Egypt. J. Chem. **Vol. 64,** No. 2 pp. 605 - 622 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

A Rapid Sensitive and Selective GC-Ms/Ms Method for Multi Residue Analysis of A Large Number of Pesticides in Chamomile

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Abstract

Multi-residue methods for pesticide residues analysis in herbal plants, using gas chromatography tandem mass spectrometry (GC–MS/MS), usually carried out by a long run time. These longer run times of analyses are performed to avoid the overlapping of the co-extracted natural components with the analyzed pesticides in herbal samples. In the current study, a rapid sensitive and selective GC-MS/MS method, of run time 25 m, has been developed for the analysis of 212 pesticides in chamomile. The oven temperature program has been optimized to give a better distribution for the eluted pesticides along all the run time. Besides, the back flush technique has been used to remove the less volatile compounds and to decrease the analysis runtime. In addition, the sample preparation was a modification of the known QuEChERS extraction method by applying a freezing step at -20 °C for 20 m before adding the salting out mixture. The developed method enables food safety laboratories to increase the number of analyzed samples per day with a reduction of the total analysis cost. The developed method has been fully validated on chamomile according to SANTE/11813, 2018. The obtained results showed that, more than 206 pesticides have average recoveries between 70-120 % at a concentration level of 50 µg kg^{-1}. Limit of quantitation for 160 of the studied pesticides equal 10 µg kg^{-1}. The developed method was also employed for the analysis of real chamomile samples collected from Al-Fayoum governorate, Egypt. The obtained results showed that most of the collected samples were positive by different pesticide residues. There were three samples contaminated by five to six different pesticides, indicating the presence of uncontrolled pesticide practices.

Keywords: Pesticides Residue; Rapid GC-MS/MS Method, Chamomile; Herbs.

Introduction

Indeed, pesticides play an important role in the yield increment of agricultural products [1, 2] However, intensive and uncontrolled pesticides usage usually contaminates these products [3-5]. Therefore, many governmental laboratories for pesticide residue control carry out monitoring programs to ensure that at least the founded pesticides in the agricultural products don't exceed the allowed maximum residue limits (MRL) [6-8]. A high number of studies have carried for the analysis of pesticides in fresh products (vegetables and fruits) compared to that in herbal medicinal plants, which may be attributed to the high consumptions of fresh products.

Recently, there is an increment in the consumption of herbal products [9-11]. Since, it has many health benefits include; ant-microbial, ant-oxidant, ant-carcinogenic, and ant-diabetic potential [12-14]. In addition, herbs can be taken during pregnancy [15] and for children [16, 17]. For these reasons, it is important to focus on the development of more reliable methods for pesticide residue analysis in herbal plants. One of the most commonly used herbs is the chamomile plant [18] which can be used for treating various human ailments, as it contains several classes of biologically active

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Receive Date: 30 November 2020, Revise Date: 17 December 2020, Accept Date: 23 December 2020
DOI: 10.21608/EJCHEM.2020.51066.3046

compounds [19-21]. It was recently reported that [22], patients with type two diabetes mellitus could get an improved glycemic control with a good antioxidant status by short-term intake of chamomile tea.

The complexity of herbal matrices (containing large amounts of natural active components) usually introduces a large number of ions in the commonly used electron impact ionisation (EI) unit of the GC-MS/MS technique. Therefore, the run time of pesticide residue analysis in herbal samples using GC-MS/MS is usually longer than that for fresh products, to avoid the overlapping of the naturally active co-extracted components with the analysed pesticides in herbal plants. Such a situation creates a pressure on food safety laboratories, which need to make a rapid response for the analysed of herbal samples to their customers and the related governmental authorities. Analysis run time of GC-MS/MS can be largely minimized using the Back-flushing technique (reversing the direction of the GC carrier gas flow through the capillary column after eluting the compounds of interest) [23]. Using this technique keeps the MSD source clean and decreases the chemical background by removing the less volatile matrix from the capillary column [24]. Furthermore, lowering the length of the GC column leads to shorting the analysis run time. Anna et al [25] have reported a rapid GC-MS/MS method of run time 20 m using backflush and a shorter HP 5 MS column of 10 m for detection of only 56 pesticides in teas and chamomile. Also, Tomas et al [26] have developed a fast GC-MS/MS method of run time 21 min using backflush for detection of 135 pesticides in dry tea by using an HP 5 MS of 15 m length. However, using such short columns will give lower chromatographic resolution for the detection of a higher number of pesticides in heavy matrices like herbs, especially after a long term of routine application.

The main objective of this study is to develop a rapid and sensitive GC-MS/MS method, using a backflush technique, for the determination of a wide scope of pesticides (212 pesticides) in chamomile. Chamomile was selected since it resembles one of the most complex herbal matrices. The oven program temperatures for chromatographic separation will be optimized to give highly separated pesticides in a short run time as possible. A validation study has carried out for the developed method based on measurements of the following parameters: linearity, trueness, precision, and limit of quantitation.

Materials and Methods

Chemicals and reagents

Methanol was purchased from Merck Chemicals. Acetonitrile and toluene were obtained from Sigma–Aldrich (USA). The ready QuEChERS salts for solvent partitioning (4.00 g anhydrous magnesium sulfate, 1.00 g sodium chloride, 1.00 g sodium citrate, and 0.50 g sodium hydrogen citrate sesquihydrate), and a mixture for the clean-up step (0.15 g anhydrous magnesium sulfate and 0.25 g Primary Secondary Amine, PSA) were purchased from Agilent Technologies (USA). Deionized water (DIW >17.6 Ω cm) was supplied by the Millipore water purification system (Milli-Q). All the studied pesticide standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). A stock solution (1000 µg mL^{-1}) for each pesticide standard was prepared in 100 mL toluene. The working standard solution mixture of the studied pesticides (2.50 µg mL^{-1}, each) was prepared by diluting a suitable aliquot of the stock solutions with toluene and stored in a refrigerator at 4 ºC for the fortification of chamomile samples.

Sample preparation

Blank chamomile sample (stems and flowers, previously tested for pesticide residues) was finely ground. A little modified QuEChERS (citrate buffered method) was used [27]. In brief, 2 g of ground homogenized chamomile was weighed into a 50 mL polypropylene tube. For recovery experiments, the sample was fortified by adding appropriate volumes of working mixture (2.50 µg mL^{-1}), then left for 30 m (to allow pesticide absorption). These samples wetted by adding 10 mL of DIW and shacked for 1 m by hand. Then, 10 mL acetonitrile added and mixed by hand for 1 m. After that, all samples cooled in freezer at -20 °C (for 20 m) before adding the ready salting out mixture. Where, it is known that, adding the salting out mixture increases the heat of the sample. This increment in temperature will be higher in case of herbs sample, since a lower amount of sample (2.00 g) was collected compared to that for fresh samples (10 g). The ready QuEChERS salt for salting out was added on the cooled samples with immediately

shaken for 1 m. The tubes were centrifuged at 15, 000 × g and 4 ºC for 5 m. The acetonitrile extracts were collected into a 15 ml tube containing the ready clean up mixture. This tube was shaken for 1 m and centrifuged for 2 m at 15, 000 × g and 4 ºC. Finally, 2.00 mL of the supernatant was transferred into 50 mL round bottom glass flask and evaporated under vacuum at 40 ºC till complete dryness. The residue was then reconstituted by 2.00 mL of hexane/ acetone (9:1 v/v) which containing 100 µg L^{-1} Aldrin (Injection standard). Samples were then ultra-sonicated and filtered through 0.45 µm PVDF Millipore filters into an amber glass vial being ready for GC-MS/MS analysis.

Gas chromatography tandem mass spectrometer

Pesticides analyses were performed using Agilent 7890A gas chromatograph coupled with 7000B triple quadrupole mass spectrometer (Agilent Technologies, USA) using Mass Hunter software. The mass ionization was carried out using electron ionization mode at + 70 eV, with a sample injection volume of 1 µL. The temperatures of the transfer line and ion source are 280 ºC and 300 ºC, respectively. The analysis was carried out with a solvent delay of 2 m with applying multiple reaction monitoring (MRM) for the studied pesticides. Most MRM parameters for the studied pesticides (Table 1) were obtained from previous studies [28] with exchanging between the selected quantifiers and qualifiers for many pesticides. In addition, few pesticides have been optimized to get more sensitive and selective MRMs include biphenyl, penconazole, and ethion.

Chromatographic separations carried out using HP-5ms Ultra Inert column (30 m × 0.25 mm, 0.25 µm) which obtained from Agilent Technologies (USA). A pure Helium gas (>99.999 %) was used as carrier gas with a constant flow rate of 1.83 mL/m. The optimized oven temperature program and back flushing were used to shorten the analysis time with reducing the times of system maintenance. Backflush parameters were installed as follow; holding for 3 m; inlet pressure of 1 psi; three way splitter pressure of 40 psi; at oven temperature of 280 ºC.

Previously reported oven temperature program

The GC-MS/MS analysis was carried out using a previously reported oven temperature program [28], which carried out in QCAP Laboratory. Where, the temperature was initially held at 70 ºC for 2 m, 25 ºC /m to 150 ºC , 3 ºC /m to 200 ºC, 8 ºC /m to 280 ºC(hold for 10 m). The total run time is 42 m.

New optimized temperature program

The oven temperature was initially held for 1 m at 70 ºC, 40 ºC/m to 150 ºC, and 6 ºC/m to 250 ºC. Finally, the oven temp was programed to 315 ºC by 15 ºC/m (hold for 1min). The total run time was 25 m**.**

Method validation

To elucidate the performance of the developed GC-MS/MS method, a validation study has been carried out according to SANTE/11813, 2018[29]. Linearity was evaluated using four matrix-matched calibration solutions prepared by spiking blank chamomile extracts at the following concentrations 2, 10, 50, and 100 µg L^{-1}. Trueness was obtained by recovery measurements of five spiking blank chamomile at the following levels 10, 50, 250, and 500 µg kg^{-1}. These concentrations appears fifth fold lowered on the instrument (2, 10, 50, and 100 µg kg^{-1}), giving the dilution factor of five. Precision was evaluated as intra-day (same day) and inter-day precision (five repeated days), which represented as relative standard deviation (RSD %). Intra-day precision was obtained from the injection of the five repeated spiked samples at the four different spiking levels in the same day. Inter-day precision was studied by the analysis of five spiked samples at concentrations of 50 and 250 µg kg^{-1}. Limit of quantitation (LOQ) was determined as the lowest spike level that obeys the method performance criteria for trueness and precision [29]. Finely, a blank chamomile extract was analyzed in every run, to ensure that there are no interfering peaks with the selected MRM transitions for the target pesticides.

Results and Discussion

Optimization of GC oven temperature

In this study, 212 pesticides were selected to cover a wide analytical scope of pesticides analysis. A standard mixture of 250 µg Kg^{-1} was prepared in a blank chamomile extract (appear on the instrument as 50 µg Kg^{-1}, giving the dilution factor of five) was analyzed by GC-MS/MS, using the previously reported oven temperature program [28]. The total ion chromatogram (TIC) of this analysis is shown in Fig. (1), as shown in this figure, there are poor distributions for the eluted pesticides at each program

rate. Where, there is a slow ramping temperature of 3 ºC/ m for the increment of oven temp from 150 to 200 ºC (acquisition time of 5.2 to 21.8 m) to elute 89 pesticides. On the other hand, a higher ramping temperature of 8 ºC/ m was applied for the increment of oven temp from 200 to 280 ºC (acquisition time of 21.8 to 31.8 m) although there were a higher number of pesticides (112 pesticides) eluted between these temps. Furthermore, there were six minutes from the acquisition time of 36 to 42 m used for cleaning the used column after eluting all the tested pesticides.

In the current study, oven temperature programs were modified in order to give a good distribution for the eluted pesticides, which subsequently minimize the overall time of GC analysis. The GC oven temperature was started at 70 ºC, hold for one m, and fast ramped by 40 ºC/ m to 150 ºC. In this program temperature, a rate of 50ºC/ m has also been tried in the current study (using a HP 5 MS of 30 m). But, the ramping of 40 ºC/ m was preferred since it may maintain a higher resolution for eluted pesticides especially after several routine injections. After that, the oven temp was increased from 150- 250 ºC (acquisition time of 2.6 to 10 m), at a rate of 6 ºC/ m. At this program temperature, the oven temperature reaches 200 ºC with a twofold faster rate than that in the previously reported method [28]. Where, by raising the temperature from 150 to 200 ºC (from acquisition time of 3.00 and 11.33 m) only 47 pesticides were eluted with no interfering peaks from matrix components. So, there is no need for slowing the ramping at this section as done in the previous method [28].

Fig. 2A and 2B show the MRM chromatograms for formothion (RT 6.71) and diazinon (RT 10.49), respectively, which analyzed by the newly developed method. These MRM chromatograms don't differ largely from those obtained by the previous reported method [28] in Fig1A and 1B respectively. In addition, the current program temp with a rate of 6 ºC/ m slows down the increment of oven temp from 200-250 ºC (acquisition time of 11.3 to 19.66 m) by 25 % than that in the previous method (8 ºC / m). This slowdown is highly needed at this program temperature (200-250 ºC) since it elutes a higher number of pesticides (120). Therefore; the eluted peaks for penconazole at RT 14.29 (Fig.2C) and ethion at RT 17.33 (Fig.2D)

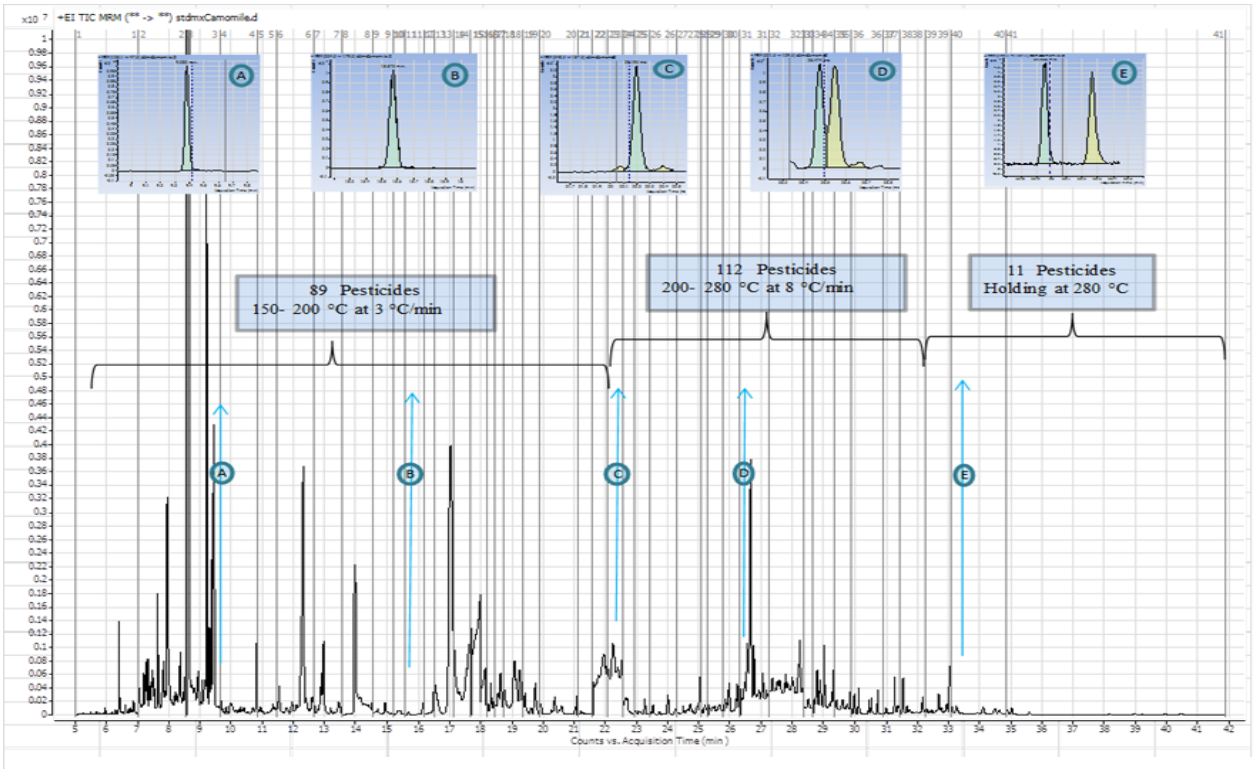

Fig.1. Total ion chromatogram for the MRM analysis of a standard mixture of 250 µg/ Kg, in a blank chamomile extract, by the previous reported GC oven temperature program [28] with MRM chromatograms for formothion (A), diazinon (B), penconazole (C), ethion (D) and flucythrinate (E)

achieved a good separation from matrix interference peaks contrary to that obtained during analysis by the previously reported method [28] (Fig. 1C and Fig.1D). Even though, new MRMs for penconazole (Fig 2F) and ethion (Fig 2G) have been optimized in the current study with almost no interferences. The last temperature program in the new method is increment the oven temp from 250 to 315 ºC with a moderate ramping of 15 ºC / m, since it elutes only 44 pesticides of high selectivity. However, the two isomers for flucythrinate (one of the late eluted pesticide) were still separated, as shown in Fig. 1E.

Method Validation

Linearity

For the linearity evaluation, four calibration levels were prepared in chamomile extract at 2, 10, 50, and 100 µg L^{-1}. Correlation coefficients (R^2) for each pesticide were calculated by plotting signal responses against concentrations of each pesticide. As presented in table 1, R^2 for each studied pesticide was ≥ 0.9988, indicating good linearity for the analyzed pesticides using the developed GC-MS/ MS.

Recovery

The recoveries of 212 pesticides in chamomile extract were carried out at four concentration levels of 10, 50, 250 and 500 µg kg^{-1}. At each level, five replicates were tested by calculating mean recovery and precision evaluation (RSD). Adding a freezing step at -20 °C for 20 m before the addition of the salting-out salt mixture in the procedure of pesticide extraction (the known QuEChERS method) is very important step that decreases the large increment of sample temperature after the addition of this salt, especially with the low weight of the herbal sample of 2 gm. This temperature affects largely the recovery of the thermal labile pesticides, especially at lower concentration levels. At levels of 250 and 500 µg kg^{-1}, nearly all of the studied pesticides have recoveries between 70-120 % with RSDs ≤ 20 which is in agreement with SANTE/11813, 2018 [29]. Only omethoate has very low recovery (35 %) at all the studied levels. This is maybe attributed to its hydrolysis by high pH [30] during the clean-up step by PSA. Even though, its analysis has RSD < 20 that enables its qualitative analysis by the currently developed method. While, quantitative analysis of this pesticide can be carried out by LC-MS/MS technique (using soft ionization mode). In addition, samples can be directly analysis by LC-MS/MS without using PSA [31, 32]. At a lower concentration level of 50 µg kg^{-1}, only highly polar pesticides (six pesticides) can't be calculated at this concentration. Where, it may interact with the liner glass surface leading to its degradation [33]. The recoveries for the studied pesticides have been carried out also at a much lower conc. level of 10 µg kg^{-1}. Even though, nearly 75% of the studied pesticides show good performance at this concentration level.

Precision

Intra-day precision was evaluated by calculating RSD of the obtained results for the analysis of five fortified replicates at four levels 10, 50, 250, and 500 µg kg^{-1} in the same day and by calculating RSD of the obtained results for the analysis of five fortified replicates at two levels 50 and 250 µg kg^{-1} over 5 days. As presented in table 2, most of the studied pesticides have RSD < 20 for both intra-day and inter-day precision.

Limits of quantitation

Most of the studied pesticides have a low LOQ of 10 µg Kg^{-1}. Only six pesticides have a much higher LOQ of 250 µg Kg^{-1}, as presented in table 2. However, the LOQ value for these six pesticides is equal or lower than their MRLs values, except for oxadiazinon, which have a low MRL of 50 µg Kg^{-1} [34].

Analysis of real samples

In order to elucidate the effectiveness of the developed method, fifteen chamomile samples were analyzed by this method in one batch, which includes: a blank chamomile extract, five calibrations levels (prepared in a blank chamomile extract), the fifteen chamomile samples and ended by a calibration level of 10 µg L^{-1} (to check the performance of the instrument). These chamomile samples were obtained from different stores at Al- Fayoum governorate, the largest Egyptian governorate for chamomile production [35].

The results of the collected chamomile samples are present in table 3. Most of the collected samples were contaminated by pesticides except one sample, which was free from any of the studied pesticides. Values of the founded pesticides were below its MRLs [34]. However, the presence of three pesticides or more in many samples refers to uncontrolled pesticide practices. Sample number fifteen was contaminated by six pesticides (Table 3); the result of metalaxyl in this sample was 70 % from its MRL.

Conclusion

A fast run time of the GC-MS/MS method, equal 25 m, was developed for the determination of 212 pesticides in a complex herbs matrix, chamomile. Where, a new oven temperature has developed using the back-flush technique. The developed GC-MS/MS offers high selectivity and adequate sensitivity for the studied pesticides since the developed oven temperature program gives good distribution for the

eluted pesticides along all the run time. Especially, for pesticides like penconazole and ethion which can't be analyzed at lower concentrations by the previously reported methods. This developed method is of high demanding for both food safety laboratories and their customers as it shortens the required time for pesticide residue analysis and subsequently results in fast trade and export of such valuable herbal products. Analysis of real chamomile samples at the intensive production area in Egypt, Al-Fayoum governorate, showed that only one sample was free from any of the studied pesticides, while eleven pesticides were detected in the other samples. Three samples were contaminated by five to six different pesticides, which refer to the presence of uncontrolled pesticide practices.

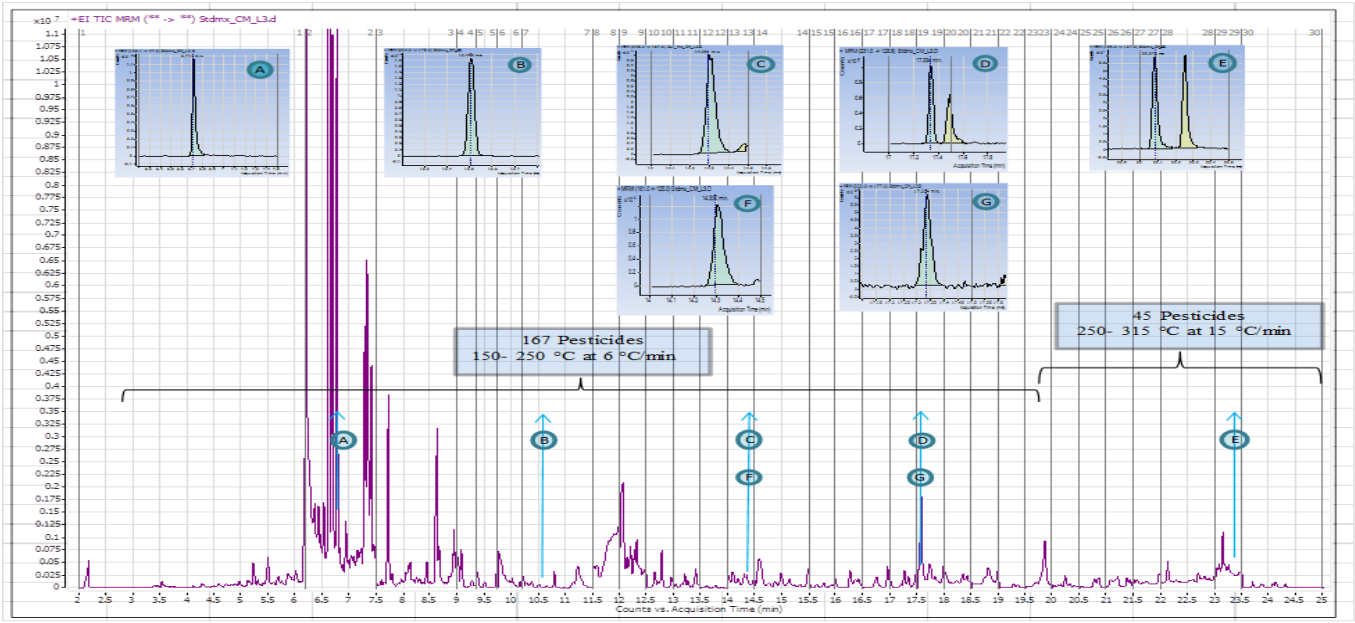

Fig.2. Total ion chromatogram for the MRM analysis of a standard mixture of 250 µg/ Kg, in a blank chamomile extract, by the new GC oven temperature program with MRM chromatograms for formothion (A), diazinon (B), penconazole (C, F), ethion (D, G) and flucythrinate(E).

Table 1. Acquisition and MRM parameters for the analysis of studied pesticides by GC -MS/MS.

N	**Pesticides**	**TS**	**RT**	**Quantifier**			**Qualifier**			**R**
				MRM	DT	CE	MRM	DT	CE	
1	Dichlorvos	1	4.60	185/93	10	10	185/109	10	10	0.9998
2	Dichlobenil	1	5.47	171/100	10	25	171/136	10	15	0.9997
3	Biphenyl	1	5.67	154/126	10	40	154/102	10	20	0.9998
4	Mevinphos	1,2	6.01	127/95	10	15	127/109	10	10	0.9998
5	Folpet degradation	2,3	6.67	147/103	10	5	147/76	10	25	0.9958
6	Captan degradation	2,3	6.69	151/80	10	5	151/122	10	10	0.9999
7	Formothion	2	6.71	125/47	10	15	125/79	10	5	0.9997
8	Methacrifos	2	6.71	208/180	10	5	240/180	10	10	0.9995

9	Phenylphenol	2,3	7.05	169/115	10	35	170/141	10	30	0.9999
10	Pentachlorobenzene	2	7.14	250/215	10	25	250/213	10	15	0.9998
11	Methiocarb	2,3	7.39	168/153	10	10	153/109	10	10	1
12	Heptenophos	2,3	7.61	250/89	10	15	250/124	10	25	0.9999
13	Omethoate	3,4	8.04	156/110	10	5	156/79	10	15	1
14	Tecnazene	3,4	8.05	203/83	10	35	203/143	10	20	1
15	Demeton-s-methyl	3,4	8.18	88/60	10	10	142/79	10	10	0.9999
16	Diphenylamine	3	8.25	169/167	10	10	169/77	10	35	0.9996
17	Ethoprophos	3	8.30	158/97	10	15	158/114	10	5	0.9999
18	Chlorpropham	3	8.57	213/127	30	5	213/171	30	5	0.9999
19	Trifluralin	3	8.78	306/264	10	10	306/160	10	25	0.9997
20	Sulfotep	3,4	8.92	322/146	10	25	322/174	10	15	0.9997
21	Cadusafos	3,4	8.99	213/73	10	10	159/131	10	10	0.9998
22	Phorate	4	9.08	231/129	10	20	260/75	10	5	0.9997
23	HCH alpha-	4,5	9.27	181/145	10	15	219/183	10	10	0.9996
24	Thiometon	4	9.37	88/60	10	5	125/47	10	20	0.9999
25	Disulfoton	4,5	9.37	88/59	10	25	88/60	10	25	0.9998
26	Hexachlorobenzene (HCB)	5	9.50	284/214	10	35	284/249	10	25	0.9995
27	Pentachloroanisole	5	9.58	265/143	10	15	265/235	10	25	0.9995
28	Atraton	5,6	9.69	211/196	10	15	211/169	10	15	0.9999
29	Ethoxyquin	5,6	9.70	202/174	10	15	202/159	10	30	0.9996
30	Dazomet	5,6	9.74	162/89	10	15	162/42	10	15	1
31	Dicloran	5,6	9.75	206/176	10	5	206/124	10	25	0.9999
32	Dimethoate	5,6	9.84	229/87	10	10	125/47	10	20	0.9993
33	Prometon	6	9.85	210/168	10	5	225/168	10	10	1
34	Atrazine	6	9.96	200/94	10	20	200/122	10	10	0.9999
35	Terbuthylazine	6	10.02	214/104	10	20	214/132	10	10	0.9999
36	Propazine	6	10.02	214/172	10	10	214/94.4	10	25	0.9997
37	Terbumeton	6	10.03	225/169	10	5	169/159	10	5	
38	Monolinuron	6,7	10 28	214/61	10	5	126/99	10	15	0.9998
39	HCH beta-	6,7	10.14	181/145	10	15	181/109	10	30	0.9999
40	Terbufos	6	10.21	231/129	10	25	231/175	10	10	0.9997
41	Profluralin	6,7	10.25	318/199	10	20	318/55	10	20	0.9989
42	Cyanophos	6,7	10.27	243/109	10	10	243/116	10	5	0.9997
43	Quintozene	7	10.28	295/237	10	20	237/119	10	30	0.9993
44	HCH gamma-	6,7	10.34	181/145	10	15	181/109	10	30	1
45	Diazinon	7	10.50	304/179	10	15	179/137	10	20	0.9996
46	Pyrimethanil	7	10.51	198/156	10	25	198/118	10	25	0.9999
47	Tefluthrin	7	10.80	177/127	10	20	177/137	10	20	0.9995

48	Iprobenfos	7	11.13	204/91	10	10	204/122	10	10	0.9997
49	HCH delta	7,8	11.16	181/145	10	15	181/109	10	30	0.9999
50	Pirimicarb	7,8	11.29	238/166	10	10	166/96	10	15	0.9998
51	Chlorothalonil	7,8	11.33	264/168	10	25	266/231	10	20	1
52	Dichlofenthion	8	11.58	279/223	10	10	279/205	10	25	0.9998
53	PCB 028	8	11.67	258/186	10	15	258/150	10	25	0.9999
54	Metribuzin	8,9	11.95	198/82	10	20	198/89	10	15	0.9998
55	Vinclozolin	8,9	11.99	212/172	10	15	212/145	10	20	0.9999
56	Linuron	8,9	12.00	187/124	10	30	187/159	10	10	0.9999
57	Propanil	8,9	12.01	161/99	10	25	217/161	10	10	0.9997
58	Chlorpyrifos-methyl	8,9	12 08	286/93	10	20	286/271	10	20	1
59	Parathion-methyl	8,9	12.05	263/109	10	15	263/79	10	30	1
60	Heptachlor	8,9	12.08	272/237	10	25	272/117	10	25	0.9997
61	Tolclofos-methyl	8,9	12.11	265/250	10	15	265/93	10	25	0.9994
62	Alachlor	9	12.15	188/160	10	10	160/130	10	30	0.9996
63	Ametryn	9	12.18	227/152	10	20	227/170	10	30	0.9999
64	Prometryn	9	12.26	241/184	10	5	241/111	10	5	0.9998
65	Metalaxyl	9	12.27	206/132	10	5	206/162	10	20	0.9997
66	Paraoxon-ethyl	9	12.30	149/102	10	20	109/81	10	10	0.9992
67	Prosulfocarb	9	12.37	128/43	10	5	128/41	10	5	1
68	Terbutryn	9,10	12.62	185/170	10	5	241/170	10	10	0.8245
69	PCB 052	10	12.64	292/220	10	25	292/255	10	10	0.9999
70	Fenitrothion	10	12.69	277/260	10	5	277/109	10	20	0.9997
71	Pirimiphos-methyl	10	12.70	290/125	10	25	305/290	10	10	0.9999
72	Ethofumesate	10	12.74	286/207	10	5	286/161	10	15	1
73	Malathion	10,11	12.94	158/125	10	10	173/127	10	10	0.9999
74	Thiobencarb	10,11	12.97	257/72	10	20	257/100	10	20	0.9999
75	Diethofencarb	11	13.13	267/225	10	5	196/168	10	5	0.9999
76	Fenpropimorph	11	13.20	128/70	10	15	128/110	10	10	0.9999
77	Chlorpyrifos	11	13.25	314/258	10	15	197/169	10	15	1
78	Parathion-ethyl	11	13.31	291/109	10	10	291/81	10	10	0.9995
79	Triadimefon	11,12	13.37	208/181	10	5	208/127	10	15	0.9999
80	Chlorthal-dimethyl	11	13.40	299/221	10	25	330/299	10	10	0.9999
81	Tetraconazole	11,12	13.59	336/218	10	15	336/204	10	30	0.9999
82	Butralin	12	13.71	266/220	10	10	266/190	10	10	0.9989
83	Bromophos-methyl	12	13.76	331/316	10	20	331/286	10	35	0.9999
84	Pirimiphos-ethyl	12	13.88	318/109	10	35	333/318	10	5	1
85	Isofenphos-methyl	12,13	14 05	199/121	10	15	199/65	10	15	0.9999
86	Cyprodinil	12,13	14 71	225/224	10	10	224/208	10	20	0.9999

87	Chlorfenvinphos I	13	14.13	267/159	10	20	267/81	10	40	0.997
88	Heptachlor-exo-epoxide (cis-)	13	14.17	353/263	10	15	353/282	10	15	0.9999
89	Pendimethalin	13	14.19	252/161	10	20	252/162	10	10	0.9987
90	Metazachlor	13	14.20	209/132	10	20	133/117	10	25	1
91	Penconazole	13	14.29	161/125	10	25	159/123	10	25	1
92	Heptachlor-endo-epoxide (trans-)	13	14.31	183/119	10	25	183/155	10	25	1
93	Pyrifenox I	13	14.33	171/100	10	25	262/227	10	10	1
94	Tolylfluanid	13	14.34	238/137	10	10	137/91	10	15	1
95	Chlozolinate	13	14.35	186/145	10	15	188/147	10	15	0.9999
96	Chlorfenvinphos II	13,14	14.47	267/159	10	20	267/81	10	40	0.9999
97	Mecarbam	13,14	14.50	329/131	10	10	329/160	10	5	1
98	Phenthoate	13,14	14.53	274/121	10	10	274/125	10	20	1
99	Quinalphos	13,14	14.56	146/118	10	15	146/91	10	25	0.9999
100	Triadimenol I	14	14.63	168/70	10	15	128/65	10	20	1
101	Procymidone	14	14.76	283/96	15	10	283/255	15	10	1
102	Triflumizole	14	14.86	206/179	10	10	278/73	10	5	1
103	Triadimenol II	14	14.86	168/70	10	15	128/65	10	20	1
104	Chlordane trans- (gamma)	14	14.90	373/266	10	30	373/264	10	25	1
105	Chlordane cis- (alpha)	14	14.90	373/266	10	30	373/264	10	25	1
106	Methidathion	14	14.97	145/58	10	15	145/85	10	5	1
107	Bromophos-ethyl	14	15.00	359/303	10	15	359/331	10	5	0.9999
108	Pyrifenox II	14	15.10	171/100	10	25	262/227	10	10	1
109	PCB 101	14	15.13	326/256	10	35	326/291	10	10	0.9999
110	Endosulfan alpha-	14	15.22	241/206	10	15	239/204	10	15	1
111	Butachlor	14	15.35	237/160	10	25	237/188	10	25	1
112	Ditalimfos	14	15.48	130/102	10	15	148/102	10	25	1
113	Napropamide	14	15.63	128/72	10	5	271/128	10	5	1
114	Oxadiazon	15	15.72	175/112	10	15	302/175	10	15	0.9993
115	Hexaconazole	15	15.72	214/172	10	20	214/159	10	20	0.9999
116	Prothiofos	15	15.77	267/239	10	5	162/63	10	30	1
117	Isoprothiolane	15	15.83	290/118	10	10	290/204	10	5	1
118	Profenofos	15,16	15.88	337/267	10	10	337/188	10	30	1
119	Dieldrin	15,16	15.97	263/193	10	30	263/191	10	30	0.9999
120	DDE pp`-	15	15.98	246/176	10	30	248/176	10	30	0.9999
121	DDD op`-	16	16.24	237/165	10	20	235/200	10	10	1
122	DDD pp`-	16	16.24	237/165	10	20	235/200	10	10	1
123	Buprofezin	16	16.27	172/57	10	15	105/104	10	15	0.9999

124	Carboxin	16,17	16.30	235/143	10	5	144/87	10	5	1
125	Oxyfluorfen	16	16.32	252/196	10	20	361/300	10	15	0.9991
126	Myclobutanil	16	16.34	179/125	10	15	179/152	10	5	1
127	Fludioxonil	16,17	16.35	248/127	40	30	248/182	40	15	0.9999
128	Flusilazole	16,17	16.36	233/165	10	20	233/152	10	20	1
129	Bupirimate	16,17	16.41	273/193	10	5	316/208	10	5	1
130	Kresoxim-methyl	16,17	16.41	206/116	10	5	206/131	10	10	1
131	Endrin	17	16.60	281/245	10	20	263/191	10	35	0.9996
132	Fluazifop-p-butyl	17	16.72	282/91	10	15	282/238	10	15	0.9999
133	Cyproconazole	17	16.74	222/125	10	20	222/82	10	10	1
134	Chlorfenapyr	17	16.80	408/59	10	10	247/227	10	15	0.9996
135	Endosulfan beta-	17,18	16.96	195/159	10	10	195/125	10	25	0.9998
136	Chlorobenzilate	17,18	16.96	251/139	10	10	139/75	10	15	0.9999
137	PCB 118	17,18	16.99	326/256	10	25	326/254	10	25	1
138	Diniconazole	18	17.18	270/234	10	15	268/136	10	15	1
139	DDT op`-	18	17.25	237/165	10	20	235/165	10	20	0.9998
140	DDT pp`-	18	17.25	237/165	10	20	235/165	10	20	0.9998
141	Ethion	18,19	17.33	233/177	10	5	231/185	10	5	1
142	Oxadiaxyl	18,19	17.42	163/132	10	5	163/117	10	15	1
143	Chlorthiophos	18,19	17.44	269/205	10	15	325/269	10	15	1
144	Mepronil	19,20	17.56	119/91	10	15	119/65	10	15	0.9422
145	PCB 153	19	17.61	360/290	10	25	360/325	10	15	0.9999
146	Triazophos	19	17.82	161/134	10	5	257/162	10	5	0.9999
147	Benalaxyl	19,20	18.04	148/105	10	15	204/176	10	5	1
148	Epoxiconazole I	20	18.08	192/138	10	10	192/111	10	35	0.9989
149	Endosulfan-sulfate	20	18.21	272/237	10	20	387/253	10	5	0.9999
150	Propiconazol I	20	18.21	259/69	10	15	259/173	10	15	1
151	Trifloxystrobin	20	18.34	116/89	10	20	131/116	10	15	0.9999
152	Clodinafop-propargyl ester	20,21	18.39	349/266	10	10	349/238	10	15	0.9989
153	PCB 138	20,21	18.41	360/290	10	25	360/325	10	15	1
154	Propiconazol II	20	18.41	259/69	10	15	259/173	10	15	1
155	Hexazinone	21	18.72	171/71	10	15	171/85	10	15	1
156	Nuarimol	21	18.74	235/139	10	15	314/139	10	5	1
157	Tebuconazole	21	18.78	250/125	10	25	252/127	10	25	0.9999
158	Methoxychlor	21	18.79	227/169	10	25	227/115	10	40	0.9999
159	Diclofop methyl	21	18.80	253/162	10	15	340/253	10	15	0.9999
160	Propargite	21	18.81	135/107	10	15	135/77	10	25	0.9964
161	Piperonyl-butoxide	21	18.97	176/103	10	25	176/145	10	15	0.9999

162	Epoxiconazole II	22	19.26	192/138	10	10	192/111	10	35	0.9999
163	Fenoxycarb	22	19.34	255/186	10	10	186/109	10	15	0.9998
164	Mefenpyr-diethyl	22	19.35	253/190	10	20	253/188	10	25	1
165	Spiromesifen	22,23	19.41	370/254	10	15	370/272	10	15	0.9999
166	Iprodione	23	19.64	314/56	25	25	314/245	25	25	0.9998
167	Pyridaphenthion	23	19.66	340/199	10	5	340/108	10	15	0.9999
168	Bromuconazole I	23	19.71	295/173	10	15	173/145	10	15	0.9998
169	Bromopropylate	23	19.78	341/185	10	20	183/155	10	15	1
170	Azinphos-methyl	23,24	19.80	160/77	10	20	160/132	10	5	0.9999
171	Phosmet	23,24	19.80	160/133	10	20	160/105	10	15	0.9998
172	EPN	23,24	19.82	157/77	10	25	157/110	10	15	0.9996
173	Bifenthrin	23	19.84	181/165	10	25	181/166	10	15	1
174	Tetramethrin	23	19.86	164/77	10	25	164/107	10	10	0.9999
175	Bifinazate	23	20.00	258/199	10	15	300/258	10	15	0.9993
176	Fenpropathrin	23	20.03	265/210	10	15	209/116	10	20	0.9999
177	Etoxazole	24	20.09	300/270	10	20	204/176	10	10	0.9999
178	Tebufenpyrad	24	20.14	333/171	10	20	333/276	10	5	1
179	Fenazaquin	24	20.22	160/145	10	5	160/117	10	20	1
180	PCB 180	24	20.30	394/324	10	30	396/324	10	20	0.9999
181	Bromuconazole II	24,25	20.38	295/173	10	15	173/145	10	15	0.9996
182	Tetradifon	24	20.52	229/201	10	15	354/159	10	10	0.9998
183	Triticonazole	25	20.71	235/182	10	15	235/217	10	5	0.9995
184	Phosalone	25	20.77	182/111	10	15	182/138	10	5	0.9999
185	Pyriproxyfen	25,26	20.83	136/96	10	10	136/78	10	20	1
186	Mirex	25	20.86	272/237	10	15	272/235	10	25	0.9999
187	Mefenacet	25,26	21 39	192/136	10	10	193/137	10	10	0.9999
188	Cyhalothrin lambda-	26	21.19	197/161	20	10	181/127	20	35	0.9997
189	Fenarimol	26	21.36	139/75	10	35	139/111	10	15	0.9999
190	Acrinathrin	26	21.42	289/93	20	5	209/141	20	20	0.9995
191	Pyrazofos	26	21.48	221/193	10	10	232/204	10	10	0.9999
192	Azinphos-ethyl	27	21.54	160/104	10	10	132/104	10	5	0.9996
193	Fenoxaprop-P-ethyl	27	21.72	361/288	10	10	288/119	10	10	0.9999
194	Bitertanol	27,28	21.95	170/141	10	20	170/115	10	35	0.9998
195	Permethrin I	27,28	21.97	183/168	10	15	183/115	10	10	0.9999
196	Permethrin II	28	22.11	183/168	10	15	192/136	10	10	1
197	Pyridaben	27,28	22.12	147/117	10	20	147/132	10	10	0.9999
198	Fluquinconazole	28	22.26	340/298	10	20	340/313	10	15	0.9998
199	Coumaphos	28	22.30	362/226	10	15	362/81	10	30	0.999
200	Prochloraz	28	22.35	180/138	10	10	180/69	10	20	0.9992

201	Fenbuconazole	28,29	22.68	198/129	10	5	129/102	10	10	0.9994
202	Cyfluthrin(4 isomer)	28,29	22.74	163/127	20	5	227/77	20	30	1
203	Boscalid	28,29	23 13	140/112	10	10	342/140	10	10	0.9997
204	Cypermethrin (4 isomer)	28,29	23 29	163/127	20	5	181/127	20	35	0.9994
205	Flucythrinate I	28,29	23.07	199/107	10	30	199/157	10	10	0.9995
206	Etofenprox	29	23.13	376/163	10	10	163/135	10	10	0.9999
207	Flucythrinate II	29	23.24	199/107	10	30	199/157	10	10	0.9996
208	Fenvalerate I	29	23.68	167/125	10	10	225/119	10	15	0.9995
209	Fenvalerate II	29,30	23.85	167/125	10	10	225/119	10	15	0.9994
210	Fluvalinate tau-	30	23.88	250/200	10	20	250/55	10	20	0.9991
211	Difenoconazol I	30	24.10	323/265	10	15	325/267	10	15	0.9993
212	Deltamethrin	30	24.28	253/172	50	10	253/93	50	20	0.9986

Table 2. Recoveries (Rec) and relative standard deviation (RSD) at10, 50, 250 and 500 µg/kg (n= 5) in same day and RSD at 250 and 500 µg/kg (n= 5) in five replicates day. Limit of quantitation (LOQ) was calculated according to SANTE/11813, 2018.

N	**Pesticides**	**Rec and RSD at**								**Inter day precision at**		**LOQ (µg/kg)**
		10 µg/Kgm		50 µg/Kgm		250 µg/kg		500 µg/kg		50 µg/Kg	250 µg/kg	
		Rec %	RSD	Rec %	RSD	Rec %	RSD	Rec %	RSD	RSD	RSD	
1	Dichlorvos	111	6	110	12	92	6	102	9	13	5	10
2	Dichlobenil	102	9	96	15	85	5	100	10	13	3	10
3	Biphenyl	90	25	92	22	76	9	90	11	17	7	10
4	Mevinphos	99	9	94	11	85	5	100	12	6	5	10
5	Folpet degradation	<LOQ	\	98	11	82	7	113	16	18	14	50
6	Captan degradation	<LOQ	\	122	9	115	9	120	9	16	6	50
7	Formothion	101	11	103	11	91	4	108	10	7	4	10
8	Methacrifos	110	7	110	7	90	4	109	11	7	3	10
9	Phenylphenol	96	10	91	11	85	3	101	12	4	5	10
10	Pentachlorobenzene	81	6	73	11	79	4	93	13	6	7	10
11	Methiocarb	<LOQ	\	115	15	116	4	112	14	29	7	50
12	Heptenophos	<LOQ	\	128	6	85	1	97	11	10	6	50
13	Omethoate	50	0	35	9	35	11	36	15	15	18	
14	Tecnazene	<LOQ	\	110	6	97	7	106	11	12	9	50
15	Demeton-s-methyl	117	8	70	10	85	9	100	7	7	7	10
16	Diphenylamine	<LOQ	\	64	12	100	10	98	16	14	8	50
17	Ethoprophos	112	11	94	8	91	6	99	12	5	4	10
18	Chlorpropham	101	5	100	10	92	6	103	13	7	6	10
19	Trifluralin	97	10	100	10	86	5	93	7	10	11	10
20	Sulfotep	115	10	105	9	92	6	99	12	8	7	10
21	Cadusafos	<LOQ	\	111	8	89	7	93	8	9	6	50

22	Phorate	137	14	98	5	87	6	95	9	6	6	10
23	HCH alpha-	91	19	97	7	99	8	109	11	6	5	10
24	Thiometon	102	9	109	6	79	4	93	8	5	6	10
25	Disulfoton	102	9	104	6	79	7	92	12	8	6	10
26	Hexachlorobenzene	86	4	71	6	72	6	81	12	2	9	10
27	Pentachloroanisole	<LOQ	\	<LOQ	\	90	10	92	15	<LOQ	15	250
28	Atraton	<LOQ	\	85	21	84	8	80	10	25	12	50
29	Ethoxyquin	<LOQ	\	58	8	53	7	64	15	23	8	50
30	Dazomet	<LOQ	\	70	5	26	9	28	12	6	14	50
31	Dicloran	<LOQ	\	102	12	93	8	107	10	17	7	50
32	Dimethoate	<LOQ	\	72	21	79	6	68	12	25	9	50
33	Prometon	89	15	76	12	81	6	73	13	11	9	10
34	Atrazine	113	23	88	17	81	7	82	9	9	6	10
35	Terbuthylazine	<LOQ	\	96	12	87	8	86	9	26	7	50
36	Propazine	79	17	94	10	91	6	91	9	6	5	10
37	Terbumeton	116	16	84	22	83	8	83	11	14	13	10
38	Monolinuron	80	17	79	13	79	7	81	6	12	14	10
39	HCH beta-	<LOQ	\	90	10	83	6	88	9	17	14	50
40	Terbufos	109	7	95	5	88	5	97	9	2	3	10
41	Profluralin	<LOQ	\	104	11	86	3	83	7	8	12	50
42	Cyanophos	109	9	97	9	91	5	98	10	3	4	10
43	Quintozene	117	14	89	8	84	5	85	7	7	9	10
44	HCH gamma-	127	6	88	12	82	6	88	6	10	12	10
45	Diazinon	104	12	99	12	95	8	98	9	8	3	10
46	Pyrimethanil	127	9	96	12	82	5	87	9	12	3	10
47	Tefluthrin	92	7	100	8	86	4	97	9	4	2	10
48	Iprobenfos	98	8	115	6	90	5	98	9	5	2	10
49	HCH delta	81	9	87	10	80	5	85	9	7	3	10
50	Pirimicarb	118	12	87	13	80	7	84	13	6	6	10
51	Chlorothalonil	<LOQ	\	88	10	76	5	84	8	9	7	50
52	Dichlofenthion	100	10	94	8	89	6	98	9	4	4	10
53	PCB 028	79	4	77	11	80	6	88	11	9	2	10
54	Metribuzin	<LOQ	\	103	12	80	7	83	8	2	4	50
55	Vinclozolin	107	9	97	13	91	5	94	6	6	2	10
56	Linuron	79	6	87	11	90	4	93	7	3	2	10
57	Propanil	117	17	86	9	91	5	94	7	11	5	10
58	Chlorpyrifos-methyl	92	9	87	13	86	4	87	6	7	4	10
59	Parathion-methyl	107	3	92	13	89	4	93	7	5	4	10
60	Heptachlor	<LOQ	\	64	9	67	4	65	7	26	26	50
61	Tolclofos-methyl	99	8	96	6	92	4	98	7	5	3	10
62	Alachlor	<LOQ	\	110	7	91	6	95	6	6	4	50
63	Ametryn	98	19	91	15	88	7	85	14	14	8	10
64	Prometryn	112	15	92	12	90	5	89	8	10	2	10
65	Metalaxyl	109	27	99	6	90	7	92	10	15	4	10
66	Paraoxon-ethyl	92	99	74	19	91	5	89	7	23	10	10
67	Prosulfocarb	88	15	100	11	94	4	101	6	3	3	10
68	Terbutryn	<LOQ	\	<LOQ	\	102	5	92	7	7	5	250
69	PCB 052	87	8	109	4	86	3	91	3	5	2	10
70	Fenitrothion	125	10	96	13	93	4	98	3	6	4	10

71	Pirimiphos-methyl	104	9	114	4	95	5	97	3	4	4	10
72	Ethofumesate	114	13	93	14	97	5	100	4	9	4	10
73	Malathion	94	11	97	8	94	5	99	4	5	5	10
74	Thiobencarb	109	12	95	9	94	3	98	2	6	4	10
75	Diethofencarb	116	6	102	11	94	5	102	3	6	2	10
76	Fenpropimorph	87	6	106	9	79	9	75	12	4	10	10
77	Chlorpyrifos	114	11	94	8	95	4	105	3	6	4	10
78	Parathion-ethyl	121	18	103	12	93	4	97	3	11	6	10
79	Triadimefon	94	9	103	13	94	4	97	4	9	3	10
80	Chlorthal-dimethyl	98	7	93	13	95	4	97	5	8	3	10
81	Tetraconazole	105	22	93	10	92	5	94	5	8	6	10
82	Butralin	125	10	81	12	86	4	88	3	8	8	10
83	Bromophos-methyl	110	11	91	10	95	5	102	3	5	5	10
84	Pirimiphos-ethyl	112	12	109	9	99	5	102	5	27	2	10
85	Isofenphos-methyl	84	14	104	10	97	6	101	2	8	2	10
86	Cyprodinil	99	8	88	10	88	6	92	6	4	4	10
87	Chlorfenvinphos I	98	7	104	11	103	7	100	6	18	7	10
88	Heptachlor-exo-epoxide (cis-)	89	12	98	14	95	7	99	3	9	9	10
89	Pendimethalin	119	11	105	9	108	6	100	2	8	6	10
90	Metazachlor	103	12	93	10	91	7	92	4	7	6	10
91	Penconazole	104	7	89	13	88	6	86	5	12	10	10
92	Heptachlor-endo-epoxide (trans-)	100	26	93	11	87	9	88	3	11	3	10
93	Pyrifenox I	<LOQ	\	86	12	87	8	77	7	10	12	50
94	Tolylfluanid	<LOQ	\	93	11	84	8	87	5	20	15	50
95	Chlozolinate	108	17	101	8	94	7	96	2	8	5	10
96	Chlorfenvinphos II	107	7	99	9	95	7	96	3	11	4	10
97	Mecarbam	<LOQ	\	109	15	120	7	108	3	11	7	50
98	Phenthoate	110	10	102	9	95	7	100	3	8	5	10
99	Quinalphos	<LOQ	\	140	9	115	9	113	4	16	3	50
100	Triadimenol I	<LOQ	\	104	15	91	8	94	5	10	3	50
101	Procymidone	113	10	103	13	96	9	101	3	6	3	10
102	Triflumizole	108	12	87	8	89	9	88	5	10	7	10
103	Triadimenol II	112	8	113	15	112	10	95	4	14	7	10
104	Chlordane trans- (gamma)	89	12	94	8	94	9	100	5	10	3	10
105	Chlordane cis- (alpha)	89	12	92	9	94	9	100	5	10	4	10
106	Methidathion	103	8	105	9	98	11	101	3	8	3	10
107	Bromophos-ethyl	102	10	103	8	100	10	107	4	6	8	10
108	Pyrifenox II	60	8	92	15	90	9	82	6	13	10	10
109	PCB 101	81	9	115	4	83	10	91	3	5	4	10
110	Endosulfan alpha-	<LOQ	\	101	16	91	11	96	4	7	5	50
111	Butachlor	102	24	108	20	97	8	98	3	12	3	10
112	Ditalimfos	99	8	99	14	92	10	96	3	8	5	10
113	Napropamide	106	9	104	7	96	8	102	4	7	3	10
114	Oxadiazon	<LOQ	\	<LOQ	\	97	11	105	6	<LOQ	9	250
115	Hexaconazole	<LOQ	\	102	9	87	12	91	4	6	7	50
116	Prothiofos	89	7	95	8	92	11	100	3	8	5	10

117	Isoprothiolane	111	9	107	14	96	13	102	2	23	5	10
118	Profenofos	117	9	121	3	102	12	102	3	9	11	10
119	Dieldrin	<LOQ	\	92	11	91	12	92	3	9	6	50
120	DDE pp`-	78	8	105	6	81	12	91	3	3	4	10
121	DDD op`-	79	8	96	9	87	13	95	3	10	6	10
122	DDD pp`-	79	8	96	9	87	13	95	3	10	3	10
123	Buprofezin	<LOQ	\	101	11	95	11	103	3	8	5	50
124	Carboxin	95	19	101	5	56	14	76	4	15	19	10
125	Oxyfluorfen	134	24	125	19	92	10	89	2	22	10	10
126	Myclobutanil	87	14	94	13	90	13	90	4	6	10	10
127	Fludioxonil	98	10	103	7	87	13	90	5	7	7	10
128	Flusilazole	98	6	98	12	89	14	90	5	13	11	10
129	Bupirimate	103	15	102	13	95	12	95	4	9	10	10
130	Kresoxim-methyl	103	15	108	12	92	10	100	3	8	7	10
131	Endrin	<LOQ	\	<LOQ	\	96	16	104	5	30	<LOQ	250
132	Fluazifop-p-butyl	104	13	111	8	98	14	106	2	10	5	10
133	Cyproconazole	96	11	94	10	86	15	90	4	8	6	10
134	Chlorfenapyr	<LOQ	\	122	11	100	17	115	2	23	16	10
135	Endosulfan beta-	<LOQ	\	94	23	89	17	90	4	19	13	50
136	Chlorobenzilate	107	12	109	9	96	13	101	3	7	7	10
137	PCB 118	69	13	74	9	78	11	87	2	4	8	10
138	Diniconazole	<LOQ	\	95	11	90	13	94	5	11	7	50
139	DDT op`-	84	4	101	8	84	13	89	3	10	3	10
140	DDT pp`-	84	4	101	8	84	13	89	3	10	3	10
141	Ethion	<LOQ	\	107	15	113	9	100	5	17	6	50
142	Oxadiaxyl	<LOQ	\	78	13	74	12	70	8	13	10	50
143	Chlorthiophos	98	11	102	9	95	12	100	3	5	7	10
144	Mepronil	<LOQ	\	<LOQ	\	99	22	97	7	15	14	250
145	PCB 153	62	11	113	4	77	12	85	5	3	9	10
146	Triazophos	110	13	107	10	98	12	104	7	12	6	10
147	Benalaxyl	<LOQ	\	105	17	105	14	103	6	10	9	50
148	Epoxiconazole I	<LOQ	\	108	6	110	11	117	11	10	10	50
149	Endosulfan-sulfate	85	11	101	8	91	14	93	6	13	4	10
150	Propiconazol	100	14	108	9	94	12	94	7	14	6	10
151	Trifloxystrobin	106	13	117	9	98	13	100	6	10	4	10
152	Clodinafop-propargyl ester	108	2	109	12	104	10	107	11	19	9	10
153	PCB 138	107	6	82	6	83	12	89	7	8	14	10
154	Propiconazol II	77	9	133	14	97	13	94	7	10	15	10
155	Hexazinone	65	18	77	11	75	14	68	10	13	18	10
156	Nuarimol	99	13	99	12	90	13	88	8	10	10	10
157	Tebuconazole	107	9	100	8	89	15	89	7	11	4	10
158	Methoxychlor	92	14	108	6	95	13	94	5	11	12	10
159	Diclofop methyl	108	12	109	10	96	15	98	6	12	5	10
160	Propargite	<LOQ	\	231	7	108	13	108	7	14	9	50
161	Piperonyl-butoxide	115	6	121	7	102	13	106	6	13	9	10
162	Epoxiconazole II	65	12	91	11	83	12	83	8	17	10	10
163	Fenoxycarb	<LOQ	\	130	7	100	19	102	5	20	6	50
164	Mefenpyr-diethyl	127	23	113	14	95	13	99	7	9	7	10
165	Spiromesifen	<LOQ	\	<LOQ	\	107	17	114	12	<LOQ	250	10
166	Iprodione	103	13	109	13	94	12	92	8	16	4	10

167	Pyridaphenthion	<LOQ	\	114	10	103	11	103	9	16	9	50
168	Bromuconazole I	97	20	93	13	89	12	87	8	16	7	10
169	Bromopropylate	92	5	113	11	102	13	102	8	14	11	10
170	Azinphos-methyl	100	13	123	7	90	13	90	8	14	5	10
171	Phosmet	91	16	113	10	92	11	92	9	20	9	10
172	EPN	70	17	115	17	95	12	92	7	18	10	10
173	Bifenthrin	84	8	100	9	89	13	96	6	10	4	10
174	Tetramethrin	119	16	96	22	94	14	96	6	19	4	10
175	Bifinazate	109	21	121	10	93	13	93	8	16	8	10
176	Fenpropathrin	109	19	108	11	93	12	101	5	8	7	10
177	Etoxazole	<LOQ	\	118	5	106	14	102	5	16	15	50
178	Tebufenpyrad	104	11	112	8	105	13	107	7	10	7	10
179	Fenazaquin	90	15	102	10	88	9	94	7	14	3	10
180	PCB 180	59	9	70	9	79	10	85	6	15	16	10
181	Bromuconazole II	92	12	90	16	82	14	81	11	12	6	10
182	Tetradifon	<LOQ	\	96	9	91	14	92	6	13	8	50
183	Triticonazole	77	15	99	13	88	11	81	10	15	9	10
184	Phosalone	89	19	116	8	91	14	93	7	13	10	10
185	Pyriproxyfen	89	15	101	7	93	11	97	6	10	7	10
186	Mirex	35	3	63	9	68	13	75	6	15	18	10
187	Mefenacet	<LOQ	\	91	25	94	14	89	8	25	11	50
188	Cyhalothrin lambda-	91	9	105	11	86	13	93	6	8	7	10
189	Fenarimol	89	8	105	13	83	14	81	8	11	7	10
190	Acrinathrin	104	4	108	10	90	9	98	7	11	8	10
191	Pyrazofos	91	5	119	6	94	12	97	7	12	7	10
192	Azinphos-ethyl	182	62	101	13	87	9	90	9	23	17	10
193	Fenoxaprop-P-ethyl	100	9	121	7	103	13	101	7	11	13	10
194	Bitertanol	85	13	105	20	90	11	83	9	11	13	10
195	Permethrin I	<LOQ	\	70	22	103	17	110	11	<LOQ	6	50
196	Permethrin II	<LOQ	\	53	11	76	11	91	11	<LOQ	19	50
197	Pyridaben	<LOQ	\	118	9	88	10	92	7	19	17	50
198	Fluquinconazole	97	18	105	7	92	11	89	8	17	6	10
199	Coumaphos	74	16	122	16	102	9	98	6	23	7	10
200	Prochloraz	<LOQ	\	<LOQ	\	83	7	76	14	16	9	250
201	Fenbuconazole	97	10	89	13	82	11	76	9	11	9	10
202	Cyfluthrin	102	14	124	15	86	8	93	6	15	8	10
203	Boscalid	91	11	109	8	83	13	80	9	11	10	10
204	Cypermethrin	86	14	114	8	77	22	93	8	7	5	10
205	Flucythrinate I	94	7	121	4	92	11	93	7	19	8	10
206	Etofenprox	<LOQ	\	123	19	95	12	104	9	23	5	50
207	Flucythrinate II	98	15	118	9	97	14	108	10	22	15	10
208	Fenvalerate I	107	21	108	5	81	9	84	7	9	7	10
209	Fenvalerate II	<LOQ	\	129	8	99	10	102	11	16	6	10
210	Fluvalinate tau-	121	8	82	9	82	5	85	8	16	7	10
211	Difenoconazol I	119	22	108	12	78	7	77	10	23	13	10
212	Deltamethrin	88	12	97	8	72	4	76	7	10	5	10

Table 3. Concentration of the founded pesticides and its MRL (µg/Kg) in the analyzed chamomile samples (S1-S15).

Pesticides (MRL)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
Clorpyrifos (500)		10	20	30	30	50	60	40	20	50	100	130	70	30	150
Malathion (1500)				<LOQ	<LOQ		<LOQ	<LOQ			10	20	10		20
Profenofos (50)				<LOQ	10			10	10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	20
Metalaxyl (100)					20				50						70
Cypermethrin(100)									10						
Procymidone (50)									<LOQ						
Tetraconazole (20)												10			
Diazinon (50)				<LOQ			<LOQ								<LOQ
Flusilazole (50)													<LOQ		
Tolcofos-Me (50)										<LOQ					
Myclobutanil (50)													<LOQ		10

Acknowledgment
I would like to express my sincere gratitude to my colleagues Ekramy Halawa, Tawfik Khedr, Prof. Dr. Emad At-Allah (Quality Manager), and Prof. Dr. Ashraf El-Marsafy (previous lab. director) at QCAP Egypt laboratory for their help and support.

Conflicts of interest
There are no conflicts to declare.

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