pack XR-ODSII (75 mm x 2 mm I.D., 2.2 um)
Mobile phase	: A – 5 mM ammonium acetate - water B – 5 mM ammonium acetate - methanol
Gradient program	: 10% B (0min) → 40% (1-2min.) → 95% (10-15min.) → 10% (15.01-20min.)
Flow rate	: 0.2 mL / min.
Column temperature	: 40 °C
MS conditions (LCMS-8050)	
Ionization	: ESI (Positive / Negative)
MRM	: Max MRMs simultaneously monitored: 72ch. (36 event) Max loop time: 0.442 sec Dwell time 5 msec. / Pause time 1 msec.

Result

Pesticide standards

146 compounds were analyzed in a single run by just 5 msec. MRM event with 5 msec. polarity switching. All studied compounds have shown excellent LOQs and linearity of calibration curves ranging from 0.1-100 µg/L.

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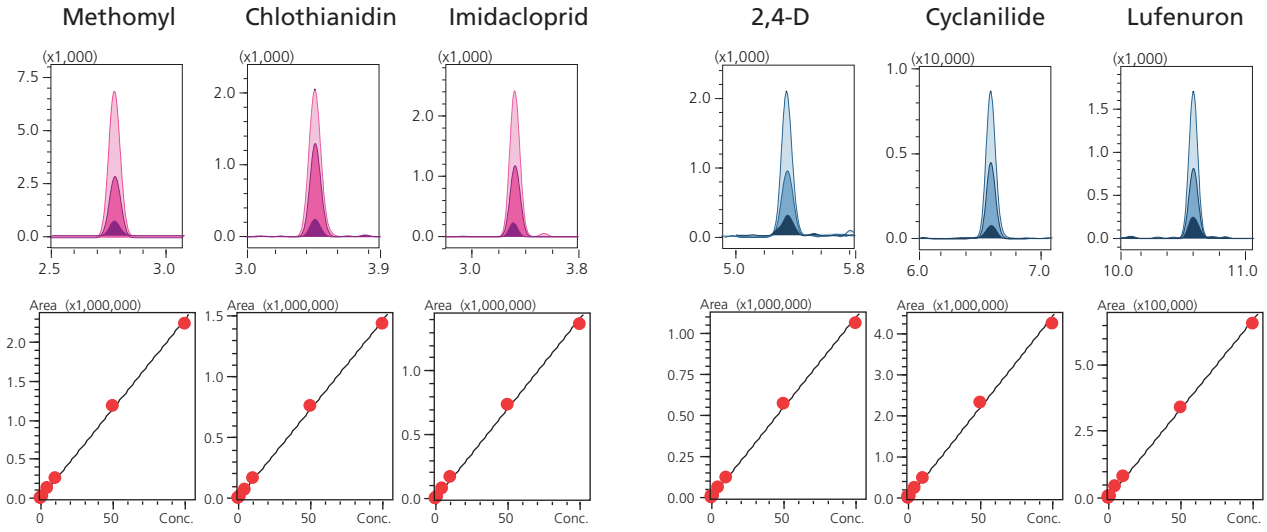

Figure 3 MRM chromatograms and calibration curves of typical pesticides
(left: positive / right : negative)

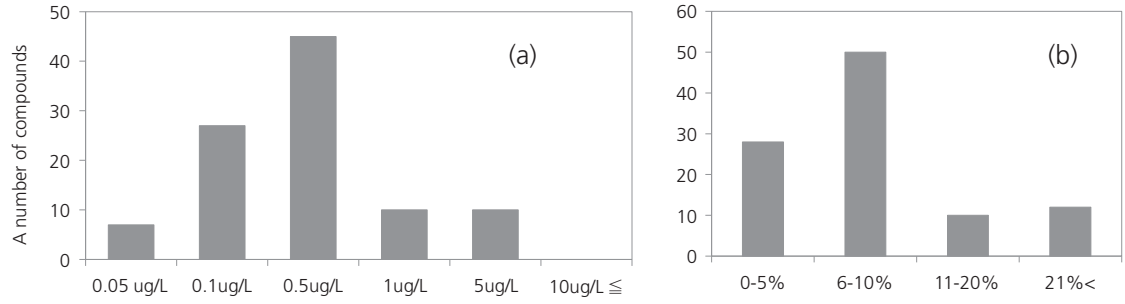

Figure 4 (a) : LOQs of all tested compounds
(b) : CV(%) of all tested compounds at 1 µg/L (n=5)

Matrix effect

The matrix samples spiked with 10 µg/L standards were prepared for the recovery test in all matrices. More than 80% of target compounds have shown good recoveries ranging from 70-120% in all matrices, neither ion suppression nor enhancement was observed.

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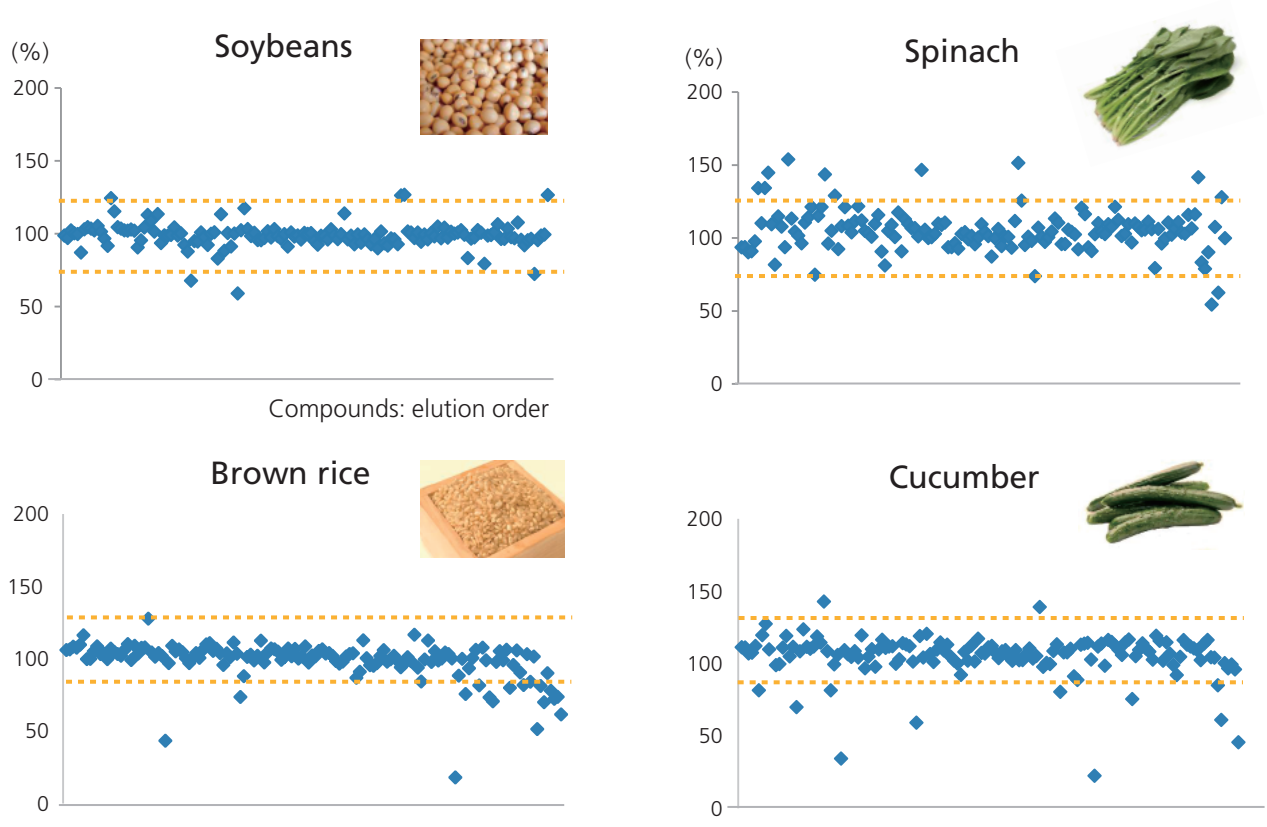

Figure 5 Recoveries of all target compounds in each matrix

Extraction efficiency

Extraction efficiency was determined from ratios of peak area of pre-extraction / post-extraction spiked sample (10 µg/kg). Almost all compounds have shown the good recoveries in high water content foods such as spinach and cucumber.
However, in low water content foods like brown rice and soybeans, especially, high polar compounds showed poor recovery. To improve this, 9 mL of water is added to the homogenized sample before acetonitrile extraction. As a result, recoveries of these compounds were dramatically improved.

Foods	Water content (%)
Soybeans	13
Brown rice	15
Spinach	92
Cucumber	95

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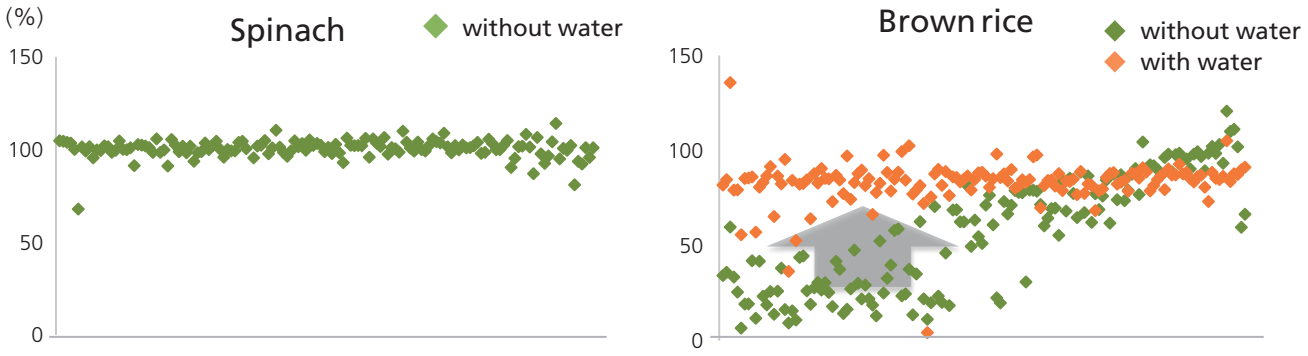

Figure 6 Recoveries in each matrix

Comparison between LCMS-8050 & LCMS-8060

■ Sensitivity

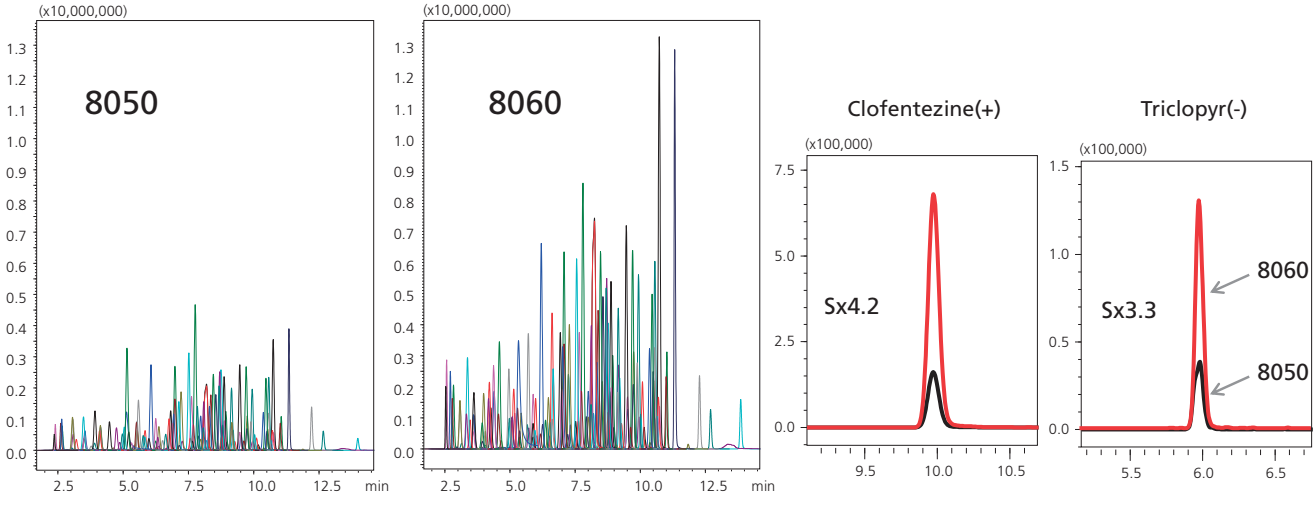

Figure 7 MRM chromatograms in LCMS-8050 and LCMS-8060

The sensitivity of pesticides was compared between LCMS-8050 and 8060 under the same analytical conditions. In LCMS-8060, signal response was improved average about 3 times higher than LCMS-8050, and lower LOQs were achieved. The increased sensitivity of the LCMS-8060 enables the accurate quantitation below MRLs even in high degree of dilution in the matrix.

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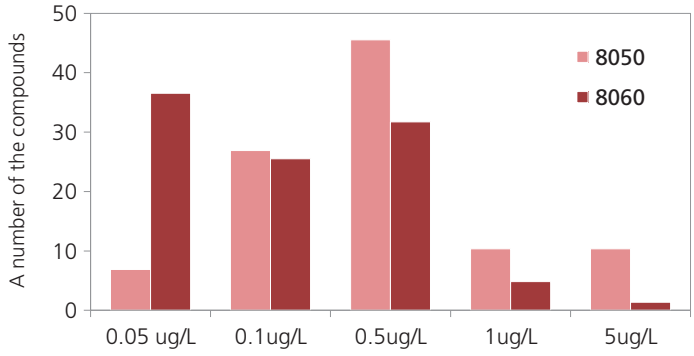

Figure 8 LOQs of the compounds

■ Matrix effect

The matrix effect was also compared between LCMS-8050 and 8060. As a result, there is no difference of the recoveries between two instruments.

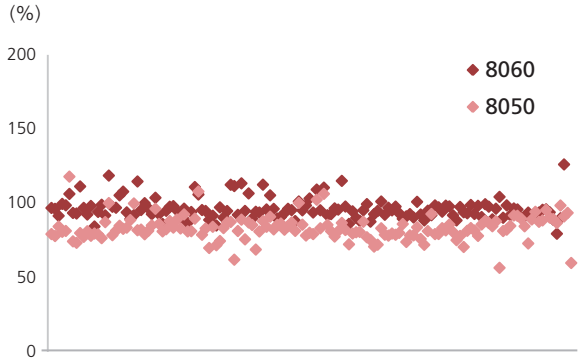

Figure 9 Recoveries of pesticides in soybeans

Figure 10 LCMS-8060

Conclusions

- This method is able to be applied to the quantification of pesticides in complex food matrices.
- The increased sensitivity of the LCMS-8060 enables the accurate quantitation below MRLs even in high degree of dilution.

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