

Development and Validation of Analytical Method for Carbamate Pesticide Residues in Vietnam Agricultural Products

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Abstract

For the purpose of determining the residues of some recently registered pesticides in Vietnam agricultural products, a quick and precise approach based on a modification of QuEChERS extraction and liquid chromatography tandem mass spectrometry (LC-MS/MS) has been studied. QuEChERS stands for “quick, easy, cheap, effective, rugged and safe”, using acetonitrile as an extraction solvent and MgSO₄/PSA for cleaning. By using the LC-MS/MS method, carbamate pesticide residues were identified and measured on a variety of sample matrices. The approach performed well in the concentration ranges between 0.1 and 200 ppb. All the pesticides used in the testing had LOQ values that were less than 10 ppb and repeatability of less than 20% RSD. For a variety of agricultural goods, including cabbage, truffle, rice, and grape, the approach has been successfully used and detected 21/100 samples containing pesticide residues. There were 4 samples with pesticide residues exceeding the allowable levels, namely DL09, DL14 (Propamocarb), and DL10, DL15 (Metalaxyl).

Keywords: LC-MS/MS, carbamate group, residues pesticides, QuEChERS

1. Introduction

Plant protection chemicals (PPC) include some main groups of substances as follows: organochlorine, organophosphates, pyrethroid, carbamate, neonicotinoid, macrocyclic lactone, inorganic, group of plant origin [1]. Some representatives of the carbamate group are bendiocarb, centhiocarb, carbaryl, diethofencarb, fenobucarb, isoprocarb, pirimicarb, propoxur, aldicarb, carbofuran, methomyl, indoxacarb [2]. Carbamates have common characteristics of high toxicity, narrow spectrum of action, short potency, and poor stability, but can be combined with other plant protection substances to enhance the spectrum of action. Therefore, carbamate compounds are used very commonly today. A small amount of PPC residues can also cause great harm to the environment and human health [3-5]. Thus, it is necessary to have suitable analytical methods to accurately determine pesticides residues (PR). PR analysis consists of two steps, sample extraction and sample analysis. The QuEChERS method is a sample extraction method published in 2003 by Anastassiades and Lehotay [6]. The sample was extracted once with acetonitrile, the solution was pH stabilized during extraction. Then, magnesium sulfate was used for removal of water from the sample. Samples were cleaned from residual acids and water by PSA, MgSO₄, GCB adsorbent. This extraction method gives good recovery results. Lesueur *et al.* used the QuEChERS

extraction method according to CEN/TC 275 to extract 4 matrices of grapes, lemons, onions, and tomatoes. Then analyze the GC/SQ-MS with HPLC/IT-MS. The results show that the extraction method has a recovery of 70-110 % [7]. The authors Kyung Junn Lee's team used the QuEChERS extraction method to identify 234 pesticides in Korean herbs and the recovery rates were all from 62-119 % [8]. Thus, QuEChERS is a fast, effective, highly reproducible, and safe method for the user.

Liquid chromatography coupled with electrospray mass spectrometry (LC-MS/MS) is a highly sensitive and selective analytical technique that is widely used for qualitative and quantitative research applications. [9-11]. The authors, Mi Young Yun, used the LC-MS/MS system to identify residues of 118 pesticides. The method Limit of detection (LOQ) for each substance was less than 0.5 µg/kg. It can be seen that the LC-MS/MS method achieves very high sensitivity and stability [8]. Carbamate group pesticides in fruit juice were analyzed by Gianni Sagratini by LC/MS and LC/QIT-MS methods [12]. Thus, LC-MS/MS is a very good technique for quantitative analysis of trace and ultratrace pesticide residues. The detection limit of the method is very small, possibly down to ppb concentrations.

The purpose of this study is to survey and select the optimal conditions to conduct the LC-MS/MS method for the analysis of 15 substances belonging to

the carbamate (aldicarb, aldicarb sulfoxide, aldicarb sulfone, carbofuran, carbosulfan, fenobucarb, iprovalicarb, isoprothiolane, metalaxyl, methomyl, oxamyl, pirimicarb, propamocarb, propboxur, indoxacarb) in Vietnam agricultural products.

2. Experiment

2.1. Research Subjects

Research subjects are agricultural products of plants, including samples which has water content over 80% such as cucumbers; sample containing acid which has water content over 80 % such as oranges and dry sample.

2.2. Chemicals

Acetonitrile (CH_3CN), formic acid (HCOOH), ammonium acetate ($\text{CH}_3\text{COONH}_4$), primary secondary amine (PSA) (particle size 40-60 μm), magnesium sulfate (MgSO_4), sodium chloride (NaCl), sodium hydrogencitrate sesquihydrate ($\text{Na}_2\text{C}_6\text{H}_6\text{O}_7 \cdot 1.5\text{H}_2\text{O}$) and Tri – sodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) were purchased from Merck.

The standard pesticides including aldicarb-sulfone, aldicarb, aldicarb sulfoxide, aldicarb sulfone, carbofuran, carbosulfan, fenobucarb, iprovalicarb, isoprothiolane, metalaxyl, methomyl, oxamyl, pirimicarb, propamocarb, propboxur, and indoxacarb was provided by Dr. Ehrenstorfer (Augsburg, Germany) with purity more than 95 %.

Standard stock solution with a concentration of 1000 $\mu\text{g}/\text{ml}$ was prepared in acetonitrile (ACN) and stored in the dark at a temperature of 5 °C average. The intermediate solutions of 10 $\mu\text{g}/\text{mL}$ (solution A) and 1 $\mu\text{g}/\text{mL}$ (solution B) were prepared from the standard stock solution.

2.3. Equipment and Tools.

Samples after a sample preparation were injected to LC-MS/MS Shimadzu 8040 triple quadrupole mass spectrometer coupled liquid chromatography system. The system has auto sample pumping equipment SIL-2QACXR Nexera, Low pressure pump LC-20ADXR Nexera, Oven CTO-10ASvp Shimadzu and system control CBM-20Alite. The column ZORBAX SB RPC18 150 mm x 4,6 mm, 5 μm was used in the system.

A binary mobile phase was composing of solvent A (ACN/ H_2O ratio of 9:1 and 5 mM ammonium acetate) and solvent B (ACN/ H_2O ratio of 1:9 and 5 mM ammonium acetate).

Analytical balance (XT22A, Precisa), grinding machine (PAXD-MX-AC400WRA, Panasonic), centrifuge (Rotina 38R, Hettick), machine swirling (IKA),

micro pipettes, and centrifuge tubes (50 ml and 15 mL) were used in this research.

2.4. Sample Preparation

Based on the method EN 15662 we made some changes to QuEChERS extraction to fit the pattern of agricultural matrix. Schematic overview of the sample processing process is shown in Fig. 1.

The raw samples about 2 kg were taken, cut into small pieces, and then 500 g representative samples were homogenized by a grinding machine. About 10 g of sample (2 g for dry sample) homogenized was transferred into 50 mL centrifuge tube, then added standard solution, soaked for 30 minutes. X (mL) NaOH was added to the orange sample (acid sample). For rice samples, it was soaked in water. Then 10 mL ACN, 1 g of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 1 g NaCl and 0,5 g $\text{Na}_2\text{C}_6\text{H}_6\text{O}_7 \cdot 1.5\text{H}_2\text{O}$ were added sequentially. The mixture was shaken for about 15 minutes, then Y(g) anhydrous MgSO_4 was added and centrifuged at 3000 rpm for 5 min. After that, 4 mL of sample was transferred to a 15 mL centrifuge tube which had Z:K ratio PSA/ MgSO_4 , shaken for about 30 seconds, and centrifuged it at 3000 rpm for about 5 minutes. Finally, the extracted sample was transferred to a 2 mL vial and added V (mL) formic acid. X, Y, Z, K, V are survey information.

2.5. Assessment Methods

Surveys of the method through specificity, linearity, limit of detection, limit of quantification, accuracy, and measurement uncertainty.

3. Result and Discussion

3.1. Survey Conditions LC - MS/MS

3.1.1 Spectral fragment condition

By immediately injecting a mixture of standard mix pesticides with a concentration of 10 ng/mL into MS and using software for evaluation, the conditions for the molecular ion, product ion bombardment, and ideal energy were established. The results are listed in Table 1.

3.1.2 Mobile phase solvent ratio

At 100 % mobile phase ratio of A channel for high signals, all substances are eluted. However, for some substances such as Carbofuran, Isoprothiolane, Propoxur the signal is more sensitive in different ratios like 70 %A. Therefore, it is necessary to set the solvent gradient so that the active substances are all eluted with the highest signal. Through the survey, the segmented gradient profile for the gradient elution of the sample is presented in Fig. 2. The program shows that the substances were all eluted with good shape peaks and high intensity peaks.

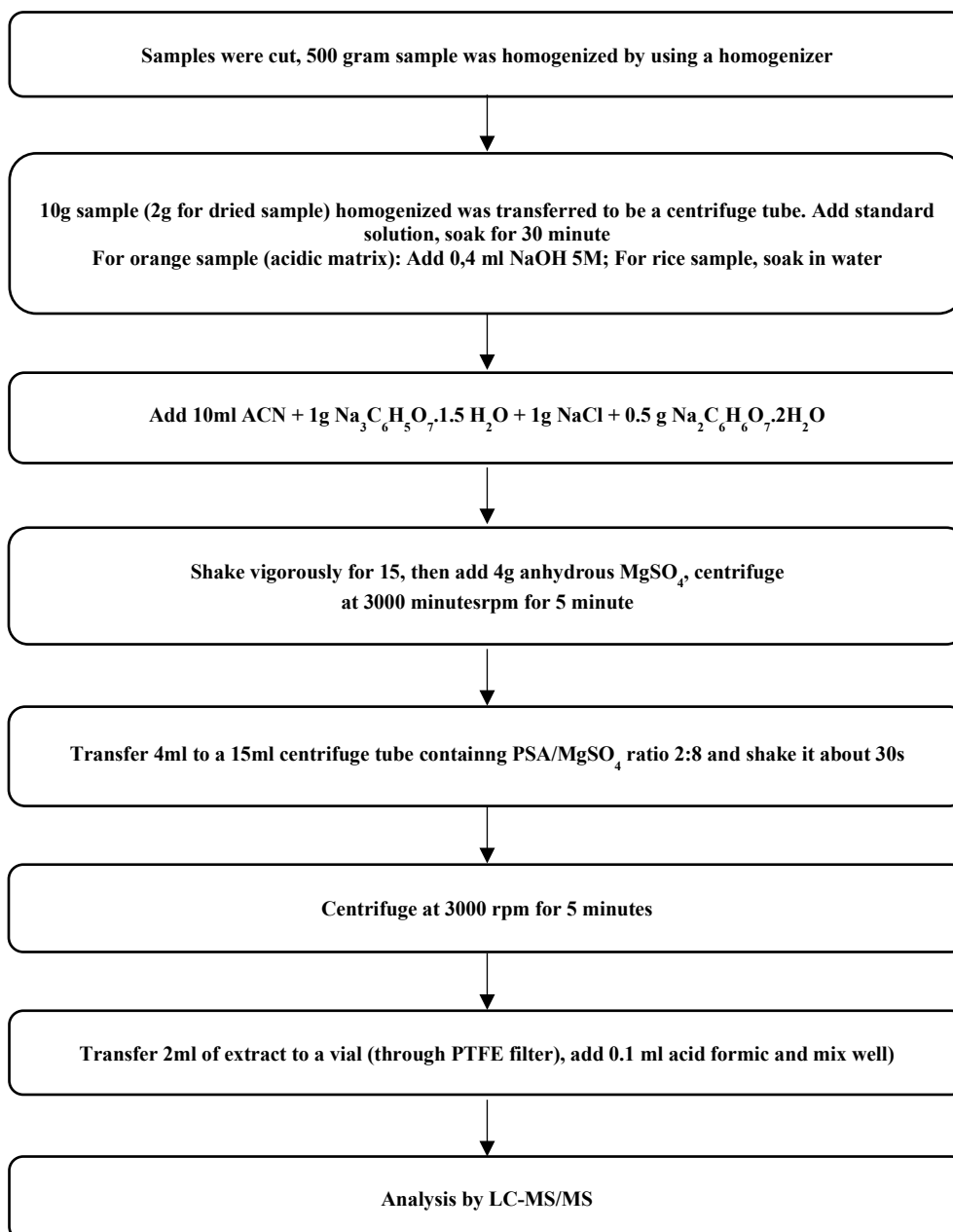


Fig. 1. Schematic overview of the sample preparation for LC-MS/MS analysis

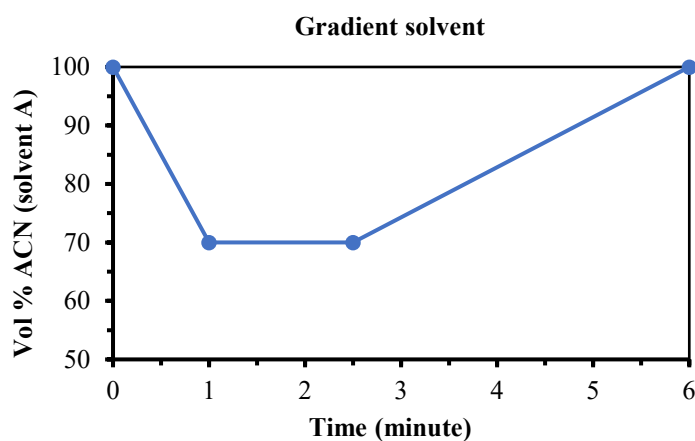


Fig. 2. The segmented gradient profile for the gradient elution of the sample

Table 1. The conditions MS analysis for 15 pesticides of carbamate group by LC-MS/MS

Pesticide	Precursor Ion	Product Ion	Dwel (ms)	CE (V)	Q1 Pre Bias (V)	Q2 Pre Bias (V)
Aldicarb sulfone	240.1	149.00	3	-18	-26	-26
		86.10	3	-24	-13	-23
Aldicarb sulfoxide	207.10	132.10	11	-6.0	-14	-27
		89.00	11	-14.0	-13	-15
Carbofuran	222	164.90	11	-12	-10	-30
		122.80	11	-20	-10	-22
Carbosulfan	381	117.90	11	-20	-17	-20
		159.90	11	-15	-17	-30
Fenobucarb	208	152.00	14	-25	-30	-30
		95.00	14	-53	-30	-30
Iprovalicarb	321	119.00	11	-21	-21	-22
		202.90	11	-9	-22	-11
Isoprothiolane	291	213.00	11	-11	-10	-14
		189.00	11	-12	-21	-17
Metalaxyl	280.10	219.90	11	-14	-10	-20
		160.00	11	-24	-20	-14
Methomyl	163	106.10	11	-12	-11	-22
		87.90	11	-11	-11	-16
Oxamyl	237.00	90.00	11	-8	-11	-15
		71.90	11	-12	-11	-27
Pirimicarb	239.10	72.10	11	-23	-16	-27
		181.90	11	-15	-17	-16
Propamocarb HCL	189.20	102.00	11	-17	-12	-18
		144.00	11	-13	-15	-12
Propoxur	210.10	111.00	11	-14.0	-15.0	-18.0
		168.00	11	-8.0	-16.0	-14.0
Aldicarb	208.10	89.10	11	-13.0	-14.0	-16.0
		116.00	11	-8.0	-14.0	-16.0
Indoxacarb	528.0	218.20	3	-14.0	-11	-17
		249.10	3	-27.0	-11	-26

3.1.3. Mobile phase flow rate

The results of the flow rate investigation of the compound is that the compounds' peak signal is significantly impacted by the mobile phase flow rate. High speeds cause the active ingredient to elute quickly, overlapping area was occurred, the sensitivity of the method was decreased. Most compounds are eluted and have high measurement signal at a flow rate of 0.3 to 0.5 mL/min, and the peaks are symmetrical. Some compounds, such carbosulfan and propamocarb HCL, exhibit substantially smaller signals at 0.3 mL/min. In order to simultaneously identify plant protection active ingredients with the highest stability and peak signal, a flow rate of 0.5 mL/min was chosen.

In summary, measurement conditions of the LC-MS/MS system for the analysis of carbamate group are shown in Table 2.

Table 2. Schematic of the sample preparation for LC-MS/MS analysis

STT	Parameters	Conditions
1	Analysis column	ZORBAX SB RPC18 150 mm × 4,6 mm, 5 μm
2	Suction volume	5 μl
2	Column temperate	40 °C
4	Ionization mode	ESI/MRM
5	Carrier gas flow	3.0 L/min
6	Drying air flow	8.0 L/min
7	Interface Voltage	4.5 kV
8	DL pipe temperature	250 °C
9	IG Vacuum	1.8e-003 Pa
10	Speed line	0.5 L/min
11	Detector potential	1.98 kV

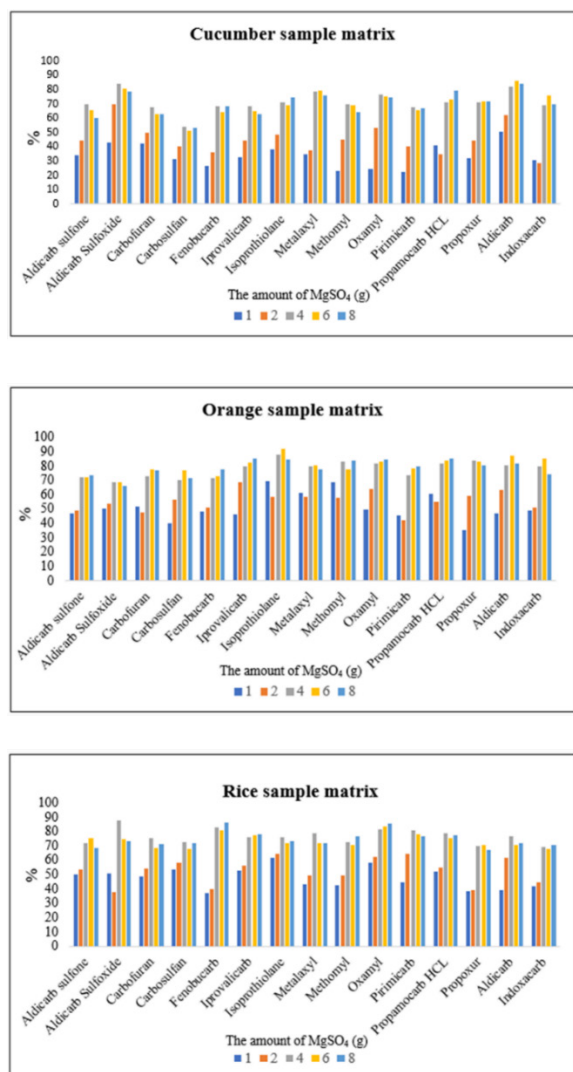


Fig. 3. Effect of the amount of MgSO₄ on the recovery on different matrix

3.2. Investigation of Sample Extraction Conditions

3.2.1. The effect of the amount of MgSO₄

The effect of the amount of MgSO₄ on the recovery results on cucumber, orange and rice samples are shown in Fig. 3. The results show that, with all 3 samples in the rough cleaning stage, if a small amount of MgSO₄ (1 and 2 g) is used, most of the substances have low recovery, because the MgSO₄ content is not enough to absorb all the water in the sample, leading to the pesticide content being partially dissolved into the aqueous phase. In addition, the excess water content in the column affects the process of spreading in the column, leading to poor separation of substances, so the recovery is low. At higher levels of MgSO₄ (4, 6, 8 g), the recoveries were not significantly different. Therefore, to save chemicals, we choose to use 4 g MgSO₄ in this period.

3.2.2. Effect of PSA/MgSO₄ ratio

At the stage of purification, the ratio of PSA/MgSO₄ also affects the recovery of the active ingredients. Experimental results show that with all 3 matrices, at the ratio of 2:8 for the highest recovery of active ingredients, the PSA content is enough to clean the substrates.

3.2.3. The effect of the amount of formic acid

The results show that in all 3 samples, if the formic acid content is low (0.05), the recovery of the active ingredients is low, due to the solution. The final extract is not stable. At the formic acid content of 0.1-0.3 mL, the best recoveries were obtained, not much different from each other. Therefore, for the purpose of optimizing the extraction process to achieve efficiency and economic efficiency, we choose 0.1 mL of formic acid to add to the final extract.

3.2.4. Effect of pH on Orange Matrix Sample (Acid Sample)

The QuEChERS method is the most effective when extracting at pH of 5. Some pH-sensitive substances may give low recovery, so for samples with high acidity such as oranges, lemons, pH adjustment must be investigated by NaOH 5M.

The influence of the amount of 5M NaOH added to the orange matrix on the recovery is shown in Fig. 4. The results that the amount of acid added was about 0.3-0.4 stable, with high recovery efficiency. However, at 0.3 level, some recoveries are not as good as Aldicarb sulfone, so to optimize the process for the highest efficiency, choose the content of NaOH to be 0.4 mL.

3.2.5. Effect of soaking time on the recovery of rice sample matrix

The effect of soaking time on the recovery of rice samples are shown in Fig. 5. The results show that, at different time of soaking in water, the recovery of active ingredients does not have a significant difference, so to optimize in terms of time, we just need to add water and perform the next stage.

3.3. Method of Validation

3.3.1. Selectivity and specificity

The selectivity and specificity of the method are demonstrated in analyze blanks, standards and increments. The blank sample does not give an analytical signal, and the spike sample gives the same analytical signal as retention time on standard sample. A chromatogram of blank Metalaxy in cucumber matrix is shown in Fig. 6. and a chromatogram of LOQ Metalaxy in cucumber matrix is presented in Fig. 7.

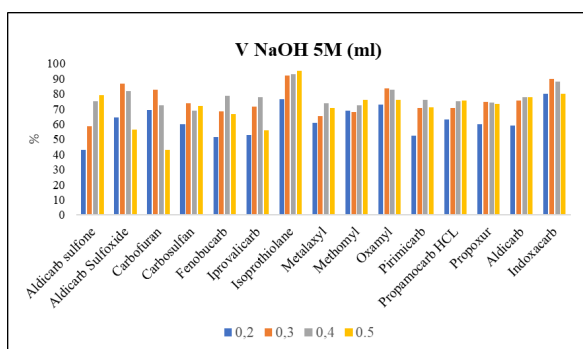


Fig. 4. Effect of the amount of 5M NaOH on the recovery

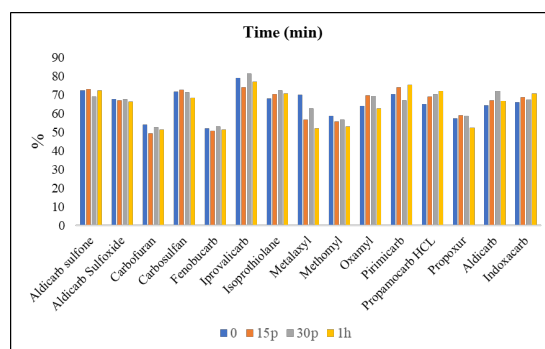


Fig. 5. Effect of soaking time on the recovery of rice sample matrix

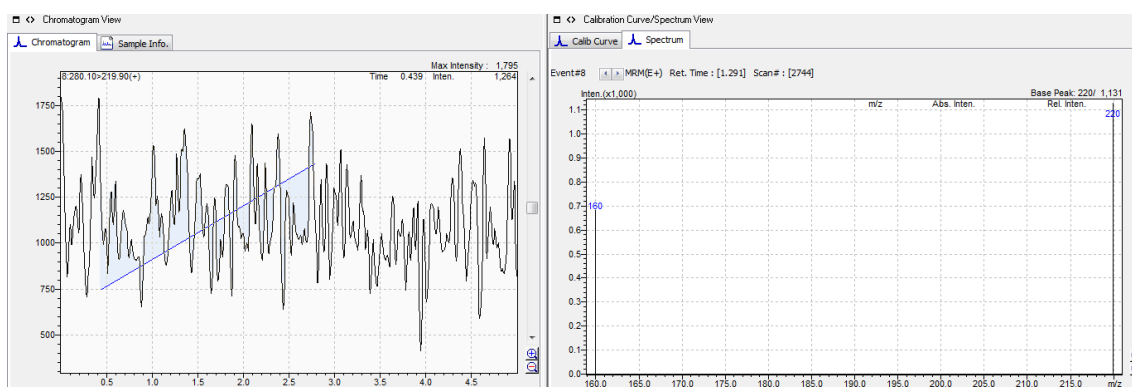


Fig. 6. Chromatogram of blank Metalaxyl in cucumber matrix

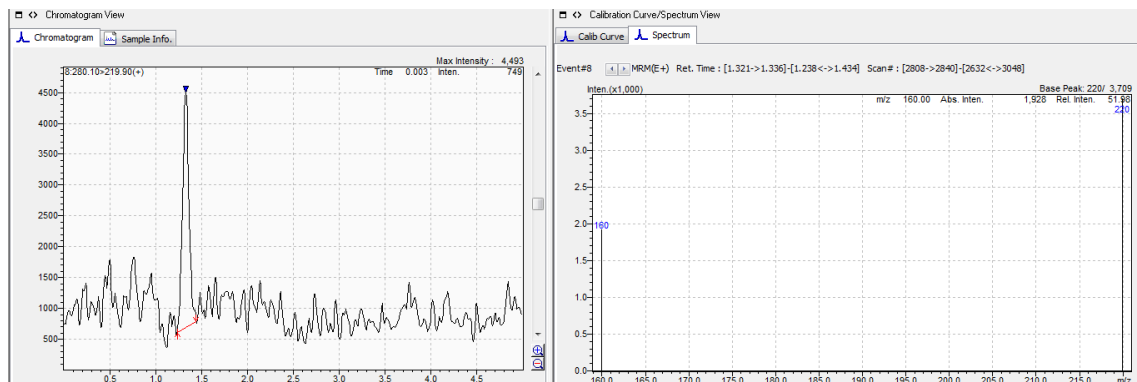


Fig. 7. Chromatogram of LOQ Metalaxyl (0.1ppb) in cucumber matrix

3.3.2. Linearity and standard curve

The linearity of each active ingredient at the estimated LOQ was investigated. The lowest point of the calibration curve of all compounds was 0.1 ppb. A standard curve consisting of 10 points at concentrations of 0.1, 0.5, 1, 2, 5, 10, 25, 50, 100, and 200 (ppb) from original solution A and original solution B in section 2.2 was constructed.

Standard addition curves in three different blank matrix were also constructed to compare to the standard curve using ACN solvent. The standard concentration of 0.1, 0.5, 1, 2, 5, 10, 25, 50, 100, and 200 (ppb) was

added to the tubes containing blank matrix. The tubes was soaked for 30 minutes. The next step was followed the conditions showing in Fig. 1.

As can be seen in Table 3, the square of correlation coefficient (R^2) is very close to 1. It represents a linear fit. The main concentration range was wide from 0.1-200 and 1-200 ppb, it is suitable for the application of pesticide determination.

Therefore, we use the standard curve on the sample matrix to validate the method (Fig. 8).

The sample matrix has an effect on the detection sensitivity of each active substance, which is confirmed through the linearity values and the slope “a” of the calibration curve. For example, on cucumber samples, Aldicarb sulfoxide could be detected at 0.1 ppb, but on orange and rice matrix it was only detectable at 1 ppb, Sl_a/Sl_{std} of Carbosulfan less than 30%, lower than regulation: 70-120%.

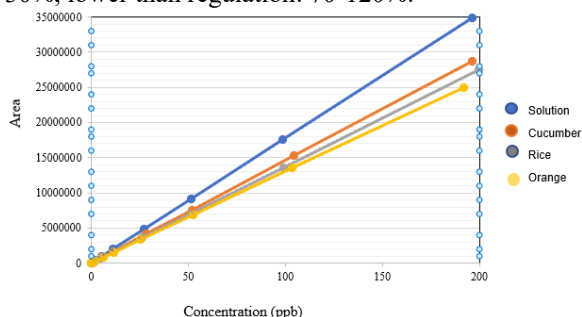


Fig. 8. Aldicarb-Sulfone's standard curves in different blank matrices

3.3.3. Limits of Detection and Quantitation

The limit of detection (LOD) and limit of quantitation (LOQ) values of the samples on 3 different matrices are shown in Table 4. The results show that the LOQ of the method ranges from 0.1-5 ppb, all less than 10 ppb, so the method can quantify the active substances in the matrix at concentrations lower than the specified MRL value

(0.01 mg/kg or 10 ppb). Compared with the LOQ of other studies also using LC-MS/MS as author Gianni [12] for the LOQ of the method ranges from 10-50 ppb, it can be seen that the LOQ of the construction method is better, completely suitable for ultratrace analysis of plant protection active ingredient.

3.3.4. Precision, repeatability, and spike recovery

The results of repeatability are shown in Table 5, at different matrices of the plant protection active ingredients, the recovery ranges from 70-120%, within the allowable limit for the analysis of ultratrace content according to the regulations documents EN 15662 [13]: % RSD (relative standard deviation) of the active ingredients are all less than 20%, so it is possible to confirm that the repeatability of the method is satisfactory, and at the same time gives high accuracy, suitable for determining the amount of residues of protective drugs. plants in agricultural products.

The accuracy of the method is calculated based on bias b %, the results show that the bias is less than less than 20 %, which is in line with the requirements of trace analysis. In addition, the accuracy of the method is also certified through the results of interlaboratory testing with the certified standard sample (CRM) Kiwi Fruit Puree under the FAPAS program 2022 with pesticide residue containing Carbamate group. The result that has high accuracy, z -score values is less than $|2|$.

Table 3. Linearity and slope of standard curve in different matrices

Pesticide	Linear interval (ppb)	Cucumber		Linear interval (ppb)	Orange		Linear interval (ppb)	Rice	
		Slope a	Sl_a/Sl_{std}		Slope a	Sl_a/Sl_{std}		Slope a	Sl_a/Sl_{std}
Aldicarb sulfone	0.1-200	145965	82.10	0.1-200	130067	73.16	0.1-200	137299	77.23
Aldicarb sulfoxide	0.1-200	4346.28	86.55	1-200	4321.22	86.05	1-200	6431.17	128.06
Carbofuran	1-200	2029.28	102.85	1-200	1467.60	74.38	1-200	3207.67	162.58
Carbosulfan	0.1-200	11100.3	13.56	1-200	8696.81	10.62	0.1-200	20585.3	25.14
Fenobucarb	1-200	36170.1	40.38	1-200	34869.8	38.93	0.1-200	61225.6	68.36
Iprovalicarb	0.1-200	158461	80.59	0.1-200	150982	76.78	0.1-200	171672	87.31
Isoprothiolane	1-200	23876.4	86.17	0.1-200	21851.2	78.86	0.1-200	20845	75.23
Metalaxyl	0.1-200	131446	98.16	0.1-200	113863	85.03	0.1-200	135592	101.26
Methomyl	1-200	3042.13	74.49	1-200	2396.89	58.69	1-200	5344.71	130.87
Oxamyl	0.1-200	36011.8	54.06	0.1-200	35162.2	52.78	0.1-200	57034.1	85.61
Pirimicarb	0.1-200	167914	90.74	0.1-200	165648	89.52	0.1-200	178792	96.62
Propamocarb HCL	1-200	33925.1	13.91	1-200	34843.2	14.29	1-200	174653	71.62
Propoxur	1-200	3564.70	86.58	1-200	2504.51	60.83	1-200	5217.6	126.73
Aldicarb	5-200	320.694	67.92	5-200	314.970	66.71	5-200	467.564	99.03
Indoxacarb	1-200	6068.75	29.56	1-200	6268.91	30.53	1-200	5990.6	29.18

Table 4. The LOD and LOQ values of the samples (ppb)

Pesticides	Cucumber		Orange		Rice	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
Aldicarb sulfone	0.03	0.10	0.06	0.19	0.03	0.11
Aldicarb sulfoxide	0.42	1.37	0.35	1.16	0.27	0.89
Carbofuran	0.39	1.29	0.50	1.66	0.14	0.47
Carbosulfan	0.29	0.95	0.33	1.10	0.02	0.07
Fenobucarb	0.13	0.43	0.12	0.41	0.01	0.03
Iprovalicarb	0.02	0.06	0.03	0.12	0.02	0.07
Isoprothiolane	0.24	0.79	0.04	0.12	0.05	0.16
Metalaxyl	0.05	0.15	0.04	0.13	0.03	0.09
Methomyl	0.29	0.98	0.37	1.23	0.40	1.31
Oxamyl	0.01	0.04	0.02	0.07	0.03	0.11
Pirimicarb	0.03	0.11	0.04	0.14	0.02	0.08
Propamocarb HCL	0.29	0.95	0.55	1.84	0.15	0.49
Propoxur	0.27	0.89	0.35	1.14	0.33	1.10
Aldicarb	1.34	4.43	1.28	4.22	1.10	3.64
Indoxacarb	0.16	0.53	0.18	0.60	0.41	1.36

Table 5. Repeatability of active ingredients at concentrations of 50 ppb on different matrixes (n=10)

Pesticides	Cucumber Matrix			Orange Matrix			Rice matrix		
	SD	RSD%	%R _{tb}	SD	RSD%	%R _{tb}	SD	RSD%	%R _{tb}
Aldicarb sulfone	4.23	7.74	109.27	0.97	1.86	104.84	1.03	1.98	104.22
Aldicarb sulfoxide	3.99	7.32	109.08	1.51	2.75	109.84	2.27	3.94	115.27
Carbofuran	3.52	6.81	103.42	6.32	11.75	107.53	4.09	7.46	109.81
Carbosulfan	2.53	4.56	110.84	1.22	2.26	108.17	3.11	5.66	110.2
Fenobucarb	1.45	3.13	92.84	0.89	1.85	96.84	1.04	1.96	105.80
Iprovalicarb	4.25	8.24	103.03	2.38	4.18	113.85	3.09	6.11	100.99
Isoprothiolane	6.27	12.28	102.10	1.71	3.00	114.38	3.70	6.78	109.31
Metalaxyl	3.28	6.14	106.63	2.50	4.38	114.28	2.01	3.91	102.69
Methomyl	1.67	2.93	114.18	4.15	7.53	110.19	3.09	5.72	107.99
Oxamyl	2.58	4.79	107.75	4.40	8.13	108.33	2.12	3.85	109.93
Pirimicarb	3.45	6.87	100.30	2.16	4.64	93.07	2.37	4.49	105.29
Propamocarb HCL	4.27	8.63	98.97	2.13	4.58	93.26	1.03	1.98	104.21
Propoxur	3.39	6.08	111.39	3.87	6.96	111.29	2.60	4.79	108.40
Aldicarb	4.36	8.15	107.07	2.97	5.35	110.97	3.26	5.88	110.76
Indoxacarb	3.47	6.27	110.50	1.32	2.43	109.05	1.92	3.50	109.83

Table 6. Analysis results of actual samples

Sample	Symbol	Samples with residues of pesticides	
		Pesticides	Detection concentration (mg/kg)
Cabbage	DL 05	Isoprothiolane (0.17)	
	DL 08	Metalxyl (0.11); Propamocarb (0.222)	
	DL 09	Metalaxyl (0.36); Propamocarb (1.75);	
	DL 10	Metalaxyl (1.47); Propamocarb (0.26)	
	DL 11	Metalaxyl (0.39); Propamocarb (0.19)	
	DL 12	Propamocarb (0.157)	
	DL 13	Propamocarb (0.246)	
	DL 14	Propamocarb (2.420)	
	DL 15	Metalaxyl (0.705)	
	Truffle	DL 28	Carbofuran (0.09); Indoxacarb (0.04)
DL 30		Carbofuran (0.17); Indoxacarb (0.01); Metalaxyl (0.24)	
DL 32		Carbofuran (0.24)	
DL 37		Indoxacarb (0.03)	
DL 75		Isoprothiolane (1.06), Carbofuran (0.07)	
Rice	DL 61	Methomyl (0.04)	
	DL 64	Methomyl (0.02)	
	DL 70	Isoprothiolane (0.83), Methomyl (0.19)	
	DL 75	Isoprothiolane (1.06), Carbofuran (0.07)	
	DL 98	Indoxacarb (0.20)	
Grape	DL 80	Metalaxyl (0.15)	
	DL 89	Methomyl (0.02), Indoxacarb (0.04)	
	DL 91	Metalaxyl (0.12)	

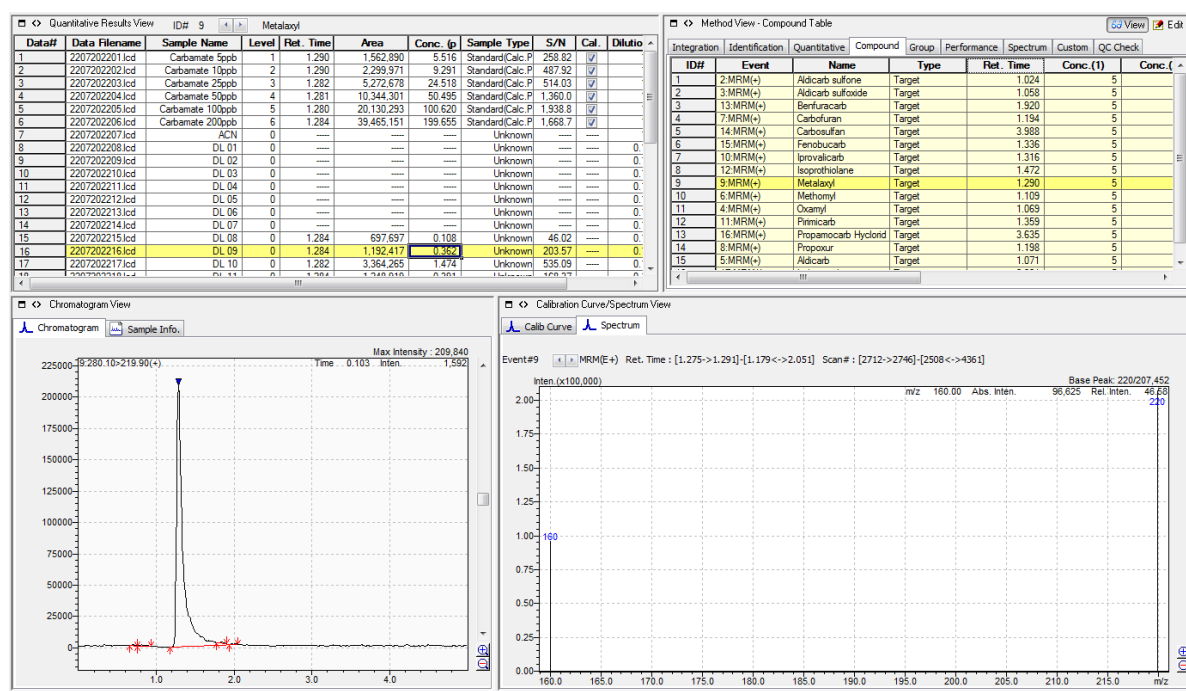


Fig. 9. Chromatogram of Metalaxyl sample

3.4. Pesticides Residue Analysis in Sample

The results of residue analysis were calculated according to the formula:

$$X = X_o \times \frac{V}{m} \times \frac{P}{100} \times k$$

where X_o is concentration of test portion displayed on meter ($\mu\text{g/mL}$); V is Solvent volume to extract sample (mL); m : sample weight (g); P : Purity of standard substance; k : Dillution coefficient

The analysis results of actual samples are presented in Table 6 and Fig. 9. There were 21/100 samples collected in the Northside Vietnam to detect residues of Carbamate pesticides, in which Metalaxyl, Propamocarb, Carbofuran appeared the most. According to FAO standards regulating residue levels in agricultural samples, the allowable residue level of Propamocarb in cabbage is 1 mg/kg, so samples DL09 and DL14 are exceeding the allowable level. The samples DL10 and DL15 exceeded the allowable level of Metalaxyl in cabbage (0.5 mg/kg). The remaining samples all have residue levels within the allowable limits (According to FAO and TT 50/2016-BYT).

4. Conclusion

Our findings showed that the method for concurrently determining residue levels for fifteen carbamate pesticides had been developed with strong sensitivity (LOQ from 0.1 to 5 ppb), recovery, and good repeatability. The technique has been successfully used to quickly and simultaneously determine the presence of pesticide residues in various agricultural crops. The actual experiment showed that there were 4 samples with pesticide residues exceeding the allowable levels, namely DL09, DL14 (Propamocarb) and DL10, DL15 (Metalaxyl).

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