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Analysis of Pesticides in *Solanum macrocarpon* Fruit by Ultrahigh-Performance Liquid Chromatography-Tandem Mass Spectrometry

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Abstract

A UPLC-MS/MS was developed for the analysis of 11 pesticides in Vietnamese cannon eggplant. Pesticides were extracted by QuEChERS and then cleaned up with solid phase extraction. 11 pesticides in the sample solution were separated by reversed phase column and detected by positive ionization mass spectrometry utilizing with multiple reaction monitoring (MRM). Validation of the developed analytical method was performed by linearity range, limit of detection (LOD), limit of quantification (LOQ), repeatability, recovery, etc. LOD and LOQ ranged from 0.03 µg/kg to 0.1 µg/kg and 0.11 µg/kg to 0.33 µg/kg for wet weight samples, respectively. Repeatability and reproducibility of the analytical method were achieved below 12.3% and 19.1%, respectively. Recovery ranged from 75.5% to 86.6%. Matrix effect was investigated and presented. The validated analytical method was then applied to analyze 11 pesticides in five Vietnamese cannon eggplant samples. Experimental results indicated that some pesticides were detected in the samples analyzed. However, the concentration of these compounds was below the Vietnam Ministry of Health and EU standards.

Keywords: Matrix effect, MS/MS, pesticides, QuEChERS, UPLC.

1. Introduction

Pesticides are widely used in agricultural activities to protect crops and improve productivity. However, uncontrolled use of pesticides leads to residues of these compounds in vegetables, especially in edible vegetables. In addition, some pesticides are persistent organic contaminants, toxic, and bioaccumulate compounds. Some compounds are listed in the potential compounds that caused cancer according to the International Agency for Research on Cancer (IARC) [1]. In Vietnam, the Ministry of Agriculture and Rural Development [2] and the Ministry of Health [3] have published the ban and restricted list of pesticides and the maximum level of residual pesticides in plant-related food.

Vietnamese cannon eggplant (*Solanum macrocarpon,* Ca phao in the Vietnamese language) was popularly used as fermented eggplant or salad. Vietnamese cannon eggplant is also used in combination with other foods, like a mixture of cannon eggplant and fermented shrimp. Therefore, the determination of pesticides in these samples is important in terms of food safety and human health. However, a few works focus on the development of the analytical method for the analysis of pesticides in this sample. In addition, most methods are only used for the analysis of pesticides in general eggplant [4].

To date, many analytical methods have been developed and introduced for the analysis of pesticides in vegetable samples, especially eggplant samples, such as liquid chromatography (LC), gas chromatography (GC) using several detectors [5]. Mass spectrometry (MS) detection, especially high-resolution mass spectrometry, was the most popular because of selectivity and sensitivity [6]. In addition, LC-MS and GC-MS in combination with stable isotopically labelled internal standards were used to improve the robustness of the analytical method. In general, LC-MS is the most popular method than GC-MS for the analysis of water-soluble and polar pesticides [7]. The limits of detection and limit for quantification of these methods

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for analysis of pesticides were ranged (from 1 µg/kg to 3 µg/kg) and (from 3 µg/kg to 10 µg/kg), respectively.

In this work, an ultrahigh performance liquid chromatography (UPLC) in combination with electrospray ionization tandem mass spectrometry (MS/MS) was used for analysis of pesticides in Vietnamese cannon eggplant samples. Pesticide in the samples was extracted by QuEChERS AOAC 2007.01 kit, and sample matrix was cleaned up using an Oasis HLB cartridge. Pesticide in the extract solution was separated on a reverse phase LC column and detected by a mass spectrometer equipped with positive electrospray ionization in multiple reaction monitoring mode. The developed method was validated according to the guidelines of the EU and SANTE 2021 through spiking experiments [8, 9]. Finally, the validated method was used for the determination of 11 pesticides in five Vietnamese cannon eggplant samples that were collected in the local market in Gia Lam, Ha Noi.

2. Chemical, Instrument, and Method

2.1. Chemical

Pesticides, including: acetamiprid, buprofezin, diflubenzuron, diuron, hexaconazole, imidacloprid, metribuzin, mevinphos, myclobutanil, and propoxur were purchased from Sigma Aldrich (Singapore). Three stable isotopically labelled internal standards, including dimethoate-D6, dichlorvos-D6, and malathion-D6, were collected from Toronto Chemical Research, Canada. Single stock solution (1000 µg/mL) of pesticides and internal standards was separately prepared by dissolving solid substances in either methanol or acetonitrile. A mixed standard solution was prepared by dilution of single stock solutions in a mixture of methanol and water (1/1 by volume). Working solutions with concentration from 0.5 ng/mL to 100 ng/mL containing three internal standards with concentration 50 ng/mL were prepared by dilution mixture standard solution and internal standard solution in a mixture of methanol and water (1/1 by volume). All of the standard solutions were stored in an amber LC vial and kept in a freezer at -20 °C until use.

Ammonium acetate, methanol, and formic acid, LC-MS grade chemicals were purchased from Sigma Aldrich, Singapore. QuEChERS kit (AOAC 2007.01) was purchased from Thermo Scientific, Germany. Oasis Prime HLB SPE cartridge (60 mg/3 mL) was collected from Waters, USA. Mobile phase was prepared pre-weighed amount of ammonium acetate and concentrated formic acid (LC-MS grade 98%, Sigma Aldrich, Singapore) in deionized water or methanol. Mobile phase was filtered through 0.22 µm syringe filter (Regenerate cellulose) and degassed by ultrasonic before use.

2.2. Instrument and Method

A Shimadzu LC-MS/MS system model 8050 (Japan) was used for analysis of pesticides. The LC-MS/MS system includes an online degasser model DGU 405, quaternary pump model LC-40S X3, low-pressure gradient mixer, automatic liquid sample autodampler SIL40C X3, column oven CTO-40S, mass spectrometer model 8050 equipped with an electrospray ionization source was used for detector. LabSolution version 5.1.18 (Shimadzu, Japan) was used for control of the LC-MS/MS system, data handling, and processing.

Table 1. Operating conditions of UPLC-MS/MS for pesticide analysis on the Shimadzu 8050 LC-MS system

Parameter	**Value**
UPLC parameter	
Column	Shimadzu XRD ODS II (2.1 µm, 2.1 mm×100 mm)
Column temperature	40 ºC
Mobile phase	Channel A: 5 mM ammonium acetate and 0.1% formic acid in deionized water Channel B: 5 mM ammonium acetate and 0.1% formic acid in methanol
Elution mode	Gradient
Flow rate	0.3 mL/min
Sample compartment temperature	10 ºC
Injection volume	5 µL
MS parameters	
Ionization source	Electrospray ionization ESI
Polarity	Positive (+ESI)
Ionization temperature	300 ºC
Ionization voltage	+ 4kV
De-solvating temperature	525 ºC
Dry gas flow	10 L/min
Nebulizer gas flow	3 L/min
Heated gas flow	10 L/min
Measurement mode	MRM (multiple reaction monitoring)
Quantification mode	Ratio of peak area

A Shimadzu XRD ODS II (100 mm × 2.1mm × 2.1µm) column was used for the separation of pesticides. Mobile phases were 5 mM ammonium acetate and 0.1% formic acid in deionized water (Channel A), and 5 mM ammonium acetate and 0.1% formic acid in methanol (Channel B). A 5 µL of standard/sample solution was injected by the autosampler. The temperature of the column was kept at 40 ^{o}C. The flow rate of mobile phase was constantly kept at 0.3 mL/min throughout the whole chromatographic separation time. The analyzed pesticides were eluted from the column by gradient elution mode. The detailed information about the elution gradient program is as follows: an initial of 2% B was maintained for 0.5 min, increased linearly to 20% B within 1 min, and to 100% B within 24 min, and further maintained for 5 min, returned to 2% B immediately, and equilibrated for 8 min for the next injection. More details about chromatographic conditions and detection by MS/MS are listed in Table 1.

2.3. Samples

Five Vietnamese cannon eggplant samples were collected in the local market in Gia Lam, Ha Noi, in April 2024. The collection of samples followed the guidelines of the ISO 874: 1980 standard [10]. Samples were coded and transported to the laboratory. Non-edible parts were removed, and then samples were homogenized by a food processor. The homogenized sample was freeze-dried at -55 ^{o}C. Water content in the wet sample was calculated by the weight difference before and after being freeze-dried. The sample was analyzed as soon as possible or kept at -20 ^{o}C in aluminum foil in the zipped polypropylene bag for further analysis.

The sample was prepared by QuEChERS and then cleaned up by SPE according to a previous study with some modifications [11]. In brief, homogenized samples were kept at room temperature for at least 2 hours before weighing. 2.0 g of the homogenized sample was exactly weighed, and internal standards were spiked in the samples, and then the samples were kept at room temperature for equilibrium for at least two hurs before extraction. 8 mL of deionized water and 10 mL of acetonitrile were added to the samples and well-mixed with a vortex mixer. The sample was then extracted by QuEChERS (AOAC 2007.01, containing 6 grams of magnesium sulfate and 1.5 grams of sodium citrate). The sample was centrifuged at 5000 *xg* for 10 minutes, and the supernatant was collected in a new 15 mL PE tube. The solution was pre-concentrated under a gentle nitrogen flow to approximately 1 mL. The pH of solution was adjusted to 3 with concentrated formic acid and subjected to clean-up by solid phase extraction. Oasis Prime HLB 60 mg/3 mL (Waters, USA/) was used for solid phase extraction. The SPE cartridge was conditioned first with 5 mL of deionized water, 5 mL of methanol, and 5 mL of acidified deionized water (pH 3 adjusted by concentrated formic acid). The sample solution was loaded on the SPE cartridge using vacuum manifold. Chemical interferences were washed with 5 mL of acidified deionized water. Target analytes were eluted by a mixture of methanol and water (4:1 by volume), then evaporated under a gentle nitrogen flow to nearly dryness and reconstituted to 1 mL by a mixture of methanol and water (1:1 by volume). The sample solution was filtered through a syringe filter (0.22 µm regenerated cellulose membrane) and subjected to analysis by UPLC-MS/MS. The ratio of peak area was used for the quantification of pesticides in the sample.

2.4. Data Processing

LabSolution version 5.18 (Shimadzu, Japan) was used for control UPLC-MS/MS system, optimization, data handling, and data processing. The asymmetric factor of the peak was calculated by the European Pharmacopeia. The peak area of the analyte was integrated by LabSolutions software and used for quantification. Identification of the analysis pesticdes in the real sample was simultaneously performed by three parameters: retention time, two MS/MS transitions, and relative ion ratio associated with a given measurement uncertainty. In addition, selectivity of the method was defined by identification points according to the EU validation guideline [8] and the guideline for analysis of pesticides in vegetable, fruit samples SANTE 2021 [9].

Recovery of pesticides in the samples was conducted by spiking at three concentrations ((limit of quantification *(LOQ)*, *3*LOQ*, and *10*LOQ*). Limit of detection (*LOD*) and *LOQ* were determined by signal to noise ratio (*S/N*) of pesticides in spiked samples at low levels, where *S* was peak height and *N* was baseline. Both *S* and *N* were determined in the extracted ion chromatogram of the quantification MS/MS transition. *LOD* and *LOQ* were defined by 3**S/N* and 10**S/N*, respectively. For the assessment of repeatability and reproducibility, two sets of spiked samples were prepared. One set was analysed on the day that the sample was prepared. Another set was analysed the next day by the above UPLC-MS/MS method. The peak areas of 11 pesticides and the internal standard in the quantification MS/MS transition were integrated, and the standard deviation of peak area ratio was calculated in the following equations:

$$SD = \sqrt{\frac{(S_i - \overline{S})^2}{n-1}} \qquad (1)$$

$$RSD(\%) = \frac{SD}{\overline{S}} * 100 \qquad (2)$$

in which S_i and $\overline{S}$ were the peak area ratio of sample *i* and mean peak area ratio of all samples, respectively. The relative standard deviation (RSD) of the analysis of 5 spiked samples in one day, and the reproducibility was analysis of 5 spiked samples in three days was calculated and presented for repeatability and reproducibility.

Matrix effect (ME) was calculated as in the following equation:

$$ME(\%) = 100 * \frac{a'-a}{a}\text{ME} \qquad (3)$$

in which a' and a are slopes of calibration curves in solvent and in matrix-matched solution, respectively. Positive and negative values of matrix effect are presented enhancement and suppression of ionization in tandem mass spectrometry, respectively. All experiment was conducted at least in triplicate and mean value (peak area, retention time ...) was used for calculation. Blank sample was used for assessment of carry-over effect in sample preparation and sample injection in UPLC-MS/MS measurement. Data processing was performed by Shimadzu Labsolution, Microsoft Office Excel 2024 (Microsoft, USA), and Skyline MS (MacCross Lab, University of Washington, USA).

3. Results and Discussion

3.1. Optimization of UPLC-MS/MS for Analysis of Pesticides

3.1.1 Optimization of mass spectrometry

A mixture of standard solution containing 11 pesticides and three internal standards with a concentration of 1.0 µg/mL in a mixture of methanol and deionized water (1:1 by volume) was used for optimization of tandem mass spectrometry employing positive electrospray ionization. Operating conditions of tandem mass spectrometry were optimized by flow injection analysis using a mixture of channel A and channel B (1:1 by volume) as a carrier at a flow rate of 0.3 mL/min. Injection volume was set at 2 µL. Precursor ion was selected with a mass to charge ratio (*M*+1) Da, in which *M* is the molecular weight of pesticides. Product ions were selected by fragmentation of precursor ions at a suitable collision energy. For each analyte, one precursor ion and at least two product ions were selected as exception special analytes (for example, diuron, hexaconazole, and dichlorvos-D6 in this work). Information about precursor ions, product ions, collision energy, and other parameters of all analyzed pesticides after optimization is listed in Table 2.

Table 2. Precursor ion, product ion, collision energy, and other parameters of all analyzed pesticides in Shimadzu LC-MS 8050

No	Analyte	t_R, (min)	MW (g/mol)	Precursor ion, Da	Product ion, Da	CE (eV)	Q1 Pre Bias (V)	Q2 Pre Bias (V)
1	Imidacloprid	5.6	255.7	256.1	**175**	**-21**	**-19**	**-18**
					209	-16	-13	-24
2	Mevinphos	6.0	224.2	225.1	**193**	**-6**	**-18**	**-15**
					126.9	-25	-25	-15
3	Acetamiprid	6.3	222.7	223.2	**126.1**	**-21**	**-27**	**-15**
					128.1	-31	-20	-30
4	Metribuzin	9.6	214.3	215.2	**187.1**	**-19**	**-15**	**-15**
					84.1	-25	-11	-15
5	Propoxur	9.8	209.2	210.2	**110.9**	**-16**	**-22**	**-20**
					168.1	-8	-16	-21
6	Isoprocarb	12.2	193.2	194.2	**95.1**	**-17**	**-15**	**-30**
					137	-11	-23	-23
7	Diuron	12.9	233.1	233.1	**72**	**-23**	**-21**	**-30**
				235.1	72	-25	-11	-22
8	Myclobutanil	16.6	288.8	289.1	**70**	**-23**	**-21**	**-27**
					125	-33	-29	-25
9	Diflubenzuron	16.9	310.7	311.1	**141**	**-31**	**-11**	**-30**
					158	-10	-21	-20
10	Hexaconazole	19.4	314.2	314.1	**70.1**	**-24**	**-16**	**-13**
				316.1	70.1	-20	-15	-13
11	Buprofezin	21.2	305.4	306.3	**201.1**	**-13**	**-16**	**-12**
					116.1	-17	-26	-18
12	Dimethoate-D6 (IS1)	6.3	235.3	236	205	-10	-17	-13
13	Dichlorvos-D6 (IS2)	9.7	227.0	229	115	-20	-25	-22
				227	115	-20	-16	-21
14	Malathion-D10 (IS3)	15.9	340.4	341	100	-26	-13	-19

Note: for a given pesticide MS/MS transition with m/z in bold format was used for quantification and the other was used for confirmation.

3.1.2. Optimization of chromatographic separation

Analysis of pesticides by reverse-phase liquid chromatography, the mobile phase, including water, methanol, and acetonitrile, is used, especially in combination with mass spectrometry. The component of mobile phase should be compatible with operating conditions of mass spectrometer. In this work, the Shimadzu XRD ODS II was used for separation of pesticides. Mobile phase was deionized water and methanol, both solutions contained 5 mM ammonium acetate, and 0.1% formic acid. Many elution gradient programs were tested for separation of pesticides. Peak shape and sensitivity, two important parameters, were taken into account during the optimization process. The final optimized elution gradient program is as follows: an initial of 2% B was maintained for 0.5 min, increased linearly to 20% B within 1 min, to 100% B within 24 min, and further maintained for 5 min, returned to 2% B immediately, and equilibrated for 8 min. With these gradient chromatographic separation conditions, all peaks were in good shape (asymmetric factor at 10% of peak height was from 0.9 to 1.2). Therefore, these chromatographic separation and detection conditions were selected for the next experiments. Fig. 1 depicts a chromatogram of 11 pesticides in the standard solution that was separated at the optimized operating conditions.

3.2. Validation of the UPLC-MS/MS

3.2.1. Linear range

Eight independent standard solutions of 11 pesticides with concentrations from 0.5 ng/mL to 100 ng/mL and containing three stable isotopic labelled internal standards at 50 ng/mL were prepared in mixture of methanol and deionized water (1:1 by volume). These standard solutions were injected into the UPLC-MS/MS at the above optimized operating conditions. Peak areas of all pesticides and internal standards were integrated, and the ratio of peak area between pesticide and appropriate internal standard was calculated. The ratio of peak area was plotted as a linear function of pesticide concentration. The regression equation and correlation coefficient are listed in Table 3.

3.2.2. Limit of detection and limit of quantification

LOD and LOQ were calculated by *S/N* and this ratio was automatically exported from Shimadzu LabSolution in this work. As can be seen in Table 3, LODs of all analyzed pesticides are from 0.03 µg/kg to 0.1 µg/kg for the wet weight sample. LOQs were from 0.11 µg/kg to 0.33 µg/kg for wet weight samples. It could be concluded that the UPLC-MS/MS has been sensitive enough for analysis of pesticides in real samples according to Vietnamese Ministry of Health standard and comparable with a recent publication [12].

3.2.3. Repeatability and reproducibility

RSD was used for assessment of repeatability and RSD was calculated and listed in Table 4. As shown in Table 4, RSD ranges from 5.8% to 12.3%. RSDs fall in the acceptable range according to AOAC guideline for validation of the analytical method [13]. It could be concluded that the repeatability of the developed UPLC-MS/MS is suitable for analysis of pesticides in vegetable samples. Reproducibility was also investigated and listed in Table 4. RSDs of the reproducibility experiments range from 7.8% to 19.1%. In summary, the repeatability and reproducibility of the UPLC-MS/MS were suitable for analysis of pesticides in vegetables according to AOAC Guideline for the validation of the analytical method.

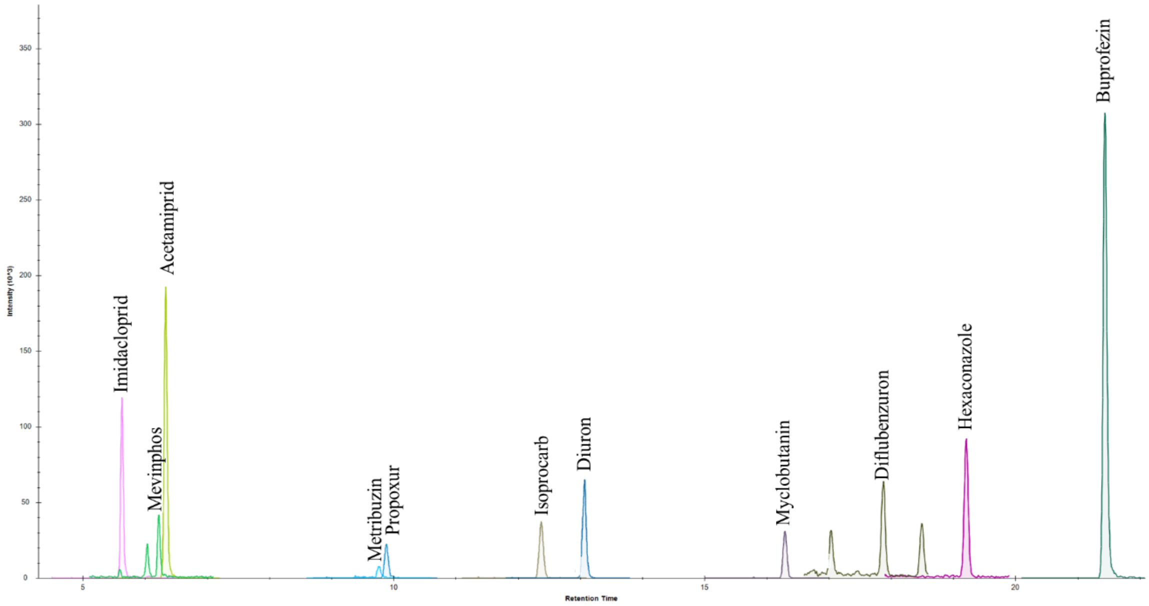

Fig. 1. UPLC-MS/MS chromatogram of 11 pesticides in standard solution

Table 3. Analytical characteristic parameters of the UPLC-MS/MS based method for pesticide analysis in *Solanum macrocarpon* fruit

No	**Analyte**	**Internal standard**	**Regression equation**	R^2	LOD^* **µg/kg**	LOQ^* **µg/kg**
1	Imidacloprid	IS1	$y = 0.0057x + 0.0029$	0.9997	0.10	0.33
2	Mevinphos	IS1	$y = 0.0022x - 0.0005$	0.9999	0.06	0.19
3	Acetamiprid	IS1	$y = 0.008x + 0.0052$	0.9991	0.03	0.11
4	Metribuzin	IS1	$y = 0.044x - 0.0209$	0.9996	0.09	0.31
5	Propoxur	IS2	$y = 0.0422x - 0.0191$	0.9995	0.05	0.16
6	Isoprocarb	IS2	$y = 0.068x - 0.0202$	0.9993	0.05	0.18
7	Diuron	IS2	$y = 0.1517x + 0.0246$	0.9998	0.06	0.20
8	Myclobutanil	IS3	$y = 0.0309x - 0.003$	0.9999	0.10	0.32
9	Diflubenzuron	IS3	$y = 0.0378x + 0.0128$	0.9995	0.07	0.24
10	Hexaconazole	IS3	$y = 0.031x + 0.001$	0.9999	0.05	0.15
11	Buprofezin	IS3	$y = 0.091x + 0.0196$	0.9998	0.04	0.14

In which: y ratio of peak area, x concentration of pesticide, LOD, and LOQ present in µg/kg for wet weight sample.

Table 4. Repeatability, reproducibility, recovery, and matrix effect of the UPLC-MS/MS based method for analysis of pesticides in *Solanum macrocarpon* fruit

No	**Analyte**	**Recovery (%)**	**Matrix effect (%)**	**Repeatability (%RSD)**	**Reproducibility (%RSD)**
1	Imidacloprid	78.6 ± 9.4	-12.3	5.8	7.8
2	Mevinphos	75.5 ± 14.4	-4.5	7.1	9.4
3	Acetamiprid	81.9 ± 8.9	+8.7	8.1	9.5
4	Metribuzin	86.6 ± 9.6	-3.4	7.4	9.1
5	Propoxur	81.5 ± 10.4	-21.6	9.1	11.1
6	Isoprocarb	80.9 ± 16.4	-11.3	9.7	12.1
7	Diuron	78.7 ± 8.8	-10.5	9.7	12.9
8	Myclobutanil	81.2 ± 13.8	+15.2	9.8	13.7
9	Diflubenzuron	82.6 ± 13.3	-13.5	10.3	11.5
10	Hexaconazole	78.5 ± 4.7	+5.2	12.3	19.1
11	Buprofezin	78.3 ± 8.3	-17.8	8.9	10.9

3.2.4. Selectivity

Selectivity of the analytical method was presented by identification points (IPs). IPs of all analyzed pesticides were 5 or 6 according to guideline for method validation from EU directive 808/2021. Besides, no peak was eluted in the blank sample and a peak appeared at the same retention time in the spiked sample.

3.2.5. Recovery

A QuEChERS, for example, AOAC 2007.01 kit, was recommended as an official sample preparation method for analysis of pesticides in vegetables, especially in eggplant samples. However, matrix effect was the main contribution to the total sample preparation procedure efficiency according to previous work [11]. Therefore, the extractant after QuEChERS was further cleaned up by solid phase extraction using an Oasis Prime HLB cartridge. Recovery of the whole sample preparation procedure was quantified by the spiked experiments in the real sample matrix because no commercially available certified reference materials for this kind of sample matrix so far. Spiked experiments were conducted at three concentration levels, extracted, and cleaned up as mentioned above. Mean values of recoveries associated with relative standard deviations are listed in Table 4. Overall recoveries of analyzed pesticides range from (75.5 ± 14.4)% to (86.6 ± 9.6)%.

Recoveries of all analyzed pesticides fell in the acceptable range (from 80% to 120%) according to EU 808/2021 and SANTE 2021 Guideline for validation of analytical method for analysis of pesticides in vegetable and fruit samples. It should be concluded that the QuEChERS in combination with solid phase extraction clean-up was an intended-use sample preparation procedure for analysis of pesticides in Vietnamese cannon eggplant sample by UPLC-MS/MS.

3.2.6. Matrix effect

Matrix effect is a critical parameter that needs to be assessed in UPLC-MS/MS, especially in using electrospray ionization technique. Many methods were introduced and used for the assessment of the sample matrix. In this study, matrix effect was investigated by comparing the slope of calibration curves in neat solvent and in matrix-matched solution. The sample matrix was calculated using (3) in section 2.4. The sample matrix effect of all analyzed pesticides is listed in Table 4. As clearly shown in Table 4, ionization suppression occurred in most of analyzed pesticides (approximately 73% of total number of analytes with negative ME value) and a few analytes with ionization enhancement (nearly 23% of total number of analytes with positive ME value). However, values of ME are smaller than ± 20%, except for propoxur which ME was -21.6%. In comparison with previous work, the sample matrix has been improved in this work when QuEChERS in combination with SPE was applied [11]. It concluded that the sample matrix was a negligible exception of propoxur [14, 16]. Moreover, matrix-matched calibration curve was used for quantification of pesticides in Vietnamese cannon eggplant in this work.

3.3. Pesticides in Samples

The validated UPLC-MS/MS was finally applied to analyze 11 pesticides in five Vietnamese cannon eggplant samples that were collected in the local markets. The concentration of these compounds is listed in Table 5.

As clearly shown in Table 5, some pesticides were detected in the samples analyzed. Pesticides were detected in samples CP01, CP2, and CP3 with high frequency. In samples CP4 and CP5, concentration of pesticides was below LOQs but higher than LODs with some compounds. In comparison with another study, the distribution profile of pesticides in Vietnamese cannon eggplant in this work was different [4]. It could be explained by the different growing conditions.

However, concentration of all analyzed pesticides was below the maximum residual level according to Vietnam Ministry of Health standard as well as European Union maximum residual level [3], [17]. For instance, acetamiprid was detected in two samples at concentrations of 0.36 ± 0.09 µg/kg and 0.64 ± 0.15 µg/kg, meanwhile, the maximum residual level of this compound in the vegetable was set at 0.2 mg/kg and 0.01 mg/kg for general pesticides according to Vietnam Ministry of Health and European Union regulations, respectively.

4. Conclusion

The UPLC-MS/MS method was successfully developed and applied to analyze 11 pesticides in Vietnamese cannon eggplant samples. All-important parameters of the analytical method, such as linear range, LODs, LOQs, repeatability, recovery, etc., were systematically investigated and presented. The validated analytical method was an intended-use method for the analysis of pesticides in Vietnamese cannon eggplant. The validated method was then applied for analysis of 11 pesticides in five samples that were collected in the local market.

Table 5. Concentration of pesticides in the analyzed samples

No	**Analyte**	**Concentration (µg/kg wet weight)**				
		CP1	**CP2**	**CP3**	**CP4**	**CP5**
1	Imidacloprid	0.34 ± 0.08	0.31 ± 0.07	<LOQ	<LOQ	<LOQ
2	Mevinphos	0.79 ± 0.19	<LOQ	0.38 ± 0.1	<LOQ	<LOQ
3	Acetamiprid	0.36 ± 0.09	0.64 ± 0.15	<LOQ	<LOQ	<LOQ
4	Metribuzin	<LOQ	0.54 ± 0.12	<LOQ	<LOQ	<LOQ
5	Propoxur	<LOQ	0.38 ± 0.09	<LOQ	<LOQ	<LOQ
6	Isoprocarb	<LOQ	<LOQ	0.14 ± 0.04	<LOQ	<LOQ
7	Diuron	<LOQ	<LOQ	0.49 ± 0.12	<LOQ	<LOQ
8	Myclobutanil	0.67 ± 0.16	0.57 ± 0.13	<LOQ	<LOQ	<LOQ
9	Diflubenzuron	<LOQ	<LOQ	0.31 ± 0.08	<LOQ	<LOQ
10	Hexaconazole	0.52 ± 0.13	<LOQ	<LOQ	<LOQ	<LOQ
11	Buprofezin	<LOQ	0.71 ± 0.16	<LOQ	<LOQ	<LOQ
Total		**2.68**	**3.15**	**1.32**	**<LOQ**	**<LOQ**

Experimental results indicated that some pesticides were found in the samples analyzed. However, the concentration of these compounds was lower than the maximum level according to the Vietnam Ministry of Health and the EU. For the next study, the fate of these compounds and their metabolites will be investigated and addressed.

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