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Multiresidue pesticide analysis in crude food extracts using AOC-MEPS and LC/MS/MS

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1. Introduction

Analysis of pesticide residues in food is typically tedious and time-consuming, due to the necessary extraction and clean-up procedures. In general, these processes are often conducted using SPE cartridges or QuEChERS kits. However, these methods can be costly as the majority are single use and require a large amount of solvent. We have developed new automated pretreatment equipment which has MEPS (Micro Extraction by Packed Sorbent) technology with newly developed sorbent. MEPS offers very simple operation, and can be used repeatedly.
In this study, we report the application of an automated clean-up system using the standalone type AOC-MEPS for analysis of pesticides in food by LC/MS/MS. 138 pesticides are selected as target analytes in the European Union Reference Labolatory (EURL) method. Of these 138 compounds, we analyzed 120 pesticides which could be measured by LC/MS in our previous study.

2. Methods and Materials

2-1. Sample preparation

Vegetable sample	
Carrot	Japan
Green pepper	Japan

Step 1. Sample extraction (using QuEChERS EU method)

Homogenize	Homogenize vegetables with food processor	
↓		
Weigh homogenized sample	Weigh homogenized sample into the extraction tube Add 10 mL acetonitrile and salt mixture*	
↓		
Shake	Shake vigorously by hand for 1 min.	・4 g $MgSO_4$ ・1 g NaCl ・0.5 g DHS
↓		
Centrifugation	Centrifuge for 5 min. at 4000 rpm	・1 g TSCD

Step 2. Sample clean up (using AOC-MEPS system)

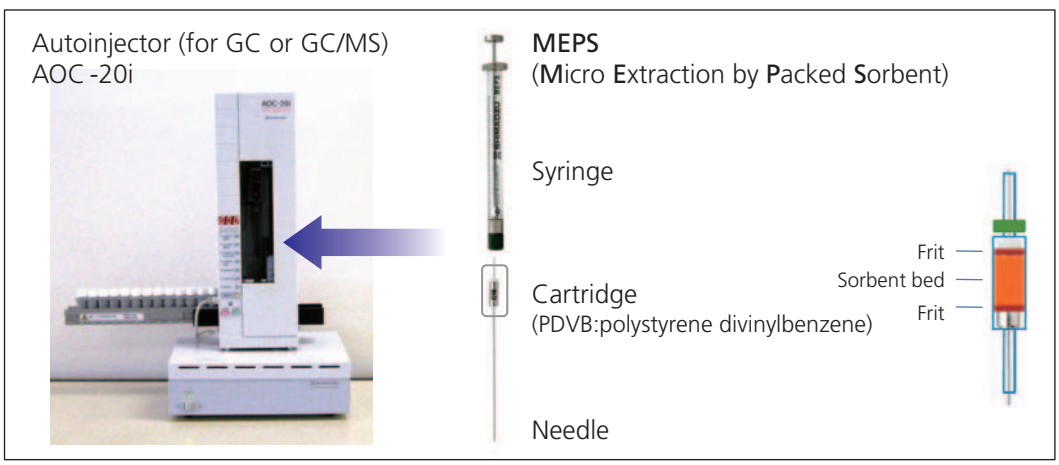

Fig. 1 AOC-MEPS system (standalone type)

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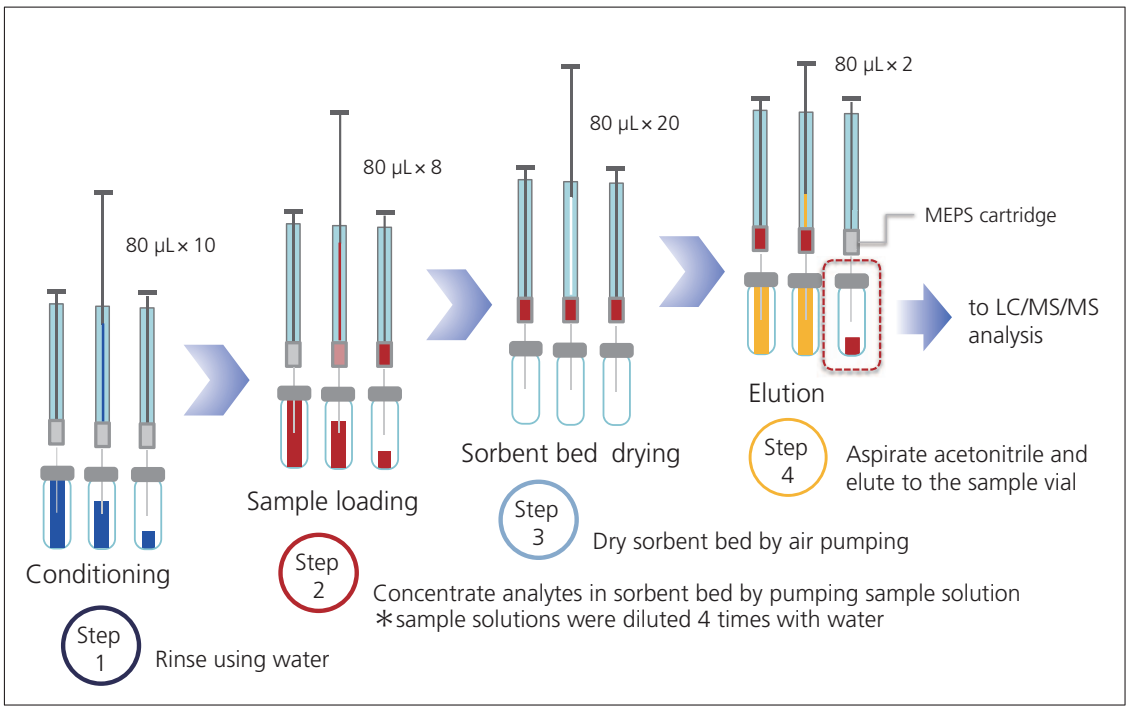

Fig. 2 Protocol of AOC-MEPS

2-2. LC/MS/MS analysis

HPLC conditions (Nexera UHPLC system)

Column	: Shim-pack XR-ODSII (75 mm × 2 mm I.D., 2.2 um)
Mobile phase	: A - Water + 2 mM ammonium formate containing 0.1 % formic acid 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 conditions (LCMS-8040)

Ionization	: ESI (Positive / Negative)
MRM	: 276 MRM transitions (2 MRMs / compound) Dwell time 5 msec. / Pause time 1 msec.

Ultra Fast Mass Spectrometer

Ultra Fast Polarity Switching
・15msec
Ultra Fast MRM
・Max. 555 transition /sec

Fig. 3 LCMS-8040 triple quadrupole mass spectrometer

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3. Result

3-1. MEPS calibration curves of pesticide standards

By using the AOC-MEPS system, approximately 80% of pesticides used in this study showed calibration curves with good linearity in the range of 5-1000 ppb.

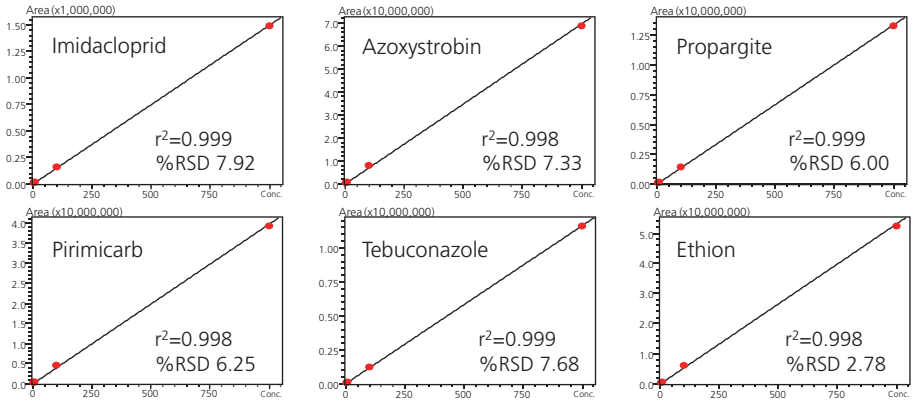


Fig. 4 Calibration curves of typical pesticides (5-1000 ppb)

3-2. Recovery of pesticides in vegetable matrices

80% of pesticides represented good recovery in the range of 70 - 120% in all studied matrices.

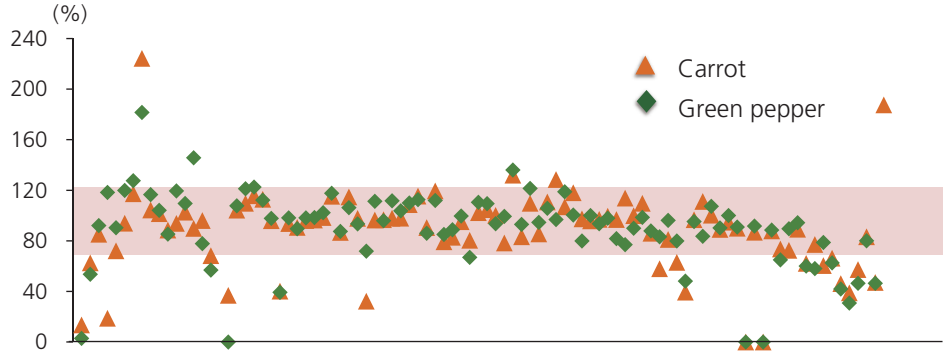
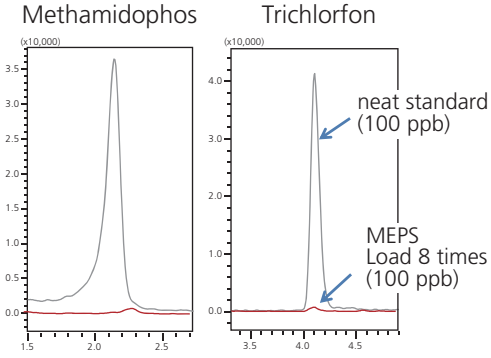


Fig. 5 Recovery of pesticides in vegetable matrices (5 ppb spiked).

3-3. Modification of MEPS protocol



Water-soluble compounds that are not retained much on the C18 column could not be trapped on the PVDB sorbent material.
Therefore, we modified the AOC-MEPS protocol.
In addition, we tested a different type of MEPS cartridge (SAX, anion exchange).

Fig. 6 MRM chromatograms of organophosphate pesticides

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Table 1 Modification of AOC-MEPS protocol

	Current method	New method
Sample solution	100% acetonitrile →4 times dilution with water	100% acetonitrile →100% water (N2purge)
Elution solution	100% acetonitrile	1N HCl / Methanol =1/4
Number of load	8	6
Number of elution	2	2
MEPS cartridge	PDVB (polystyrene divinylbenzene)	PDVB / SAX (Anion exchange)

Compounds suitable for PDVB

Fenitrothion, Tolyfluanid and Dichlofluanid could be successfully detected using the PDVB cartridge with new MEPS pretreatment method (see Fig. 7).

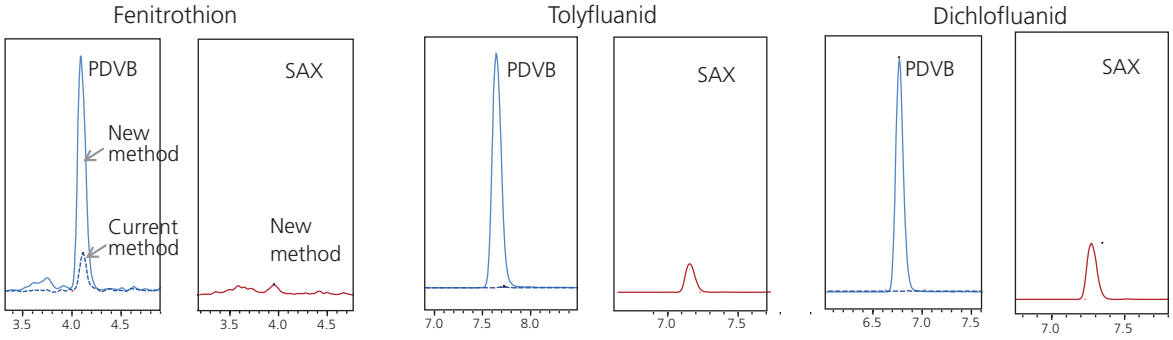

Fig. 7 Comparison of chromatogram (PDVB vs SAX)

Compounds suitable for SAX

Each calibration curve of Acephate, Methamidophos, Lufenuron and Fipronil showed good linearity by using SAX cartridge. Some compounds were successfully detected by using PDVB with the new method, however linearity in the calibration curve was not good (see Fig. 8).

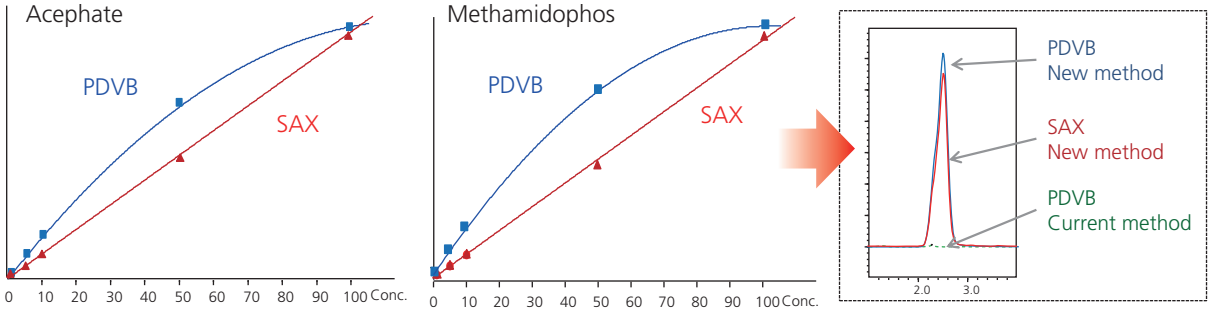

Fig. 8 Comparison of calibration curves and chromatograms (PDVB vs SAX)

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4. Conclusions

- The majority of the target compounds showed good linearity in the calibration curves and presented excellent recoveries in the vegetable matrices by the automated clean-up system using the AOC-MEPS.
- Water-soluble compounds were trapped on the MEPS cartridges (PDVB or SAX) and successfully detected by changing the AOC-MEPS protocol.

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