

Quantitative Analysis of Trace Level Pesticides in Vegetable Foods by GC/MS/MS

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1. Introduction

Multi-residue analysis of pesticides in fruits, vegetables, and other foods is always a challenge in sample preparation as well as analytical detection. The required quantitation limits for many pesticides are set below 10 ng/mL (ppb) which demands more sophisticated analytical processes.

Compared to widely used GC/MS analyses, GC/MS/MS technique provides MRM acquisition mode which can significantly improve the sensitivity and lower the method detection limits. The QuEChERS sample preparation has been accepted worldwide for multi-residue pesticide

analysis due to its special features known as Quick, Easy, Cheap, Effective, Rugged and Safe. A multi-residue pesticide analysis method by GC/MS/MS was evaluated for trace analysis of 306 kinds of pesticides in 3 different vegetable food matrices, which are apple, cucumber and tomato, extracted by QuEChERS method. The results reflect that the method is simple, rapid and characterized with acceptable sensitivity and accuracy to meet the requirements for the analysis of pesticides in vegetable foods.

2. Method and Materials

Sample Preparation

For vegetable foods, weigh about 50 g and comminute in a small disintegrator for 1 min. Transfer 10 g of comminuted sample to a 50 mL centrifugal tube. Add 10 mL of acetonitrile (containing 1% acetic acid), vortex for 5 min. Add 1.5 g of anhydrous CH_3COONa and 4 g of anhydrous

MgSO_4 , vortex for 1 min. Centrifuge for 10 min at 5000 rpm. Then transfer 1 mL of supernatant in 1.5 mL centrifugal tube, add 50 mg of PSA, 50 mg of C18 and 200 mg of MgSO_4 , vortex for 1 min and centrifuge for 2 min at 5000 rpm. Filtered with 0.2 μm membrane filter (Millipore), injection into a GC-MS/MS system.

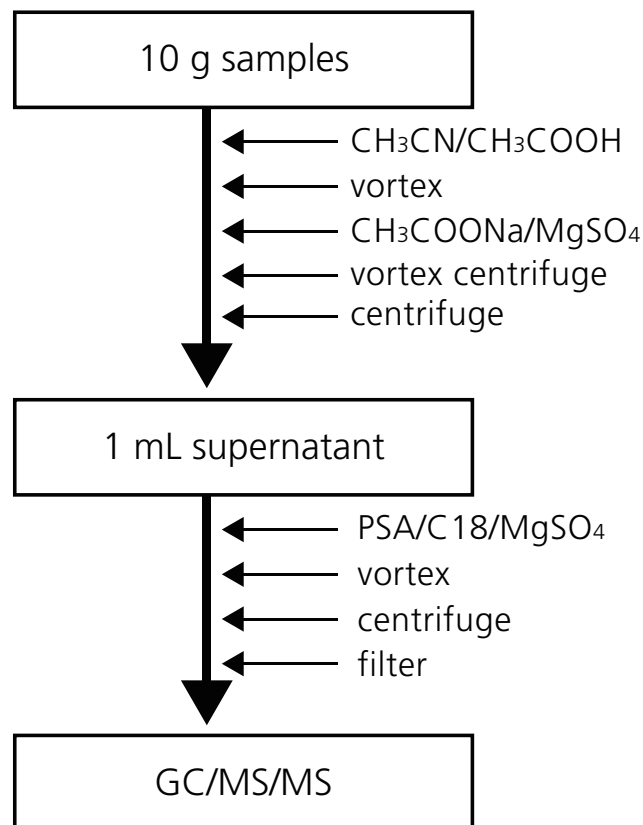


Fig. 1 Scheme of sample preparation

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Instrument conditions

A triple quadrupole mass spectrometer (Shimadzu GCMS-TQ 8030, Kyoto, Japan) was used to analyze the pesticides in vegetable samples.

GC

Column : Rxi-5 Sil MS, 30 m × 0.25 mm i.d., 0.25 μm
 Carrier gas : helium
 Injection temperature : 280°C
 Column temperature program : 50°C (1 min) 25°C/min 125°C 10°C/min 300°C (5 min)
 Flow rate : 1.69 mL/min
 Injection mode : splitless (1 min)
 High pressure injection : 250 kPa (1.5 min)

MS/MS

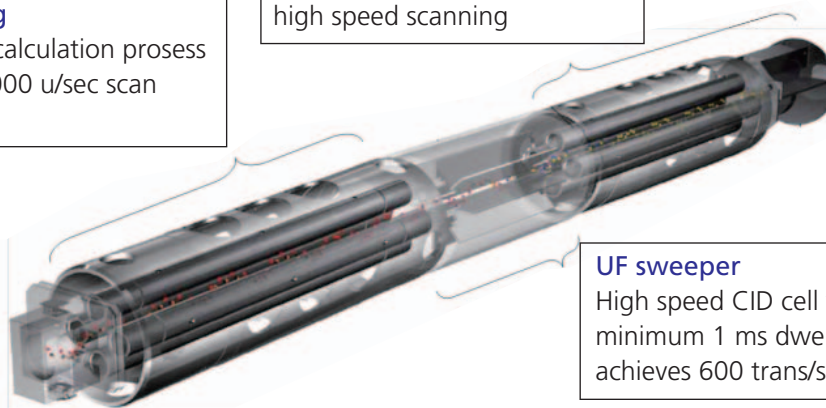
Ionization mode : EI
 Ion source temp : 200°C
 IF temperature : 250°C
 CID gas : argon
 Injection volume : 2 μL
 MRM parameters are shown in Table 1.

UF scanning

High speed calculation process enables 20,000 u/sec scan speeds

UF sensitivity

Patented ASSP function ensures high sensitivity during high speed scanning



UF sweeper

High speed CID cell with minimum 1 ms dwell time achieves 600 trans/sec

Fig. 2 Key features of GCMS-TQ 8030

Table 1 MRM parameters for pesticides

Compound name	Retention time	Precursor> Product	CE	Precursor> Product	CE
Parathion	13.760	291>109	14	291>137	6
Dicofol	13.920	251>216	8	251>139	16
cis-Chlordane	15.175	373>266	22	373>337	6
Deltamethrin	22.020	253>93	18	253>172	4

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3. Results and Discussion.

MRM chromatograms

The 306 pesticides were divided into 6 group. Fig. 3 shows MRM chromatograms of one of those groups.

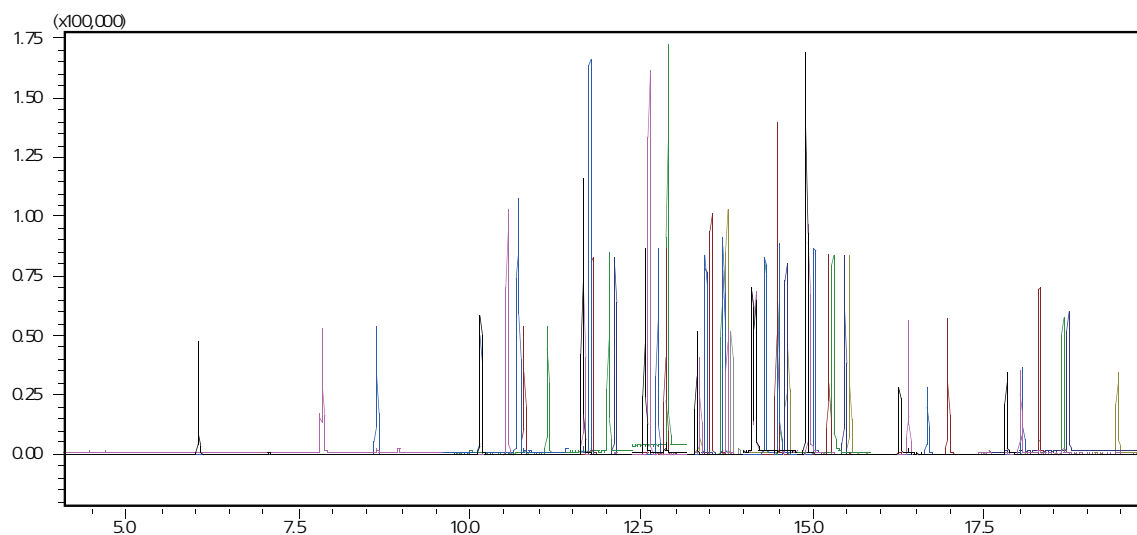


Fig. 3 MRM chromatograms of pesticide mixture (50 µg/L)

Table 2 Results of the 4 pesticide residues in apple

Compound name	R	LOD (µg/kg)	spiked 0.001 mg/kg		spiked 0.005 mg/kg	
			recovery (%)	%RSD	recovery (%)	%RSD
Parathion	0.9992	0.16	111.2	6.96	98.4	2.38
Dicofol	0.9998	0.02	97.0	7.26	103.5	4.17
cis-Chlordane	0.9993	0.04	87.2	8.23	91.26	6.60
Deltamethrin	0.9991	0.11	115.6	9.36	111.9	3.76

Linearity range, detection limits, repeatability and recoveries

For accurate quantification, representative matrix-matched calibration curves were applied to compensate matrix effects. The correlation coefficients (*r*) of the mixed matrix-matched pesticides standard solutions from 1 to 100 µg/L are above 0.999. Limits of quantification (LOQ) of mixed pesticides standards were determined by injecting a series of different matrix-matched pesticides standard solutions. Although the LOQ of the method varies with different pesticides, most of analytes can be measured at

0.001 mg/kg level in 10g of vegetable food samples. The mixed standard solutions were added into the pesticide-free vegetable food samples to make the concentration at 0.001 and 0.005 mg/kg. For most of analytes, recoveries in the acceptable range of 70-110% and repeatability (relative standard deviations, RSD) ≤ 10% (n=5) were achieved for both matrices at spiking levels of 0.01 and 0.1 mg/kg, as shown in Table 2.

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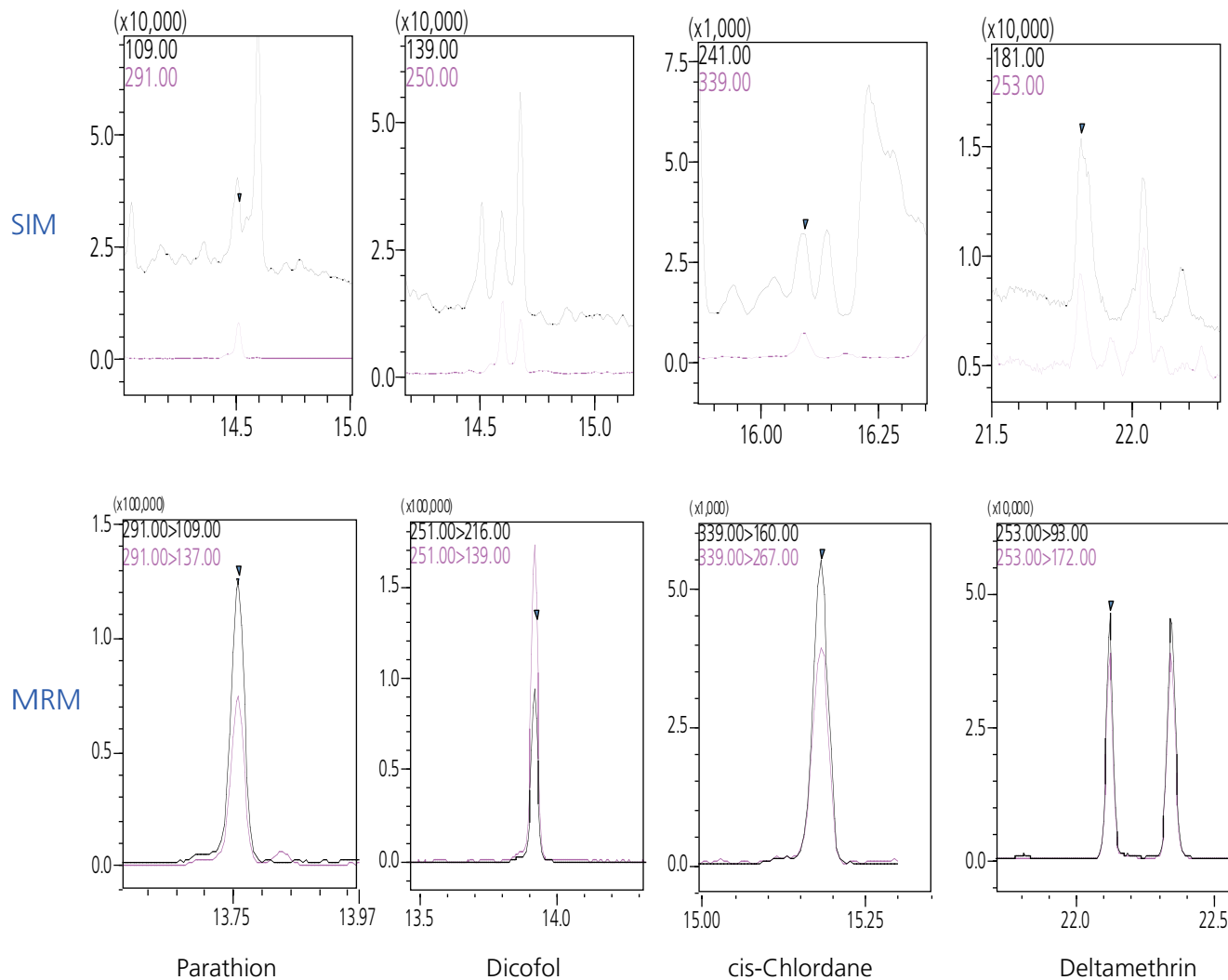


Fig. 4 Comparison between SIM and MRM of 4 pesticides in apple

Fig 4 shows mass chromatograms of the spiked sample (0.005mg/kg) using the SIM mode of GC/MS and the MRM mode of GC/MS/MS. Some of the pesticides could not be detected or identified in the SIM of GC/MS because they overlapped with co-extracted substances. On the other hand, it was possible to selectively detect and identify those

same pesticides in the MRM of GC/MS/MS. Therefore, GC/MS/MS provided an effective means for analyzing residual pesticides in complex matrices that contain a large quantity of substances co-extracted from sample, such as vegetable food samples.

4. Conclusions

A very quick, easy, effective, reliable multi-residues method in vegetable foods based on QuEChERS method was developed using a GC-MS/MS. The performance of the method was very satisfactory with results meeting

validation criteria. The method has been successfully applied for determination of vegetable food samples and ostensibly has further application opportunities, e.g. dried vegetables and herb extracts.

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