

A Method for Simultaneous Analysis of 174 Pesticides in Grape Using GC-MS/MS

Pittcon 2015 2220-12P

Feifei Tian, Xizhi Wang, Shiheng Luo, Guixiang Yang,
Taohong Huang, Shin-ichi Kawano, Yuki Hashi,
Shimadzu Global COE for Application &
Technical Development, Beijing, 100020, China

A Method for Simultaneous Analysis of 174 Pesticides in Grape Using GC-MS/MS

Introduction

With the development of science and technology, a great variety of pesticides have been used by more and more peasants and scientists. Simultaneous analysis of multi-residues such as hundreds of pesticides in agricultural products has always been a challenge. Since the detection limits for many pesticides has fallen to 10 µg/kg (10 ppb), more and more sophisticated analysis tools are required.

Due to its excellent sensitivity and selectivity, gas chromatography tandem mass spectrometry (GC-MS/MS) with multiple reaction monitoring (MRM) acquisition

mode is utilized for analysis of residual pesticides in foods. The aim of this work was to develop and validate the fast method of simultaneous analysis of 174 pesticides in grape by GC-MS/MS in MRM acquisition mode. The samples were pretreated with the QuEChERS method, then subjected to GC-MS/MS. Each compound has 2 MRM transitions (primary for quantification, secondary for qualification), totally 348 transitions in 15 minutes. The established method is sensitive, repeatable and reliable for simultaneous analysis of 174 pesticides in grape samples.

Experimental

Sample pretreatment

The samples were pretreated with QuEChERS method. Internal standard (heptachlor-endo-epoxide, 50 ng/mL) was used to eliminate the matrix effect and achieve quantitative determination.

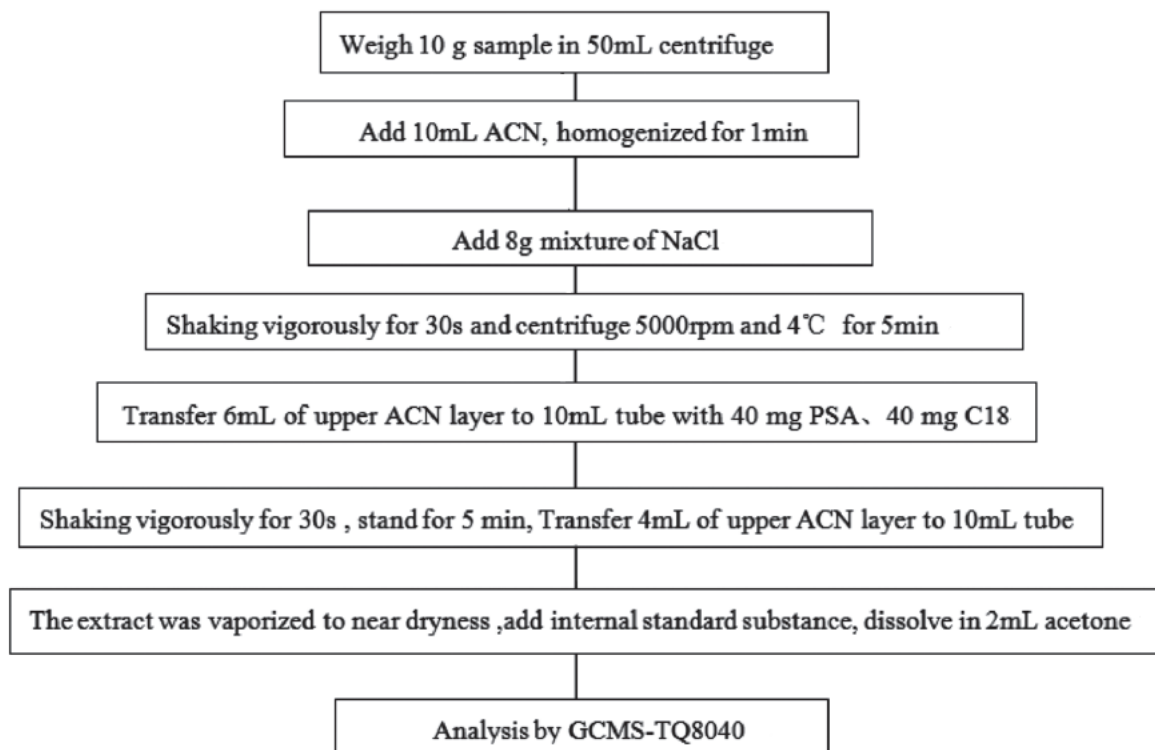


Figure 1 Schematic flow diagram of the sample preparation

A Method for Simultaneous Analysis of 174 Pesticides in Grape Using GC-MS/MS

GC-MS/MS Analysis

The treated samples were analyzed in MRM mode using GC-MS/MS (GCMS-TQ8040, Shimadzu Corporation, Japan). The MRM transitions and collision energies for each compound were acquired from the pesticides MRM database provided by Shimadzu Corporation which contains 479 pesticides.

Analytical Conditions	
GC-MS	: GCMS-TQ8040
Column	: Rxi-5 Sil ms, 30 m x 0.25 mm, 0.25 μ m
GC	
Injection port temperature	: 250 $^{\circ}$ C
Temperature program	: 50 $^{\circ}$ C (1 min)-25 $^{\circ}$ C/min-125 $^{\circ}$ C-10 $^{\circ}$ C/min-300 $^{\circ}$ C (15 min)
Injection mode	: splitless (1 min)
Injection volume	: 1 μ L
Linear velocity	: 47.2 cm/sec
MS	
Ion source temperature	: 200 $^{\circ}$ C
Interface temperature	: 250 $^{\circ}$ C
Measurement Mode	: MRM
Loop Time	: 0.3sec

Results and Discussion

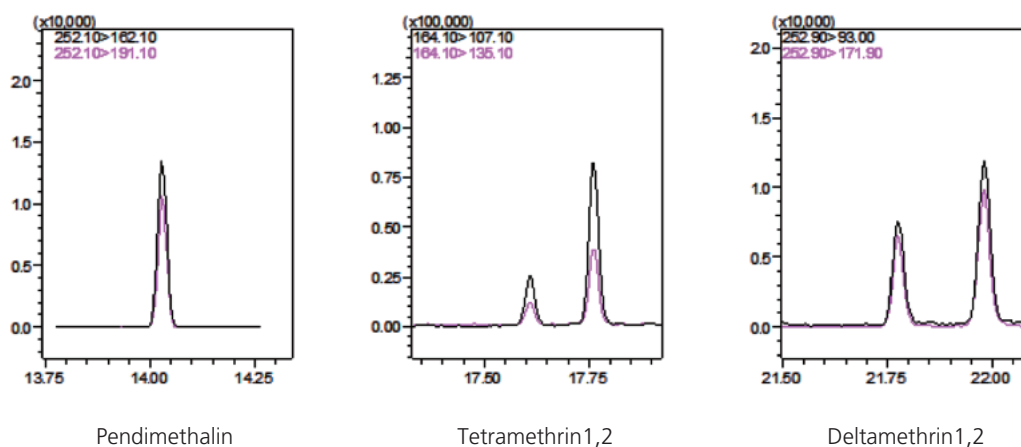


Figure 2 MRM chromatograms of pedimethalin, tetramethrin and deltamethrin spiked in grape sample (10 ng/mL)

A Method for Simultaneous Analysis of 174 Pesticides in Grape Using GC-MS/MS

The grape samples were prepared using the above method, 174 pesticides were spiked in sample extraction (10 ng/mL). Spiked samples were analyzed in MRM mode using GC-MS/MS. Fig.2 shows MRM chromatograms for pedimethalin, Tetramethrin and deltamethrin spiked in grape sample (10 ng/mL). In order to assess the method linearity, calibration curves were constructed for 174 pesticides spiked in the sample matrix, using heptachlor-endo-epoxide as

internal standard. The linear relation between peak area ratio and concentration ratio of target and internal standard substance were good from 10 ng/mL to 1 µg/mL ($r^2 > 0.99$). The limits of detection (LODs) of all the pesticides studied were 0.1 µg/kg. The average recoveries were 70%-120% of target compounds and the relative standard deviations (%RSD, n=6) were less than 10% in spiked levels at 5 µg/kg.

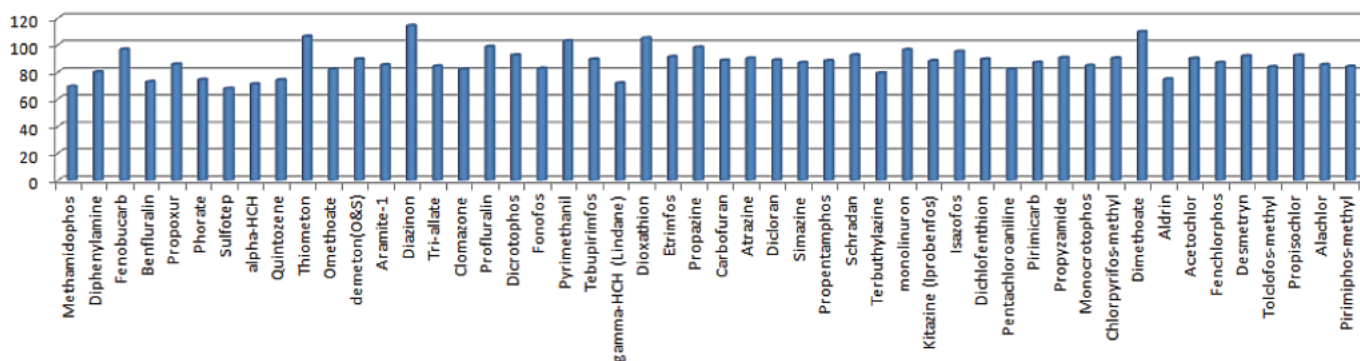


Figure 3 Recovery of pesticides at 5 µg/kg spiked in grape samples

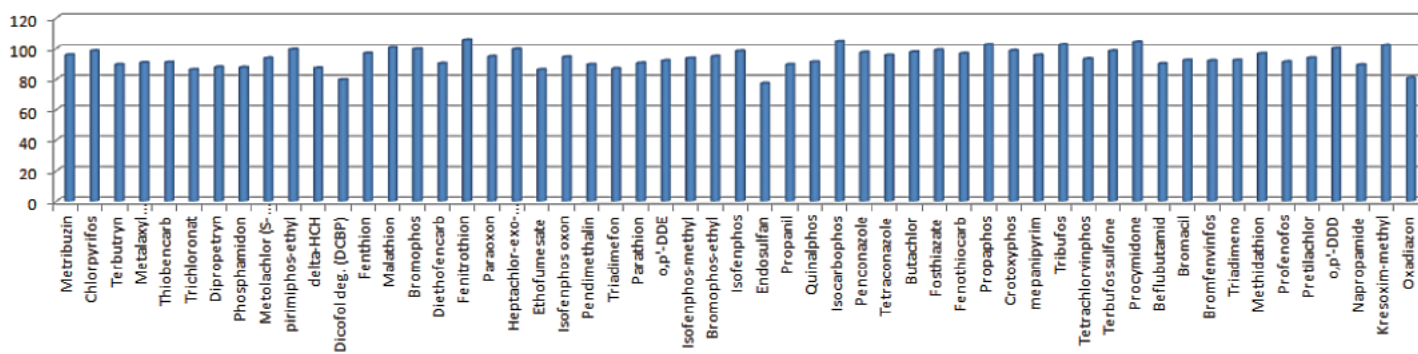


Figure 4 Recovery of pesticides at 5 µg/kg spiked in grape samples

A Method for Simultaneous Analysis of 174 Pesticides in Grape Using GC-MS/MS

Conclusions

- A fast method was developed for simultaneous analysis of 174 pesticides in grape by GC-MS/MS in MRM acquisition mode.
- The established method is sensitive, repeatable and reliable for simultaneous analysis of the 174 pesticides in grape samples.