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The use of atmospheric-pressure chemical ionization for pesticide analysis using liquid chromatography mass spectrometry

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Abstract

Based on the regulations of the Ministry of Health and Welfare (MOHW) of Taiwan in 2017, an analysis of 373 pesticides in food was conducted using the MOHW official method. The analyses involved the use of either liquid chromatography mass spectrometry (LC-MS) with electrospray ionization (ESI) or gas chromatography mass spectrometry (GC-MS) with electron ionization (EI). In this study, the applicability of detecting pesticides using atmospheric pressure chemical ionization (APCI) was investigated and evaluated. The pesticides were separated using an aqueous solution of ammonium formate with methanol as the mobile phase, and ionization efficiency was compared between APCI, ESI, and EI coupled with triple quadrupole mass spectrometer using multiple reaction monitoring (MRM) acquisition. Among the 196 pesticides that were originally analyzed by ESI, 164 could be successfully detected by APCI with 6 showing a higher sensitivity when APCI was used. Among the 177 pesticides that were analyzed by EI, 43 could be successfully detected by APCI. The results also showed that APCI gave superior ionization efficiency for pesticides containing triazine, imidazole, triazole, and pyrazole groups.

Keywords: APCI, LC-MS, Pesticides, Quantification

1. Introduction

The use of pesticides has made human civilization flourish, and its benefits have allowed crops to grow steadily and provide us with sufficient food. However, the increasing use of pesticides has resulted in the environment and the human body being exposed to different levels of toxicity, which, in turn, affects the health and sometimes, even life of our citizens. According to a recent report [1], two million metric tons of pesticides are used globally each year, with 20,000 metric tons being used in Taiwan each year, which is equivalent to a value of 120 billion NTD. For this reason, the Food and Drug Administration of the Ministry of Health and Welfare of Taiwan standardized 373 multiple pesticide residue methods in 2017 and set the Method Detection Limit (MDL) for fruits and vegetables, cereals, and tea in crops.

Because different pesticides have different physical and chemical properties, using a single ion source to analyze various types of pesticides is nearly impossible. Electron ionization (EI), a hard ionization method, many fragment ions with molecular weight less than 600 are generated before they enter the mass analyzer. Regarding analyses for polar and relatively polar compounds, soft ionization method electrospray ionization (ESI) is often adapted. On the other hand, atmospheric pressure chemical ionization (APCI) is considered to be a soft ionization technique that is complimentary to electrospray, since it enables the ionization of small and relatively less polar compounds under atmospheric pressure [2]. By heating a nebulizer probe, the analyte in solution is converted into a mist of fine droplets that passed through an ionization region with a corona discharge needle, where the analytes are ionized. Once the ions are formed, they can be transported through an additional ion-focusing voltage into a mass analyzer for subsequent mass analysis.

Carbamate, organophosphorus, and nicotine-containing pesticides are polar insecticides.

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Aminocarb, bendiocarb, zectran, and methiocarb are carbamate insecticides; azinphos-methyl, omethoat, and mevinphos belong to the family of organophosphorus insecticides. They are conventionally analyzed by liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) [3,4]. Pyrethrum insecticides such as halfenprox, permethrin, fenopropathrin, organochlorine including DDT, aldrin, and lindane are relatively nonpolar and are usually analyzed by gas chromatography electron ionization mass spectrometry (GC-EI-MS) [5,6]. It is critical to apply a suitable ionization method for the analysis of an insecticide. For example, yidaan, which causes the death of bee larvae, belongs to the nicotine family. Yidaan is difficult to analyze by GC-EI-MS because of its high polarity. In addition, it contains an N=N double bond, which is thermally unstable, making it unstable and subject to degradation in an GC-EI-MS analysis [7].

In this study, the use of APCI for the analysis of 373 pesticide compounds was investigated and evaluated. An ion source comparison was conducted on these pesticides (196 using ESI and 177 by EI in the MOHW official method).

2. Experimental conditions

2.1. Reagents and materials

HPLC-grade acetonitrile and methanol were purchased from Merck (Darmstadt, Germany), ultrapure water Milli-Q was from Millipore (Burlington, Massachusetts, USA). Reagent grade ammonium formate was purchased from Sigma (St. Louis, Missouri, USA) and formic acid was purchased from J. T. Baker (Phillipsburg, New Jersey, USA). Pesticide standards were obtained from the New Fast Technology Co. (Hsinchu, Taiwan).

2.2. LC-MS parameters

An ultra-performance liquid chromatography (AB Sciex, Framingham, Massachusetts Canada) unit was connected to an AB Sciex Triple Quad™ 5500+ LC-MS/MS, equipped with APCI and ESI interfaces. The applied voltage were as follows: Ionspray, 5500 V for ESI positive and −5500 V for ESI negative, the nebulizer current was 5 mA for APCI positive and −5 mA for APCI negative. The operating gas pressure: ion source, curtain, collision was 50, 20, 5 psi, respectively; the temperature was set at 550 °C for both APCI and ESI.

Standard solutions of pesticides were analyzed using a Kinetex EVO C18 column 2.6 μm, 150 × 2.1 mm (Phenomenex, USA). The mobile phase gradient setting was basically the same as that for the MOHW official method: mobile phase A was 0.1% formic acid and 0.04% ammonium formate in H_2O, mobile phase B was 0.1% formic acid and 0.04% ammonium formate in MeOH. The gradient for the LC was a 1% B linear ramp to 50% B in 3 min, and a linear ramp to 70% B at 10 min, and a linear ramp to 99% B at 13 min and held 2 min with a flow rate of 0.2 mL/min. The column temperature was controlled at 40 °C. The injection volume was 5 μL. The gradient for the GC was a 10% B linear ramp to 50% B in 3 min, and a linear ramp to 70% B at 17 min, and a linear ramp to 99% B at 23 min and a hold for 6 min. Data processing was using SCIEX OS-MQ software.

3. Results and discussion

The multiple reaction monitoring (MRM) scanning mode using in triple quadrupole mass spectrometer can accurately identify and quantify the target analytes [7]. The optimized voltage and parameters for the MRM transitions of pesticides are listed in the Table S1 https://www.jfda-online.com/cgi/viewcontent.cgi?filename=4&article=3392&context=journal&type=additional&preview_mode=1, and are similar to the MOHW official method with minor modifications.

3.1. Comparison of APCI and ESI

The investigation is based on a comparison of the peak areas and signal-to-noise ratios (s/n ratio) of the pesticide signals in ESI and APCI analyses. The peak area was used for evaluating the ionization efficiency of the analyte in both ion sources, and the signal-to-noise ratio was used for determining the limit of detection (LOD) and the limit of quantitation (LOQ).

The pesticides were classified into two categories, LC and GC, representing pesticides in the recommendation lists that were analyzed using LC-ESI-MS and GC-EI-MS analysis in MOHW official method. The pesticides that were originally analyzed by ESI (LC group) in the MOHW official method were divided into 10 tubes (roughly 20 pesticides each) and analyzed by LC-ESI and LC-APCI respectively. The rationale for the analysis of these pesticides as a group is that if all the pesticides were to be subjected to a single chromatographic analysis, quite a few would not be effectively separated. Which may cause severe ion suppression among the unseparated pesticides, and lead to an inaccurate evaluation of the ionization efficiency of pesticides in the ion sources. Among these

compounds, the two pesticide mixtures labeled LC09 and LC18 were analyzed using the negative ion mode because pesticides in the LC09 and LC18 cannot be ionized successfully using the positive mode. Other mixtures were ionized in the positive mode.

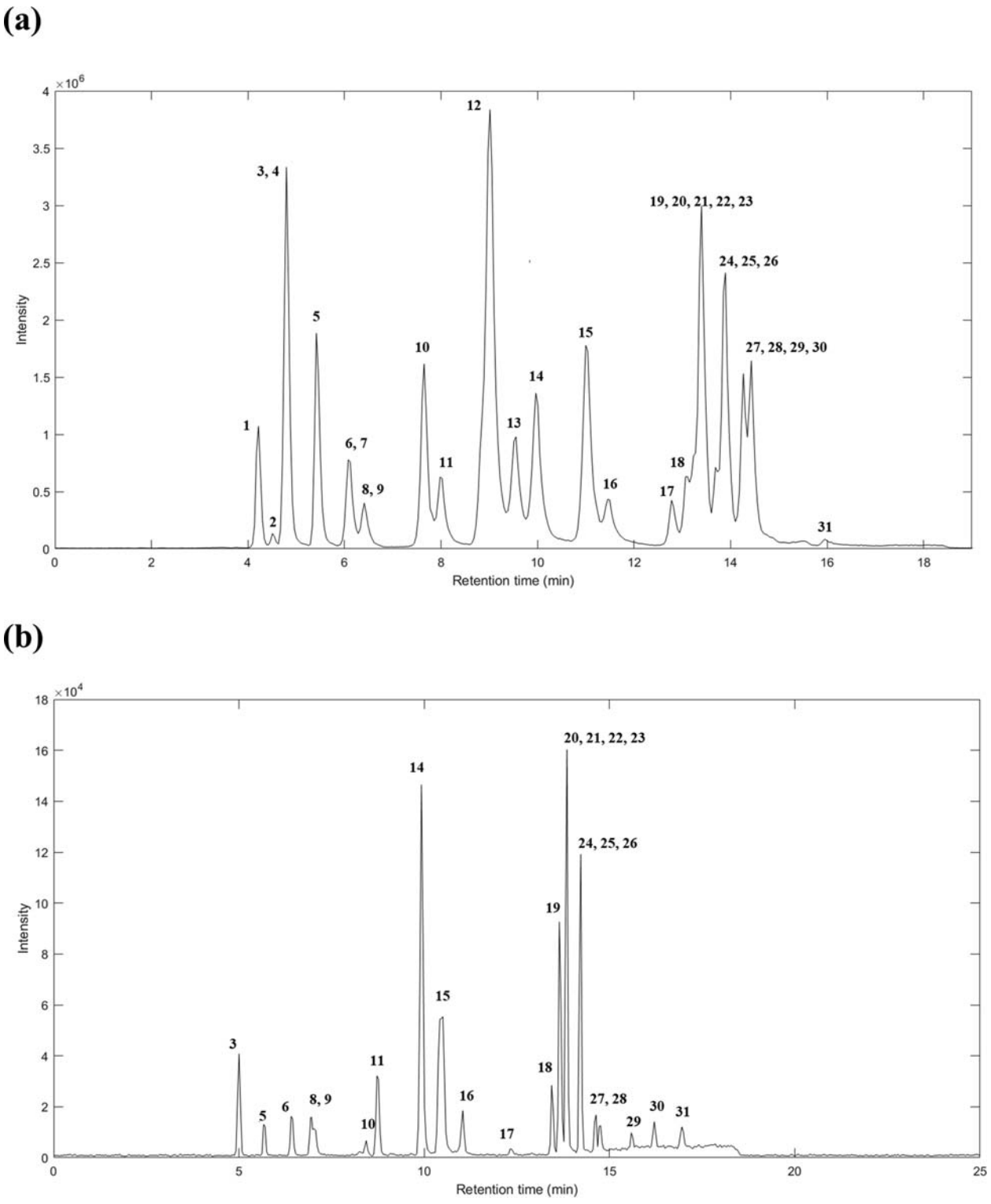

Fig. 1. Total ion chromatogram (TIC) of a sample mixture LC08 using LC-ESI (a) and LC-APCI (b). The label on the peaks and the corresponding structures are listed in Table 1. APCI showed a greater peak area for flonicamid (peak 3) while 8 pesticides including aldicarb sulfoxide, oxamyl, thiamethoxam, butocarboxim, flazasulfuron, bensulfuron-methyl, and fludioxonil (peak 1, 2, 4, 7, 12, 13, and 17), produced no signals in APCI.

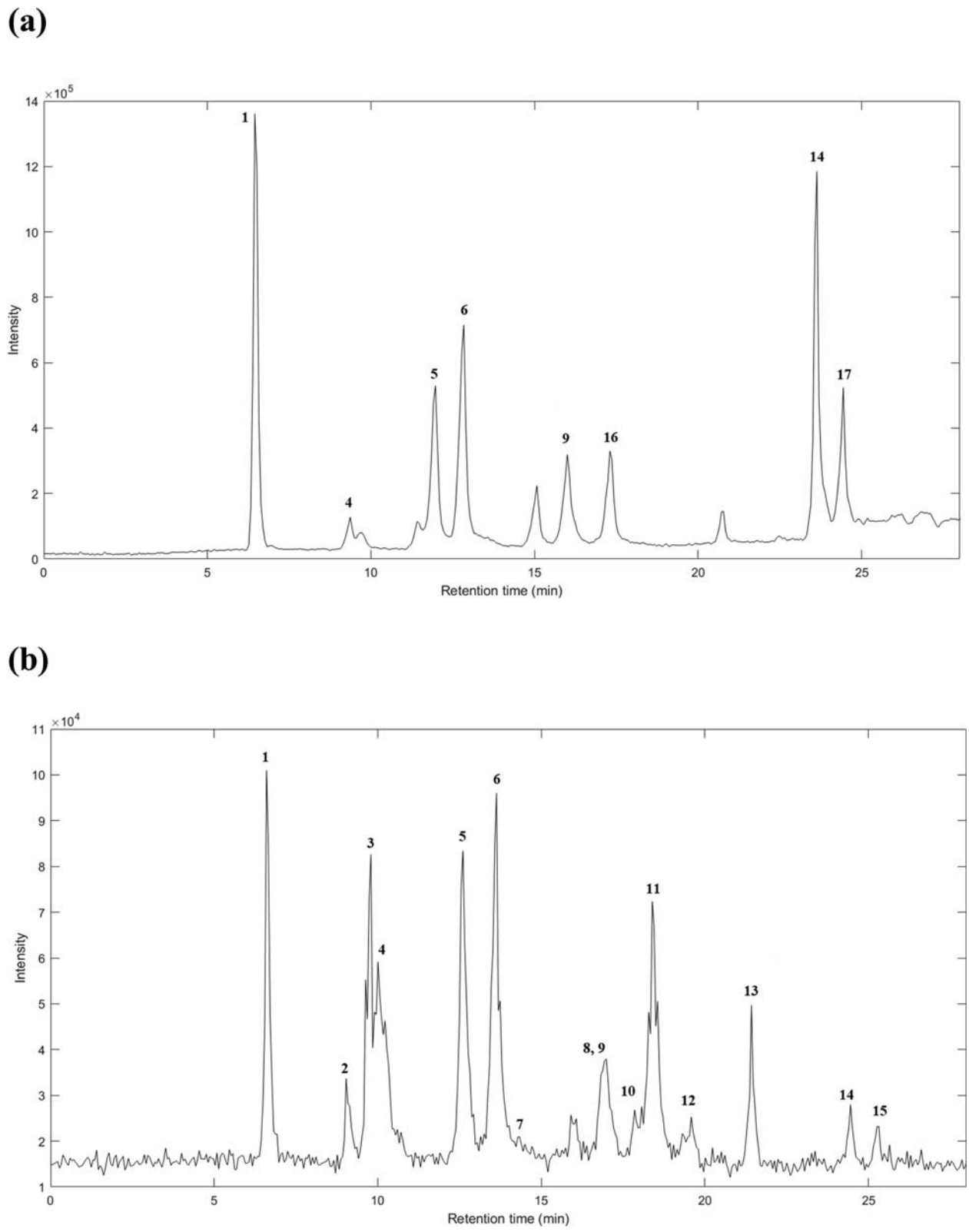

Fig. 2. The TIC of sample mixture GC01 using LC-ESI (a) and LC-APCI (b). These 31 pesticides were formerly analyzed by GC-MS. Only 17 of them could be detected by LC-MS. Among them, mephosfolan, azinphos-methyl, malathion, triazophos, fonfos, and pyraclofos (peak 1, 4, 5, 6, 9, and 14) were detected in both LC-ESI and LC-APCI; difenoconazole, pirimiphos-ethyl, and pyridaphenthion (peak 12, 13, and 15) were observed only by LC-ESI; cyanofenphos and propiconazole (peak 16 and 17) were detected only by LC-APCI.

As an example, the total ion chromatogram (TIC) of LC08 using LC-ESI (a) and LC-APCI (b) are shown in Fig. 1. Among the 31 pesticides in the LC08 group, flonicamid yields a greater peak area in APCI, while others have greater peak areas in ESI. Eight pesticides including aldicarb sulfoxide, oxamyl, thiamethoxam, butocarboxim, flazasulfuron, bensulfuron-methyl, and fludioxonil cannot be ionized by APCI (no signal was observed). Among the 196 pesticides in the LC group, only 6 pesticides including boscalid, flonicamid, flutriafol, fenthion, acibenzolar-S-methyl, and mevinphos exhibited a higher sensitivity in APCI compare to ESI. In addition, 32 pesticides in the LC group cannot be ionized using APCI. Although LOD values for the APCI were slightly inferior to those for the ESI for most pesticides, one advantage of using APCI over ESI is that it has a better tolerance for matrix effects [8–10]. APCI showed a good sensitivity to organophosphorus compounds [11,12].

A total of 177 pesticides were originally analyzed using the EI method (GC group), they were divided into tubes of mixed pesticide standards and were then analyzed by both LC-ESI and LC-APCI. As an example, the TIC of GC01 using LC-ESI (a) LC-APCI (b) are shown in Fig. 2. There were 31 pesticides in the GC01 group, but only 17 could be detected using ESI and APCI. Among them, mephosfolan, azinphos-methyl, malathion, triazophos, fonofos, pyraclofos could be detected by both APCI and ESI. Fensulfothion, methidathion, bupirimate, propiconazole, phorate, phosalone, difenoconazole, pirimiphos-ethyl, pyridaphenthion could hardly be detected by ESI, while cyanofenphos and propiconazole could not be detected by APCI. Among the pesticides that were detected in both ion sources, pyraclofos was the only one showing a better s/n in ESI; the other 5 pesticides were more sensitive in APCI. In the current MOHW official method, a total of 177 pesticides in the GC group were analyzed and 20 could be detected by ESI, 43 pesticides can be observed in APCI, and 15 can also be detected. The molecular weight distribution using ESI is wider than EI. LC-ESI-MS can be used to detect pesticides with molecular weights up to 1800 Da. To the contrary, GC-EI-MS can only detect the pesticides with molecular weights below 600 Da. If all 373 pesticides were to be analyzed by the LC system, 216 would be detected by ESI and 207 would be detected by APCI (Fig. 3). Detailed information regarding this is listed on Table S2 https://www.jfda-online.com/cgi/viewcontent.cgi?filename=5&article=3392&context=journal&type=additional&preview_mode=1.

3.2. Lipophilicity (hydrophobicity) and hydrophilicity (LogP)

In this study, the LogP value was used to determine hydrophobicity. The LogP value, the octanol–water partition coefficient, refers to the ratio of the concentration of a compound dissolved in octanol versus in water. The greater the value, the more is the compound able to dissolve in octanol (less polar), and the smaller the value, the more likely will it be for it to be dissolved in water (more polar). Table S3 https://www.jfda-online.com/cgi/viewcontent.cgi?filename=6&article=3392&context=journal&type=additional&preview_mode=1 lists the LogP values of pesticides in LC08 and GC01 groups, they seem strongly related to the sensitivity of APCI. Among the 196 pesticides in the LC group, for the 32 that could not be detected by APCI, their LogP value are either higher than 4 or less than 2. Among the 171 pesticides in the GC group, 43 that were detected by APCI have LogP values within the range of 2–4. Pesticides with a LogP value higher than 4 or lower than 2 appear to be more difficult to ionize by APCI. The LogP range of the GC and LC group are in line with the theory that a polar molecule is suitable for use in conjunction with ESI

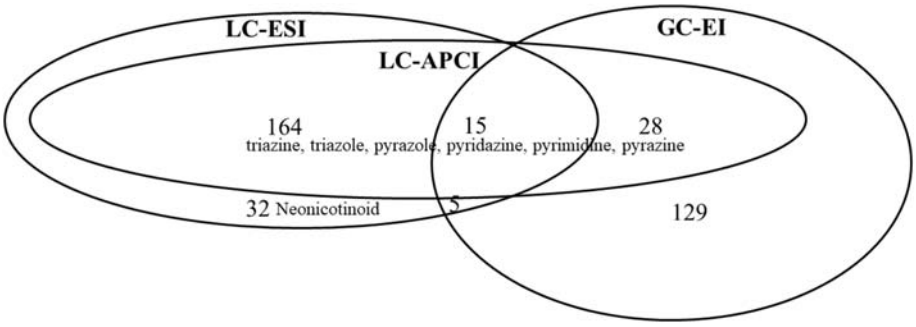

Fig. 3. The Venn diagram shows that, among 373 listed pesticides, 164 were detected by LC-APCI and LC-ESI; 5 were detected by LC-APCI, LC-ESI and GC-EI; 28 were detected LC-APCI and GC-EI. Pesticides with triazine, triazole, pyrazole, pyridazine, pyrimidine, pyrazine groups were more sensitive in LC-APCI.

Table 1. Method validation for APCI detection of 11 APCI-favorable pesticides. Linear equation, R^2, linear range, LOD, and LOQ are shown in this table.

Compounds	Linear equation		Range (ng/mL)	LOD[a] (ng/mL)	LOQ[b] (ng/mL)
	y = ax + b	R^2			
Fonofos	y = 47455x - 34846	0.998	1–200	0.1	0.1
Methidathion	y = 2248.1x - 885.9	0.998	1–200	0.5	1
Pirimiphos-ethyl	y = 4582.1x - 1579	0.997	1–200	0.1	0.5
Triazophos	y = 26796x - 12699	0.996	1–200	0.1	0.1
Triflumizole	y = 6407.3x - 2751	0.998	1–200	0.1	0.5
Acibenzolar-S-methyl	y = 30466x - 18427	0.996	1–200	0.1	0.5
Boscalid	y = 63165x - 13386	0.998	1–200	0.1	0.1
Fenthion	y = 48083x - 15078	0.998	1–200	0.1	0.1
Flonicamid	y = 9696.3x - 3898	0.997	1–200	0.1	0.5
Flutriafol	y = 63039x + 131.5	0.998	1–200	0.1	0.1
Mevinphos	y = 18418x + 7129	0.995	1–200	0.1	0.5

[a] LOD = S/N ≥ 3
[b] LOQ = S/N ≥ 10.

and less polar molecules are more suitable for use in conjunction with APCI. Of the pesticides in the LC group, 6 had a higher sensitivity when APCI was used. For example, fenthion (with a logP value of 3.86) has the greatest s/n ratio difference (APCI: 1321.9; ESI: 240.6), and this LogP value is clearly intermediate between 2 and 4.

3.3. Functional groups

Triazole and triazine are 5- and 6-membered aromatic rings that contain 3 nitrogen atoms; imidazole and pyrazole are 5-membered aromatic rings that contain 2 nitrogen atoms; pyridazine, pyrimidine, and pyrazine are 6-membered aromatic rings that contain 2 nitrogen atoms. They are not only weakly alkaline but also have a slightly weaker resonance capability than benzene rings [13]. Pesticides containing these functional groups are reported to be stable at the interface temperature (about 350 °C); moreover, their basic sites are easily protonated in the vapor state, which makes them nonionic. Hence, triazine, imidazole, triazole, pyrazole, pyridazine, pyrimidine, and pyrazine pesticides were detected with a greater sensitivity with APCI, showing a stronger signal and signal-to-noise ratio. It has been reported that neonicotinoid pesticides (thiamethoxam, clothianidin, imidacloprid, acetamiprid, and thiacloprid) can be analyzed by both APCI and ESI [14]. The findings reported herein show that their degradation products interfere with in-source fragmentation (loss of N_2O), pyrolysis (temperature sensitive) and ion/molecule reaction (based on ^{18}O-labeling experiment), thus making it impossible to conduct qualitative and quantitative analysis of neonicotinoid pesticides using APCI.

3.4. Method validation

Method validation was conducted by evaluating the linearity, LOD, LOQ, accuracy, and precision. A series of standards, in concentrations of 1, 5, 10, 50, 100, and 200 ng/mL, were used to construct calibration curves. For each standard concentration, a 100 ng/mL solution of triphenyl phosphate was added as an internal standard.

The detection of 11 pesticides, having the aforementioned functional groups showed an acceptable sensitivity when APCI was used. Among them, 5 pesticides including boscalid, fenthion, flonicamid, flutriafol, and mevinphos were from the LC group, and 6 pesticides, including fonofos, methidathion, pirimiphos-ethyl, triazophos, triflumizole, and acibenzolar-S-methyl, were from the GC group. Methidathion and acibenzolar-S-methyl are pyrazole types of pesticides, triazophos belongs to the triazole type, triflumizole belongs to the imidazole type, and pirimiphos-ethyl belongs to the pyrimidine type. As shown in Table 1, the LODs of these 11 pesticides were all higher than 0.1 ng/mL with a R^2 above 0.995. The intra-day precision was carried out three times using standard concentrations of 5, 10, 50, 100, and 200 ng/mL within the same day, and the peak area was used for calculating the coefficient of variation (Table 2). For the inter-day precision, a triplicate analysis was performed using the standards with concentrations of 10, 50 and 100 ng/mL on three consecutive days. The coefficient of variation was also calculated (Table 2). Although at low-concentrations, the accuracy and precision appeared to be poorer, they were still within a satisfactory range. Accuracy (RSD% 81.8%–138.8%) and precision (0.19%–13.87%) were both satisfactory in the case of the APCI method (Table 2).

Table 2. Accuracy and coefficient of variation, including intra-day and inter-day test for 11 APCI-favorable pesticides.

Compounds	Conc. (ng/mL)	Accuracy (%)	CV (%)	CV[a] (%)	
				Intra-day (n = 5)	Inter-day (n = 3)
Fonofos	1	27.98	1.6	–	–
	5	−13.37	0.53	1.91	–
	10	−12.24	3.11	1.51	1.1
	50	6.76	0.59	3.04	1.06
	100	2.08	0.2	3.31	1.83
	200	−1.88	2.07	3.99	–
Methiadathion	1	17.8	N/A	–	–
	5	−7.48	3.84	7.08	–
	10	−4.91	3.75	6.64	5.48
	50	6.84	0.76	1.53	1.06
	100	1.85	0.64	1.88	2.37
	200	−2.23	0.2	4.7	–
Pirimiphos-ethyl	1	7.26	8.03	–	–
	5	−10.3	4.91	5.11	–
	10	−4.4	4.23	3.87	4.21
	50	10.5	1.4	1.68	1.82
	100	3.06	1.75	1.64	2.1
	200	−3.71	0.68	7.62	–
Triazophos	1	10.46	3.25	–	–
	5	−10.07	2.16	2.35	–
	10	−8.1	4.93	1.21	0.72
	50	11.23	1.99	1.1	1.32
	100	4.28	0.96	1.96	1.76
	200	−4.33	1.18	5.33	–
Triflumizole	1	4.66	2.52	–	–
	5	−3.99	2.36	2.58	–
	10	−2.77	1.27	3.7	1.75
	50	−4.58	2.96	1.11	1.26
	100	3.22	0.48	1.41	1.75
	200	1.77	3.21	3.67	–
Acibenzolar-S-methyl	1	24	4.6	–	–
	5	−9.8	3.8	3.8	–
	10	−10.5	4.8	4.8	10.17
	50	−9.7	1.2	1.2	6.62
	100	5.8	3.8	3.8	9.02
	200	0.2	4.4	4.4	–
Boscalid	1	4.3	4.2	–	–
	5	0.3	2.8	7.59	–
	10	−3.6	3.7	6.41	3.81
	50	−5.6	2	10.16	9.09
	100	6.2	3.2	14.4	10.91
	200	−1.5	1.9	8.06	–
Fenthion	1	7.7	4.1	–	–
	5	−3.5	3.3	7.67	–
	10	−4.4	2.5	6.58	7.14
	50	−4.4	1.6	8.32	9.09
	100	6.5	1.6	7.29	8.24
	200	−1.9	1	7.47	–
Flonicamid	1	7.4	6.5	–	–
	5	−1.6	7.7	8.44	–
	10	−5.9	10	13.79	10.87
	50	−3.6	4	11.77	9.99
	100	4.9	4.3	7.55	8.36
	200	−1.3	4.3	9.35	–
Flutriafol	1	2.4	12.9	–	–
	5	−1.7	5.5	8.43	–
	10	−0.5	0.7	11.12	13.15
	50	−4.3	0.7	3.51	1.12
	100	6.1	2	12.24	13.99
	200	−1.9	2	4.22	–

(*continued on next page*)

Table 2. (continued)

Compounds	Conc. (ng/mL)	Accuracy (%)	CV (%)	CV[a] (%)	
				Intra-day (n = 5)	Inter-day (n = 3)
Mevinphos	1	3	46	–	–
	5	−3.5	5.7	13.83	–
	10	−0.4	10.9	4.29	4.15
	50	−4.8	3.4	5.28	4.7
	100	8.8	2.8	8.35	7.02
	200	−3.1	3.7	4.03	–

[a] CV: coefficient of variation. CV = (standard deviation/mean) × 100%.

Table 3. Comparison of ESI/APCI methods reported in other studies.

Number of Compounds	C18 Column	Mobile phases	Linear range	Reference
75	250 × 3 mm, 5 μm	A: MeOH/H_2O 50:50 B: ACN/H_2O 50:50	0.05–100 ng/mL[a]	[13]
10	150 × 4.6 mm, 5 μm	ACN/H_2O 70:30 + 0.05% TFA	10–50 ng/mL	[8]
53	100 × 2.1 mm, 1.7 μm	A: ACN B: 0.1% FA[b] in H_2O	5–500 ng/mL	[10]
22	150 × 2.1 mm, 3 μm	A: 0.1% FA in MeOH B: AA 5 mM in H_2O	0.5–200 ng/mL	[11]
373	150 × 2.1 mm, 2.6 μm	A: 0.1% FA + 0.04% AF[c] in H_2O B: 0.1% FA + 0.04% AF in MeOH	1–200 ng/mL	This study

[a] LOD range
[b] FA: formic acid
[c] AF = Ammonium formate.

3.5. Comparison with other methods

The development of methods for detecting pesticides has not been stopped. Comparative studies between ESI and APCI are illustrated in Table 3. In recent studies, pesticides were classified according to their acid dissociation constants, and the two ionization methods were compared.

Many researchers have been examined the sensitivity of detection with different ion sources for the detection of pesticides. Table 3 lists 4 publications that report on the sensitivity of detection on pesticides using ESI and APCI. Thurman and coworkers compared the limit of detection (LOD) of 75 pesticides using both APCI and ESI, and some LODs reached levels of 0.05 ng/mL [13]. The signal intensity was provided but the linear range was not mentioned. It was also found that neutral and basic pesticides (phenylureas and triazines) were more sensitive in APCI, and that ionic pesticides (bipyridyliumions and sulfonic acids) were more sensitive in the case of ESI. Other studies compared the detection sensitivity of pesticides in peppers [15], oranges [8], Chinese herbal medicines [10], and tea [16] using APCI and ESI and these findings are similar to the results reported in this study.

In the present work, 373 pesticides that had been analyzed by the MOHW official method were also investigated by ESI and APCI and their linear range, LOD, and LOQ were also evaluated. Pesticides reported in other studies including fonsfos, pirimiphos-ethyl, triazophos, triflumizol, acibenzolar-S-methyl, boscalid, fenthion, flutriafol, and mevinphos were found to have LOD values of 0.1 ng/mL in the case of APCI. We also found that the pesticides containing functional groups such as triazole and triazine gave better sensitivity in APCI than in ESI, which is consistent with results in other studies [13].

4. Conclusions

In this study, the sensitivity between ESI/EI and APCI detection was compared for 373 pesticides. The findings showed that 164 and 43 pesticides from the LC-ESI group and the GC-EI group, respectively, met the LOQ criteria of MOHW official method with APCI. This made up a total of 207 pesticides which can be successfully detected and quantified by an LC-APCI MS/MS analysis. The linear range was 1–200 ng/mL with a correlation coefficient r = 0.996, LOD and LOQ of 0.1 ng/mL or lower were successfully achieved. The method was further validated and met the requirements of the MOHW regulations. In summary, the objective of this study was to develop a single LC-MS analysis for the quantitative determination of APCI-favorable pesticide compounds. The findings

indicate that the method reported in this study has the potential for developing a method for rapid pesticide screening using APCI-based mass spectrometry.

Conflicts of interest

The authors have no conflicts of interest relevant to this article.

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