PO-CON1872E

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Matrix effect on pesticides in vegetables by GC-MS/MS analysis

ASMS 2019 TP304

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Overview

GC-MS/MS was applied to determine the matrix effect on pesticides in vegetables. Due to the higher sensitivity, the matrix effect has been diminished by using GCMS-TQ8050. The potential factors which influence the matrix effect has been discussed.

Introduction

GC-MS/MS have been used as a state-of-the-art method to determine pesticides residuals in agricultural products (e.g. vegetables). However, matrix effect is one of the major issues in the analysis, potentially resulting in the bias in the quantification. Matrix-paired calibration curve is a common way to diminish such effect. This indicates, theoretically, for each matrix measurement, the corresponding matrix-paired calibration curve need to be prepared, which is time- and labor-consuming. Hence, approaches that can systematically improve the matrix effect is desirable. In the present study, we compare the matrix effect of pesticides in vegetables in GCMS-TQ8050 (Shimadzu, Japan) with GCMS-TQ8040 (Shimadzu, Japan). Our assumption is due to the higher sensitivity in GCMS-TQ8050, the matrix effect can be improved by sample dilution.

Methods

Sample pretreatment

Four organic vegetables (tomato, eggplant, carrot and green vegetable) were used to compare the matrix effect of 14 pesticides by using two instruments (GCMS-TQ8040 and GCMS-TQ8050). The sample pretreatment followed QuEChERS method and samples can be divided into three groups.

(1) Matrix spiked group, samples underwent QuEChERS pretreatment and reconstituted with 1 mL external standard (conc. 10 and 1ng/mL for GCMS-TQ8040 and GCMS-TQ8050, respectively).
(2) Solvent blank group, external standard with final concentration of 10 and 1ng/mL for GCMS-TQ8040 and GCMS-TQ8050, respectively.
(3) Matrix blank group, samples underwent QuEChERS pretreatment and reconstituted with solvent.

A multiply reaction monitoring (MRM) method was established to analyse 14 pesticides by GC-MS/MS.

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High Speed Mass Spectrometer

Ultra Fast Scan Speed
- Max. 20000 amu/sec

Ultra Fast MRM
- Max. 888 transition /sec

Figure 1. GCMS-TQ8050 triple quadrupole mass spectrometer

GC-MS/MS conditions	
Column	: Rtx-5 MS, 30m×0.25mm×0.25µm
Column oven temp.	: 40°C(1min)_40°C/min_120°C_5°C/min_240°C_12°C/min_280°C(6min)
Injection mode	: Splitless mode, Injection time:1.5min
High pressure injection	: 250 kPa(1.5 min)
Injection temp.	: 280°C, Inj. Volume: 1µL
Carrier gas	: Helium
Flow control mode	: Linear velocity (36.1 cm/sec)
Initial column flow	: 1.0 mL/min
CID gas	: Argon
Ionization mode	: EI
Detector voltage	: Tuning result+0.8kV
Interface temp.	: 280°C
Ion source temp.	: 230°C

Table 1. MRM transition of 14 pesticides in the present study

No.	Compound	Retetion time (min)	MRM transition	CE (V)	MRM transition	CE (V)
1	Tecnazene	12.699	260.90>203.00	10	214.90>179.00	10
2	Ethalfluralin	13.928	275.90>202.10	5	315.90>275.90	10
3	Benfluralin	14.382	292.00>264.00	15	292.00>206.00	10
4	alpha-BHC	14.905	218.90>183.00	5	216.90>181.00	5
5	beta-BHC	15.909	181.00>145.00	15	216.90>181.00	5
6	Quintozene	16.032	295.00>237.00	20	236.90>142.90	30
7	gamma-BHC (Lindane)	16.207	181.00>145.00	5	216.90>181.00	15
8	Prometryn	19.297	226.00>184.20	5	199.00>184.10	20
9	Triadimefon	20.81	208.00>181.10	15	208.00>111.00	15
10	Pendimethalin	21.66	251.80>162.20	10	251.80>161.10	20
11	Penconazole	21.884	248.00>157.10	15	248.00>192.10	15
12	Paclobutrazol	23.078	236.00>125.10	25	236.00>167.00	25
13	Oxadiazon	24.304	174.90>112.00	15	174.90>76.00	15
14	Piperonyl butoxide	27.98	176.10>103.10	20	176.10>131.10	20

Statistics
Matrix effect (ME) is calculated as following equation : ME=[(Am/Ais)-1]×100%

Whereas Am is the average area (n=6) of pesticides in the matrix spiked group, Ais is the average area (n=6) of pesticide in the solvent blank group.
Student t-test was applied to investigate if there is any significant difference regarding the response of pesticides between matrix spiked group and solvent blank group. The significant level was set to 0.01.
Principal component analysis was used to classify the target analytes of pesticides based on the behavior of matrix effects in 4 vegetables by GCMS-TQ8050 and GCMS-TQ8040.

Result

None of target analyte was identified in the sample from matrix blank group. For matrix spiked group and solvent blank group, each sample was analysed six times consecutively, and the RSD (n=6) of the peak area was lower than 10%, implying good repeatability of the instrument. Limit of quantification (LOQ) obtained from GCMS-TQ8050 is lower than those from GCMS-TQ8040, indicating the improved sensitivity in GCMS-TQ8050 (Table 2).

Table 2. Limit of quantification (LOQ) of 14 pesticides in GCMS-TQ8040 and GCMS-TQ8050

No.	Compound	LOQ (ng/mL)	
		GCMS-TQ8040	GCMS-TQ8050
1	Tecnazene	0.39	0.14
2	Ethalfluralin	2.2	0.51
3	Benfluralin	1.83	0.24
4	alpha-BHC	0.08	0.04
5	beta-BHC	0.04	0.09
6	Quintozene	0.16	0.05
7	gamma-BHC	0.04	0.09
8	Prometryn	0.16	0.11
9	Triadimefon	0.45	0.13
10	Pendimethalin	0.48	0.14
11	Penconazole	0.19	0.02
12	Paclobutrazol	0.52	0.08
13	Oxadiazon	0.02	0.03
14	Piperonyl butoxide	0.24	0.04

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The results of matrix effect on 14 pesticides in 4 vegetables are presented in Table 3.

In brief, our results showed that in GCMS-TQ8040, for the majority of target pesticides (e.g. benfluralin and quintozene), a significant matrix-induced response enhancement was observed ($p<0.01$). In contrast, a significant matrix-induced response suppression was only observed for β-HCH ($p<0.01$). For the rest of pesticides, no matrix effect ($p>0.01$) was observed from statistical point of view.

However, for the majority of compound that matrix effect was observed in GCMS-TQ8040, such effect was declined ($p>0.01$) when the samples were diluted and run in GCMS-TQ8050 (Note: The signal response in GCMS-TQ8050 is still comparable to GCMS-TQ8040. This demonstrated that matrix effect can be somehow improved by an instrument with elevated sensitivity.

Principal component analysis (PCA) was applied to classify the pesticides in term of matrix effects (Figure 2). In general, matrix-induced response enhancement occurs, however, it is decreased with the increasing of retention index in the Rtx-5MS column. In addition, the chemical structure of pesticides might influence the matrix effect. For instance, HCHs, projected in the third quadrant of PCA plot, may have a tendency to adsorb in the injection port, leading to different behavior with respective to matrix effect as other pesticides in the present study.

Table 3. Matrix effect of 14 pesticides in 4 vegetables by GCMS-TQ8040 and GCMS-TQ8050

Compound	Tomato				Eggplant			
	GCMS-TQ8040		GCMS-TQ8050		GCMS-TQ8040		GCMS-TQ8050	
	average (%)	*p* value	average (%)	*p* value	average (%)	*p* value	average (%)	*p* value
Tecnazene	22	<0.01	-7	<0.01	5	<0.01	13	<0.01
Ethalfluralin	49	<0.01	3	0.514	24	<0.01	13	0.077
Benfluralin	53	<0.01	0	0.986	18	<0.01	10	0.027
alpha-BHC	-1	0.465	-6	0.153	-5	<0.01	7	0.036
beta-BHC	-4	<0.01	-3	0.37	-7	<0.01	4	0.338
Quintozene	36	<0.01	-4	0.45	10	<0.01	7	0.379
gamma-BHC	-3	0.011	0	0.939	-9	<0.01	6	0.02
Prometryn	17	<0.01	-5	0.188	3	<0.01	9	0.016
Triadimefon	26	<0.01	-4	0.426	7	<0.01	1	0.747
Pendimethalin	103	<0.01	17	0.141	37	<0.01	35	0.02
Penconazole	16	<0.01	-5	0.318	2	0.261	-3	0.454
Paclobutrazol	42	<0.01	-11	0.028	7	<0.01	10	0.014
Oxadiazon	-6	<0.01	-3	0.079	-11	<0.01	1	0.742
Piperonyl butoxide	2	0.16	-6	0.031	-9	<0.01	3	0.258

Table 3. Matrix effect of 14 pesticides in 4 vegetables by GCMS-TQ8040 and GCMS-TQ8050

Compound	Carrot				Green			
	GCMS-TQ8040		GCMS-TQ8050		GCMS-TQ8040		GCMS-TQ8050	
	average (%)	*p* value	average (%)	*p* value	average (%)	*p* value	average (%)	*p* value
Tecnazene	11	<0.01	-16	<0.01	11	<0.01	-3	0.804
Ethalfluralin	20	<0.01	-6	0.284	26	<0.01	4	0.196
Benfluralin	21	<0.01	-13	0.016	27	<0.01	1	0.556
alpha-BHC	5	0.055	-13	<0.01	-1	0.683	-10	0.012
beta-BHC	1	0.647	-9	0.061	-5	<0.01	-8	0.144
Quintozene	17	<0.01	-18	<0.01	24	<0.01	0	0.582
gamma-BHC	2	0.256	-17	<0.01	-8	<0.01	-13	<0.01
Prometryn	11	<0.01	-4	0.279	4	0.027	-5	0.542
Triadimefon	16	<0.01	-4	0.377	12	<0.01	-3	0.473
Pendimethalin	95	<0.01	7	0.505	78	<0.01	29	0.02
Penconazole	11	<0.01	-9	0.021	4	0.024	-1	0.725
Paclobutrazol	16	<0.01	-4	0.315	11	<0.01	-1	0.904
Oxadiazon	0	0.97	-9	0.011	-7	<0.01	-7	0.192
Piperonyl butoxide	6	<0.01	-6	0.077	1	0.411	-5	0.15

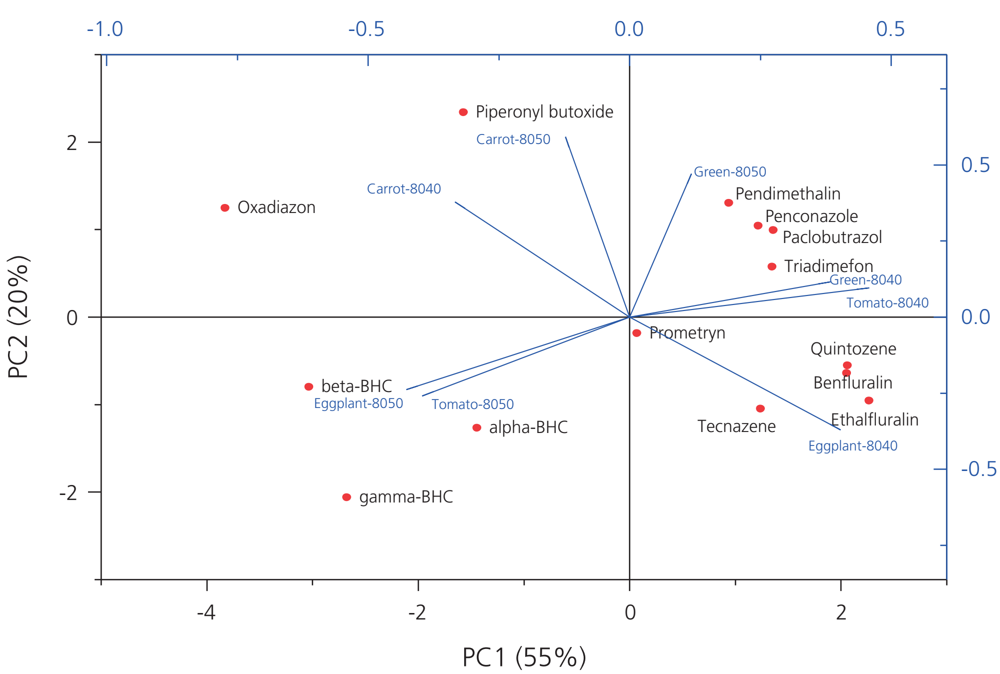

Figure 2. Projection of pesticides based on matrix effect in PCA plot.

Conclusions

Matrix effects of 14 pesticides was explored by two generation of GC-MS/MS from Shimadzu. From statistic point of view, our results indicated that the matrix effect, which was unavoidable effect in pesticides analysis, can be greatly improved by using instrumental with higher sensitivity.

First Edition: June, 2019

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