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Determination of pesticide residues in almonds by LC-MS/MS and GC-MS: A study of method validation and matrix effects☆

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ABSTRACT

This study was performed to detect pesticide residues in almond. QuEChERS method was validated for determination of 270 pesticides by liquid chromatography-tandem mass spectrometry (LC–MS/MS) and gas chromatography-mass spectrometry (GC–MS). The method had a suitable linearity ($R^2 \geq 0.99$). Limit of detection (LOD) and limit of quantification (LOQ) were ranged from 0.28 to 3.00 μg kg^{-1} and 0.92 to 9.98 μg kg^{-1} respectively. Average recoveries varied from 70.03 % to 119.82 %. Repeatability and intra-laboratory reproducibility of the method, expressed as RSDs were between 1.65–19.15 % and 1.77–19.42 %, respectively. Expanded relative uncertainties ranged from 15.82 % to 46.58 %. Although minimal matrix effects were observed in the LC-MS/MS analysis, a strong matrix effects were detected in the GC–MS analysis. The validated method was used collected for the analysis of collected 90 samples from fifteen different provinces in Turkey. The data showed that all the studied samples did not contain pesticides above the LOD values.

Introduction

The almond [*Prunus dulcis* (Mill.) D.A. Webb; syn. *P. amygdalus* (L.) Batsch] is classified as a nut belonging to the Rosaceae, subfamily Prunoideae. The cultivated almond that is commercially grown worldwide is thought to have originated in Iran, Turkey, Syria, and Palestine and spread to the world from these regions four thousand years ago (Kester & Assay, 1975; Gouta et al., 2021). Turkey is one of the genome centers of almond. Almond shells were found in archeological excavations dating back 7000 years BC (Sykes, 1975). Almond takes an important place in the world's nut production. USA is the leading country in almond production which corresponds 57.24 % of world production according to FAO data for 2020 (FAO, 2020). In the Mediterranean region Spain is the first country in almond production with% 10.7. Turkey is in the 5th place of almond production with 3.84 %.

Almonds contain several compounds that have remarkable functions in the human body. These are rich sources of carbohydrates, fatty acids, proteins, and amino acids, as well as vitamins, minerals, and secondary metabolites (Barreca et al., 2020). Unsaturated fatty acids (linoleic and oleic) in almonds reduce bad cholesterol and increase good cholesterol levels. For this reason, it reduces the risk of heart attack, cardiovascular diseases, colon, and lung cancer (Davis & Iwahashi, 2001). Almonds are eaten raw, peeled, or roasted, and are also widely used in the confectionery and pastry industries. In addition, almond oil is used extensively in the cosmetics and pharmaceutical industries.

Pests and diseases affect almond production to a great extent. *Tropinota hirta* Poda (Col.: Scarabaeidae), *Anarsia lineatella* Zell. (Lep.: Gelechiidae), *Eurytoma amygdali* End. (Hym.: Eurytomidae) *Polystigma ochraceum* (Wahl.) Sacc., *Wilsonomyces carpophylus* (Lév.) Adask., J.M. Ogawa & E.E.Butler and *Monilinia* spp. are major pests and diseases (Kurbetli & Hancıoğlu, 2009; Karaat et. al., 2021a; Karaat et. al., 2021b). Pesticides are preferred against to these pests in almond production areas. The pesticides carry the risk of threatening human health by leaving residues.

A wide variety of chromatographic methods LC, GC, capillary electrophoresis, electroanalytical, colorimetric methods, and enzyme-linked immunoassay methods) are used for the identification and quantification of pesticide residues. LC/MS-MS and GC/MS-MS have more preferred in pesticide analysis due to their greater sensitivity in recent years (Balkan, 2021).

Matrix effect occurs on the analytes during routine analysis despite the sensitive analytical instruments. The matrix effect is caused by the interfering complex matrix components at the time of measurement. Matrix effect or matrix interference is a common situation in pesticide

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Table 1
Analysis conditions for LC-MS/MS and GC-MS.

LC Conditions (Nexera X2)		MS Conditions (LCMS-8050)	
Column	Inertsil (ODS-4), C18 column (2.1 mm x 150 mm, 3 μm)	**Ionization mode**	ESI (+/−)
Oven temp.	40 °C	**Desolvation line temp.**	250 °C
Solvent A	5 mmol/L ammonium formate/ distilled water	**Interface temp.**	300 °C
Solvent B	5 mmol/L ammonium formate/ methanol	**Block heater temp.**	400 °C
Gradient	5 %B. (0 min) – 60 %B. (3 min) – 70 %B. (4 min) – 80 %B. (6 min) – 95 %B. (7 – 8.50 min) – 5 %B. (8.51–15 min)	**Nebulizer gas flow**	2.9 L/ min.
Flow rate	0.4 mL/min	**Drying gas flow**	10.0 L/ min.
Injection vol.	10 μL	**Heating gas flow**	15.0 L/ min.
Rinse solution	50 % methanol	**Dwell time**	1–33 msec
GC Conditions (GC 2010 Plus)		**MS Conditions (GC-QP2010 Ultra)**	
Column	Rxi®−5Sil MS column (30 m, 0.25 mm id, 0.25 μm	**Ionization mode**	EI
Injection temp.	250 °C	**Interface temp.**	270 °C
Gradient	90 °C (1 min) – (20 °C/min) – 150 °C – (9 °C/min) – 200 °C – (12 °C/min) – 300 °C (5 min)	**Ion source temp.**	200 °C
Carrier gas	Helyum	**Solvent cut time**	2.5 min
Linear velocity	48.1 cm/sec	**Data sampling time**	6.30–19.98 min
Purge flow	3.0 mL/min	**Acquisition Mode**	SIM
Injection vol.	1 μL	**Event time**	0.3 msec

residue studies. Interference may be specific to the determination system used, may vary in occurrence and concentration, and may be uncertain. If interference is in a form that coincides with the response of the analyte, a different cleaning or detection system may be needed. A clean-up or dilution step for sensitivity and selectivity may be necessary to reduce matrix interference and contamination of the detector. In pesticide residue analysis, co-extracted compounds may affect the quantitation of analytical results at both side (increasing /decreasing chromatographic response) by inducing matrix-effect. Best solution to eliminate matrix effect is to use matrix-matched calibration (Poole, 2007; Kruve et al., 2008; Tiryaki, 2009). Clean-up techniques are performed on the basis of differences in physico-chemical properties (eg polarity, solubility, molecular size) between pesticides and matrix components (Greer et al., 2021). Liquid-liquid extraction (LLE), solid phase extraction (SPE), and combinations of both are commonly used sample preparation methods for pesticide residue analysis in many matrices (Faraji et al., 2018; Yang et al., 2019; Zhang et al., al., 2019). The QuEChERS developed by Anastassiades et al. (2003) is the most widely sample preparation method in the world. It is quite simple and allows various modifications in almost every process of the analysis (Rejczak & Tuzimski, 2015).

Matrix effects occur frequently in gas and liquid chromatography. Therefore, the ME was evaluated in the method validation step. The samples were treated with two different sorbent mixtures in the clean-up phase of the QuEChERS method. The method validation was conducted with a sorbent mixture that gave more appropriate results. Pesticide residues were investigated in 60 samples taken from producers of Adıyaman, Ankara, Diyarbakır, Gaziantep, Kahramanmaraş, İzmir, Malatya and Şanlıurfa, Turkey in the years 2020–2021. In addition, 30 almond samples bought from seller of dried nuts were evaluated from the point of view of pesticide residue levels in Aksaray, Ankara, Aydın, Kayseri, Kırşehir, Nevşehir, Samsun, Sivas and Tokat, Turkey in 2022.

Materials and method

Chemicals and reagents

Analytical standards of pesticides (Table S1, S2) were purchased Dr. Ehrenstorfer Laboratories GmbH (Augsburg, Germany). The purities of the analytical pesticide standards were from 90 % to 99.8 %. Acetonitrile, methanol, and acetic acid (> 99 % purity) were acquired from Merck (Darmstadt, Germany). The QuEChERS kits (Acetic extraction tube containing: 6 g $MgSO_4$ + 1.5 g Na Acetate, Clean-up tube1 containing:50 mg PSA + 50 mg C18 + 150 mg $MgSO_4$, Clean-up tube2 containing: 50 mg PSA + 50 mg C18 + 50 mg GCB + 150 mg $MgSO_4$) were purchased from Restek (Bellefonte, USA).

Standard solution preparation

A total of 300 (50 pesticides for GC-MS and 250 pesticides for LC-MS-MS) pesticide reference standards were used for residue detection. A separate stock solution (1000 mg L^{-1}) in methanol for each pesticide was prepared and stored at −20 °C. The working solutions for matrix match calibrations and method validation studies were prepared by appropriate dilution of the stock solutions with methanol.

LC-MS/MS and GC-MS instrumentation

The analyses were conducted on Shimadzu UHPLC Nexera™ X2, and LCMS™−8050 triple quadrupole mass spectrometer with an electrospray ionization (ESI), and GC–MS QP2010 ultra model (Shimadzu®) with mass spectrometry system coupled with an electron ionization (EI). The final LC-MS/MS and GC-MS method conditions were listed in Table 1.

Sample extraction procedure

The official QuEChERS AOAC Method 2007.01 was used for the analyses for pesticide residue extraction and cleua-up (Lehotay, 2007). The steps for QuEChERS procedure were shown in Fig. 1.

The recovery was evaluated for the two different sorbents applied in the d-SPE clean-up step for a blank sample spiked at 10, 50 and 100 μg/kg. The effectiveness of the sorbents was evaluated according to the number of pesticides recovered in the range of 70–120 % with RSD ≤ 20 %.

Method validation

The performance criteria of the method include linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy, trueness, precision (repeatability and intra-laboratory reproducibility), uncertainty, and matrix effect. The method was validated following the European commission guideline SANTE/11312/2021 (SANTE, 2021; Balkan & Yılmaz, 2022).

Identification, quantification of residues in real samples

Pesticide residues were investigated in 60 almond samples taken from producers of Adıyaman, Ankara, Diyarbakır, Gaziantep, Kahramanmaraş, İzmir, Malatya and Şanlıurfa, Turkey in the years 2020–2021. In addition, 30 almond samples bought from nuts shop were evaluated from the point of view of pesticide residue levels in Aksaray, Ankara, Aydın, Kayseri, Kırşehir, Nevşehir, Samsun, Sivas and Tokat, Turkey in 2022. The collected almond sample (1 kg) transported to laboratory in polyethylene bags and stored in freezer at − 20 °C and analyzed as soon as possible.

Pesticides were confirmed by their retention time and their

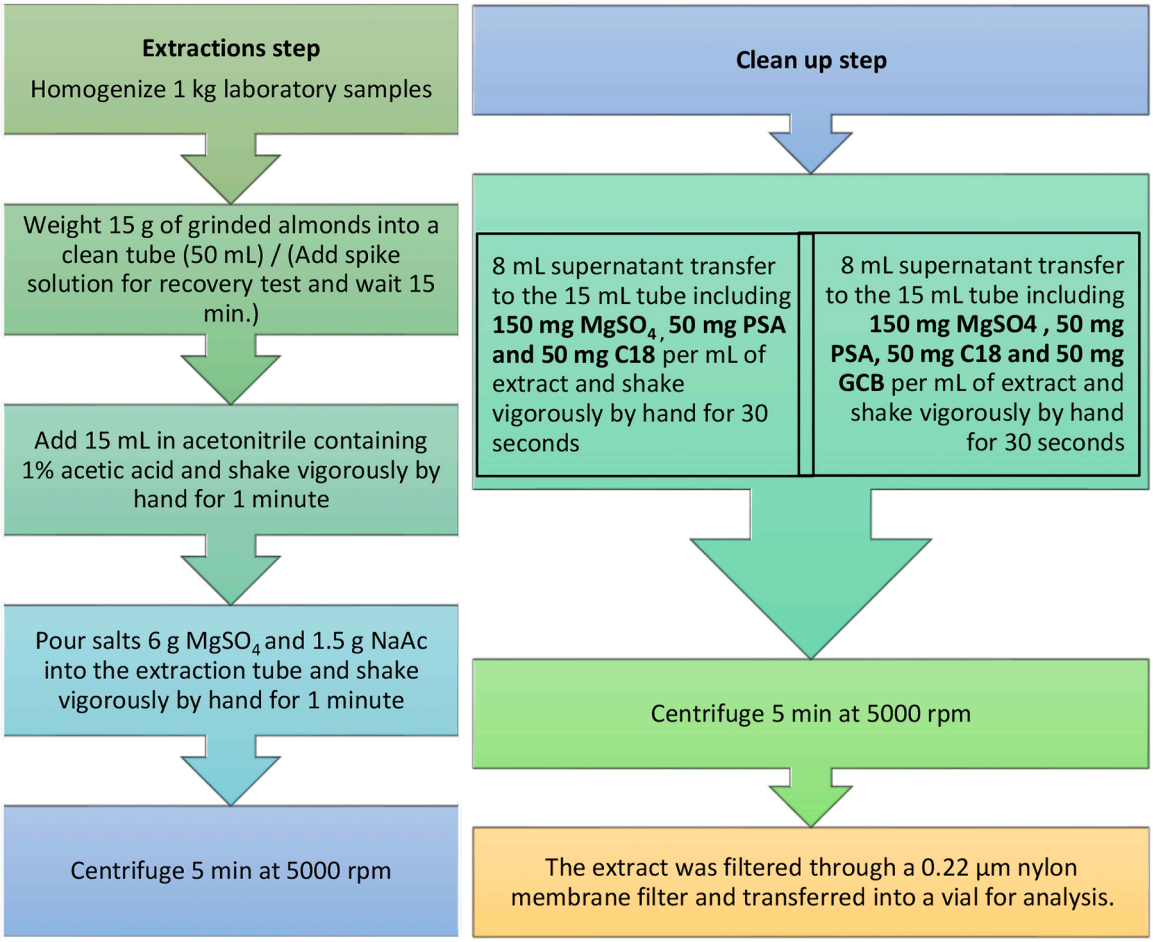

Fig. 1. Analytical steps of the QuEChERS-AOAC Official Method 2007.01.

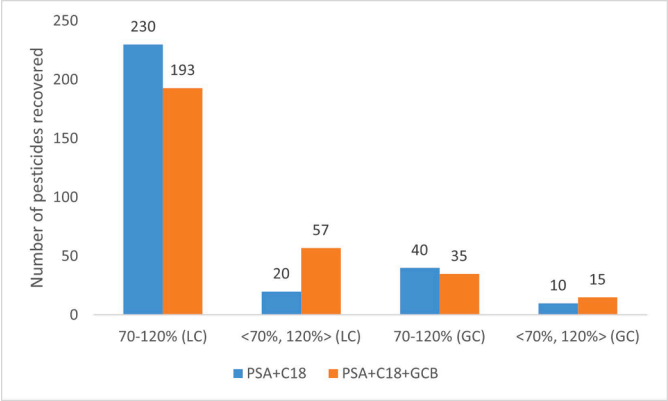

Fig. 2. Recovery response of different D-SPE clean-up sorbents (i.e., PSA and C18; PSA, C18 and GCB).

quantification and identification ions by GC-MS-selected ion monitoring or multiple reaction monitoring of two fragment ions by LC-MS/MS, respectively (Nguyen et al., 2009). Two parameters (Retention time, Ion ratio) were used as identification criteria according to the guideline (SANTE, 2021).

Results and discussion

Optimization of the clean-up

Investigation of the optimum clean-up sorbents used during the sample preparation step occurred following the extraction of spiked almond samples with two different clean-up sorbents for ten replicates. In the present study, clean-up sorbent was standardized, among two different clean-up sorbent combinations i.e., PSA + C18 and PSA + C18 + GCB used based on their polarities. A comparative picture of average percent recovery using these clean-up sorbent combinations which provided the representative data was presented in Fig. 2. Among the tested sorbents, the ones at presented the best results were the combination of sorbents PSA and C18. The combination provided the range of 70–120 % recovery in 270 of 300 pesticides. However, the combinations of PSA, C18 and GCB sorbents presented the highest number of pesticides with recovery outside the range of 70 to 120 % (Fig. 2). Based on the above results, PSA and C18 were determined to be the most effective sorbent combination for clean-up of targeted pesticides from almond samples in both LC-MS/MS and GC–MS. Similar to our study, Wang et al. (2017) reported that the most appropriate recovery in the clean-up procedure for 106 pesticides was freezing-out + 50 mg mL^{-1} C18 + 50 mg mL^{-1} PSA + 100 mg mL^{-1} $MgSO_4$ combination.

Method validation

The LOD and LOQ of the GC amenable pesticides were found to be within the ranges of 0.28–2.96 mg kg^{-1} and 0.92–9.87 mg kg^{-1} respectively. In case of LC amenable pesticides, the values for LOD and

Table 2
Method validation parameters of 270 pesticides.

Analyte	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	R^2	Repeatability ($n = 10$)						Reproductibility ($n = 10$)						U'%	ME%
				10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}		10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}			
				Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
2-phenylphenol*	2.53	8.43	0.991	71.94	7.46	78.03	5.85	102.18	4.08	78.18	3.24	82.01	5.47	93.81	6.17	39.69	165.21
Acephate	1.56	5.19	0.996	88.06	6.48	99.98	5.31	102.63	5.23	83.53	9.42	98.46	8.09	97.01	4.48	21.12	−73.06
Acequinocyl	2.21	7.37	0.997	104.42	7.81	105.31	7.31	110.01	4.68	103.07	9.66	87.80	15.53	99.73	15.80	28.79	−26.20
Acetamiprid	3.00	9.98	0.994	83.92	12.69	118.04	8.30	109.21	8.75	75.43	4.21	107.21	3.36	101.90	7.23	33.54	−1.66
Acetochlor	2.72	9.08	0.999	104.02	6.44	111.11	7.56	95.96	10.76	107.43	6.63	110.60	7.54	110.28	15.02	26.08	−13.27
Acrinathrin	0.70	2.33	0.999	112.74	14.97	103.28	8.96	92.43	14.41	79.73	13.94	74.44	16.75	95.58	11.28	38.89	−2.58
Alachlor	2.22	7.39	0.999	109.44	16.99	103.47	11.91	97.47	11.21	112.29	6.49	108.40	7.91	110.31	5.71	46.58	−28.34
Aldicarb	0.89	2.97	0.999	104.46	13.95	101.97	13.73	107.09	9.10	97.87	13.52	111.12	7.21	117.52	3.63	28.62	−13.84
Aldicarb-sulfone	2.81	9.36	0.998	101.20	12.28	118.21	7.10	110.58	9.76	87.35	6.25	110.58	5.62	105.91	7.36	28.36	−3.40
Aldicarb-sulfoxide	1.90	6.32	0.993	118.35	3.79	107.24	8.10	102.06	12.14	115.18	2.75	108.59	3.82	102.06	7.25	26.03	−10.47
Aldrin*	0.93	3.11	0.995	114.28	3.10	88.71	1.95	96.74	2.20	101.02	6.76	85.87	3.89	88.79	7.95	23.72	73.88
Alpha-BHC*	2.27	7.58	0.991	97.62	9.20	82.47	9.24	103.00	4.63	109.48	8.39	86.48	8.85	93.30	4.93	25.25	322.30
Ametoctradin	1.24	4.13	0.998	102.62	13.35	103.49	9.17	105.46	15.98	100.09	12.04	107.65	9.38	109.05	15.77	29.50	3.85
Amitraz	2.27	7.55	0.995	102.91	14.07	115.42	7.11	117.99	11.67	95.34	13.90	116.92	10.49	114.91	7.44	36.25	−6.03
Atrazine	1.79	5.95	0.999	96.06	12.10	108.56	12.12	100.35	6.27	87.28	8.50	97.91	8.44	89.68	12.38	24.66	−27.99
Azoxystrobin	1.15	3.83	0.996	110.46	9.61	114.82	8.68	111.53	15.20	98.54	12.61	113.24	9.60	102.14	17.75	33.51	−15.07
Benalaxyl	1.45	4.83	0.988	88.33	16.60	108.12	8.53	104.04	15.73	90.65	14.72	111.37	5.71	105.48	12.86	32.53	26.61
Benfuracarb	0.99	3.29	0.999	80.36	18.05	86.15	16.76	96.05	12.56	113.33	2.87	91.59	8.83	93.02	13.02	35.24	−27.01
Bensulfuron-methyl	2.43	8.08	0.998	103.83	11.42	117.02	2.85	116.11	13.20	104.00	11.57	114.26	2.56	115.14	9.39	33.67	−8.00
Bentazone	2.96	9.87	0.998	104.67	13.36	116.10	14.88	99.29	12.37	90.39	13.09	101.08	15.26	99.54	11.79	33.54	0.30
Beta-BHC*	2.96	9.87	0.998	99.07	4.82	82.32	9.16	91.70	9.80	103.71	6.86	82.53	10.60	91.55	9.92	28.27	394.65
Bifenazate	1.89	6.30	0.995	116.21	4.99	100.71	11.74	84.34	16.36	117.65	2.46	104.78	4.74	95.08	9.64	30.29	25.58
Bifenthrin*	2.28	7.60	0.992	81.96	10.44	81.93	11.25	94.91	9.29	93.73	7.11	76.21	8.06	105.94	7.41	34.16	404.11
Bitertanol	2.83	9.45	0.999	98.28	11.99	102.67	10.57	102.97	14.29	103.39	8.95	109.40	14.54	118.54	16.96	35.32	33.51
Boscalid	1.90	6.35	0.998	106.76	9.76	110.53	11.81	112.34	11.23	105.93	4.76	109.89	6.25	112.73	9.44	27.70	−12.52
Bromophos-ethyl*	1.15	3.84	0.993	110.75	2.14	75.29	8.29	96.11	8.08	104.96	1.98	77.18	7.16	92.78	8.73	32.13	525.19
Bromophos-methyl*	1.52	5.07	0.992	115.71	4.14	74.04	8.96	80.92	10.30	109.98	4.47	76.70	8.51	87.05	9.11	39.62	682.67
Buprimate	1.42	4.73	0.993	97.97	12.02	107.17	6.66	98.27	10.09	104.37	11.58	117.56	8.05	113.40	15.10	30.82	−4.28
Buprofezin	0.88	2.93	0.997	87.36	16.30	110.51	9.54	112.08	11.07	84.50	10.86	87.64	16.09	84.21	19.42	37.17	1.29
Butralin	0.88	2.93	0.999	114.05	5.46	100.47	4.94	90.52	7.78	92.12	9.51	75.23	6.61	96.64	11.91	29.83	−8.44
Butylate	0.83	2.76	0.999	82.60	11.18	79.35	9.47	79.57	5.83	77.19	9.57	98.91	6.77	116.88	11.40	39.56	−6.07
Cadusafos	1.50	4.99	0.996	102.98	11.99	107.45	7.09	103.15	9.04	95.02	11.19	108.25	10.16	115.04	18.43	32.25	−7.05
Carbaryl	1.53	5.11	0.995	72.05	6.12	116.21	13.95	112.58	6.16	80.66	7.17	110.07	3.79	105.20	10.35	38.03	−2.54
Carbendazim	2.71	9.04	0.998	92.86	12.79	113.40	5.50	108.67	10.61	79.24	8.26	94.85	10.35	84.08	5.13	30.91	−18.71
Carbofuran	1.53	5.09	0.993	75.82	10.93	117.42	3.56	114.42	5.28	87.30	6.61	112.66	5.50	108.52	8.20	34.79	−11.25
Carbofuran-3-hydroxy	2.08	6.92	0.997	73.85	11.45	102.54	10.83	109.31	7.83	80.20	5.80	96.82	9.06	98.29	13.17	33.52	−99.94
Carbosulfan	1.24	4.14	0.999	98.98	9.06	95.08	7.36	81.40	13.08	87.08	10.37	106.04	12.23	90.59	6.51	28.93	−27.59
Carboxin	1.94	6.46	0.990	78.53	5.82	114.48	12.04	115.46	9.68	81.09	9.40	103.56	11.41	108.16	11.17	36.34	−4.14
Carfentrazone-ethyl	2.93	9.75	0.996	78.93	10.54	115.27	16.69	97.30	14.60	82.93	8.53	105.58	7.27	102.58	6.66	42.36	−42.12
Chlorbufam*	2.30	7.68	0.991	106.32	5.93	81.48	2.99	100.46	4.44	104.07	5.29	85.33	6.47	96.76	4.47	23.18	5.11
Chlorfenvinhos	0.85	2.82	0.996	105.29	12.96	104.91	10.63	105.16	13.88	97.39	13.74	112.63	8.32	117.44	8.51	30.97	29.82
Chlorfluazuron	1.62	5.41	0.995	115.88	6.17	103.08	12.13	98.85	10.75	109.79	10.51	102.95	10.05	101.48	12.75	30.69	5.75
Chloridazon	2.51	8.37	0.994	74.19	7.66	116.35	7.62	107.06	10.74	75.84	3.27	103.08	12.16	101.36	8.83	36.84	−10.05
Chlorpropam*	2.08	6.95	0.992	102.52	4.41	82.01	7.83	89.16	6.31	101.31	7.70	92.51	10.50	105.56	8.53	25.65	513.15
Chlorpyrifos	1.93	6.44	0.996	105.04	9.39	104.64	6.73	108.45	5.07	81.16	8.46	77.31	9.14	94.01	15.34	32.88	−7.21
Chlorpyrifos-methyl*	1.82	6.05	0.994	110.83	3.92	80.23	9.97	90.13	11.32	103.66	4.59	85.75	10.94	94.42	9.74	28.23	593.80
Chlorpyriphos*	2.27	7.55	0.992	98.53	6.57	78.38	8.17	90.41	7.97	98.53	6.57	78.38	8.17	85.19	7.34	31.65	504.51
Chlorsulfuron	2.87	9.57	0.999	108.23	12.49	116.71	5.08	110.74	13.68	102.41	15.75	107.74	6.28	109.09	8.71	31.54	−41.39
Chlorthal-dimethyl*	0.91	3.04	0.992	113.54	3.31	83.11	5.04	95.49	5.05	110.69	4.70	77.95	3.56	88.09	6.38	30.38	144.82
Clethodim	1.56	5.20	0.995	102.39	12.19	117.64	9.11	103.44	10.55	92.16	11.31	106.51	7.04	117.44	7.03	32.20	−60.97

(*continued on next page*)

Table 2 (*continued*)

Analyte	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	R^2	Repeatability ($n = 10$)						Reproductibility ($n = 10$)						U'%	ME%
				10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}		10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}			
				Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
Clodinofop-propargyl	2.81	9.37	0.993	78.20	16.06	99.40	15.75	102.15	10.02	83.30	12.96	106.77	10.28	115.44	9.24	36.38	−10.27
Clofentezine	1.13	3.77	0.995	97.41	12.49	107.37	14.22	112.98	11.52	78.19	12.81	107.15	6.16	106.36	7.18	32.43	−0.52
Clothianidine	2.09	6.97	0.994	117.78	4.62	117.40	11.25	115.81	4.10	112.32	5.06	113.34	4.00	118.98	6.17	35.54	−7.24
Cyantraniliprole	2.88	9.61	0.998	83.67	8.72	99.68	9.74	91.48	11.85	73.06	9.60	89.78	8.24	92.33	9.98	43.05	−18.84
Cyazofamid	1.01	3.38	0.994	90.89	17.20	104.91	12.04	103.25	15.02	84.58	17.14	110.78	3.87	111.59	10.46	31.62	−0.93
Cycloate	1.02	3.41	0.999	85.85	11.03	100.77	5.04	93.95	4.61	94.55	7.16	89.64	6.02	90.65	4.22	22.53	−18.36
Cycloxydim	2.63	8.76	0.998	106.86	12.47	99.27	14.88	91.49	7.73	113.63	4.61	97.63	8.37	85.85	8.12	27.57	−8.44
Cyflufenamid	1.67	5.56	0.997	112.61	6.49	98.07	16.32	93.77	11.75	103.81	9.25	104.40	9.71	98.03	17.03	27.18	16.70
Cyhalothrin	1.42	4.73	0.999	100.73	17.05	106.13	10.72	98.08	9.11	92.03	17.52	83.64	14.91	87.00	14.90	33.14	−1.44
Cypermethrin	0.86	2.85	0.999	93.52	15.70	102.46	5.76	99.15	10.22	78.83	5.90	102.48	11.04	77.76	9.20	32.10	−26.93
Cyproconazole	1.64	5.46	0.999	98.79	12.73	101.38	16.91	99.01	9.47	96.23	7.95	88.52	3.67	84.01	4.99	25.94	−22.11
Cyprodinil	1.48	4.92	0.998	80.64	11.07	98.19	12.84	97.93	9.55	73.91	16.52	98.87	14.22	97.87	5.78	34.36	−1.02
Delta BHC*	2.79	9.32	0.998	91.78	11.98	83.59	8.11	90.56	9.51	86.89	7.22	88.12	6.69	99.47	10.41	27.47	778.78
Deltamethrin	2.88	9.60	0.996	112.32	11.51	97.44	7.49	86.01	12.15	100.33	12.67	93.35	15.95	80.28	11.94	33.86	−5.90
Demeton-s-methyl	0.92	3.06	0.999	108.72	12.00	104.91	15.88	108.32	12.13	82.77	7.51	79.62	9.76	91.45	15.46	35.26	−10.61
Desmedipham	1.93	6.42	0.999	94.81	18.36	104.23	16.50	96.18	12.93	93.64	5.82	94.99	12.29	87.96	14.20	29.19	−25.23
Diafenthiuran	0.74	2.46	0.999	100.58	14.59	93.78	12.00	97.67	6.99	78.16	7.95	74.14	4.30	96.69	13.10	37.37	10.39
Diazinon	1.01	3.38	0.999	103.29	8.19	102.04	7.68	95.12	11.35	113.24	6.22	92.54	7.63	91.14	6.74	21.89	−7.44
Dichlofluanid	1.07	3.57	0.997	79.88	13.98	96.52	16.54	81.93	13.09	83.82	9.60	101.65	7.81	99.20	10.50	34.10	−32.41
Dichlorfos	2.23	7.42	0.999	78.42	6.40	89.17	9.11	91.01	4.39	83.13	2.77	89.57	2.97	89.82	2.36	29.35	1.98
Dicrotophos	2.86	9.52	0.999	91.96	10.64	117.18	6.08	113.63	7.98	92.03	12.41	100.70	8.00	105.60	7.82	27.61	4.60
Diethofencarb	1.36	4.54	0.999	91.58	14.41	105.78	12.86	97.56	15.38	90.81	15.44	105.58	10.99	100.96	6.24	28.23	−33.46
Difenacozole	2.77	9.22	0.999	102.47	13.35	105.21	8.99	106.84	8.37	100.61	12.90	110.83	9.87	113.35	13.35	31.39	24.90
Diflubenzuran	1.49	4.97	0.997	105.92	11.79	107.71	14.59	103.74	5.85	107.01	7.98	106.37	6.72	113.72	14.01	29.44	−10.70
Dimethenamid	2.81	9.38	0.994	98.65	16.55	117.70	7.88	102.69	16.11	91.55	9.81	110.67	5.12	102.70	4.73	28.14	−18.48
Dimethoate	2.58	8.60	0.994	85.38	16.87	118.09	9.71	115.53	8.36	80.71	7.97	107.50	9.53	107.37	12.06	36.76	0.20
Dimethomorph	2.13	7.11	0.999	116.30	5.22	108.30	8.79	88.38	15.73	105.64	3.01	108.45	9.59	87.78	17.77	32.41	−21.56
Diniconazole	2.77	9.24	0.998	110.95	7.06	104.35	8.89	104.63	6.53	107.32	4.51	109.66	8.24	114.50	11.67	32.63	9.96
Dinocap	1.90	6.33	0.982	104.32	14.09	103.02	10.68	97.47	14.53	88.53	15.66	110.12	9.76	106.46	14.68	32.03	−44.74
Dioxacarb	2.37	7.89	0.993	79.79	4.42	108.33	7.89	101.06	3.47	77.48	5.88	105.78	2.52	113.62	5.03	30.48	−0.21
Diphenamid	1.27	4.23	0.997	76.48	9.00	106.20	12.91	113.25	16.17	105.40	11.35	116.19	7.46	116.95	17.53	40.86	−15.98
Diphenylamine	1.17	3.91	0.999	91.33	10.05	107.08	9.36	102.98	8.96	78.82	10.85	99.44	5.50	104.30	8.04	29.00	1.39
DMF	1.49	4.97	0.996	74.49	5.31	100.46	3.19	93.42	3.82	75.36	2.92	94.02	4.91	92.47	6.00	31.68	−10.76
Dodine	1.64	5.45	0.999	98.04	10.44	105.06	16.93	91.37	11.22	100.48	14.49	97.59	15.39	117.74	10.59	32.61	11.47
Emamectin	0.78	2.60	0.995	115.52	7.19	91.04	8.05	92.79	13.26	98.27	11.47	79.63	7.08	82.62	2.97	32.66	0.26
Emamectin benzoat	2.04	6.82	0.999	90.97	17.81	97.23	10.33	99.91	14.83	76.75	9.30	78.84	7.94	76.48	15.62	40.74	−5.98
Endosulfan sulfate*	2.18	7.28	0.993	77.63	5.67	75.06	4.23	88.57	12.63	83.17	4.02	76.89	5.68	95.52	5.32	39.01	71.70
Endrin*	1.72	5.73	0.993	106.84	7.11	83.01	4.31	90.53	5.09	103.55	5.46	78.68	5.98	87.09	7.02	29.20	199.30
EPN	1.70	5.68	0.998	100.21	13.43	93.65	11.73	85.15	14.64	74.19	6.21	94.04	11.86	113.99	3.90	34.05	−8.53
Epoxiconazole	1.72	5.73	0.999	84.81	16.33	103.43	11.74	93.09	16.63	93.13	13.53	92.81	6.94	97.08	12.93	29.92	−21.53
EPTC	2.81	9.37	0.997	76.48	15.15	94.17	11.33	93.04	5.86	87.33	11.76	98.15	11.04	96.36	11.83	32.82	−9.30
Ethiofencarb	1.28	4.27	0.995	74.46	3.01	110.98	8.39	108.27	5.86	91.52	12.02	91.87	6.61	88.64	9.37	40.90	−8.85
Ethion	0.93	3.12	0.997	91.66	11.39	103.31	11.15	101.39	11.73	74.97	9.62	83.82	8.91	95.97	2.06	32.50	−13.66
Ethirimol	2.05	6.84	0.998	83.09	13.50	95.05	17.12	92.09	11.81	92.25	3.58	102.78	7.05	116.01	3.50	31.21	−2.38
Ethofumesate*	2.09	6.97	0.991	89.91	11.72	76.79	5.51	94.23	10.10	90.86	11.39	75.12	5.64	92.31	5.88	36.08	535.91
Ethoprophos*	2.73	9.11	0.998	101.64	5.96	91.20	11.85	100.12	13.03	105.69	7.71	96.91	12.05	97.98	6.41	20.90	532.85
Etofenprox	0.91	3.03	0.999	97.76	17.29	95.87	16.43	85.84	16.89	86.05	15.31	92.68	7.16	96.77	11.91	32.82	−32.22
Etoxazole	1.60	5.32	0.999	115.50	5.08	105.15	10.64	99.02	10.32	96.75	10.95	79.64	6.49	96.13	13.79	28.83	0.09
Famaxadone	0.97	3.23	0.992	88.81	16.24	111.61	8.58	98.04	11.32	92.49	11.40	105.10	9.52	115.67	13.47	30.76	13.46
Fenamiphos	2.53	8.42	0.999	97.41	17.23	99.22	12.41	95.63	9.00	107.71	8.24	98.99	6.78	105.49	14.68	26.65	−24.29
Fenamiphos-sulfone	2.10	7.01	0.992	81.53	8.98	110.51	6.52	105.84	10.05	83.39	8.61	111.25	4.48	99.48	8.48	30.26	−5.41

(*continued on next page*)

Table 2 (*continued*)

Analyte	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	R^2	Repeatability ($n = 10$)						Reproductibility ($n = 10$)						U'%	ME%
				10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}		10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}			
				Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
Fenamiphos-sulfoxide	2.55	8.49	0.995	78.93	5.80	113.17	6.56	115.64	5.22	82.24	8.19	107.06	8.09	99.64	7.04	32.36	−2.81
Fenarimol	2.17	7.24	0.998	102.99	12.67	99.79	12.94	88.06	9.08	109.95	7.94	93.09	13.91	75.81	15.73	33.77	−12.34
Fenazaquin	0.78	2.61	0.998	100.13	7.70	95.53	5.97	84.71	14.62	87.45	9.43	105.86	6.57	81.60	11.90	30.39	−45.82
Fenbuconazole	2.22	7.40	0.996	103.39	13.39	113.74	12.59	86.16	16.79	106.97	12.12	108.34	5.65	99.95	10.86	32.46	−26.53
Fenbutatin oxide	1.62	5.41	0.997	103.02	5.69	72.93	5.15	73.03	8.09	83.22	11.45	83.48	19.01	75.81	16.39	45.92	−9.47
Fenhexamide	1.82	6.08	0.999	113.80	10.16	104.22	7.75	91.53	15.33	113.11	2.97	113.59	3.30	100.09	11.80	28.26	2.87
Fenoxycarb	1.45	4.83	0.996	79.12	16.33	86.66	19.15	95.27	13.66	95.11	10.00	101.31	11.36	99.42	6.63	31.88	−22.69
Fenoxyprob -ethyl	2.91	9.72	0.997	99.36	16.59	106.45	4.80	110.98	13.55	86.49	13.51	105.52	9.17	113.64	9.56	31.83	−16.36
Fenpropathrin	1.33	4.42	0.999	103.02	11.21	102.27	10.14	100.42	8.20	81.08	15.41	76.16	6.93	90.86	14.90	34.94	−8.49
Fenproxymate	1.98	6.61	0.995	114.64	2.94	105.65	6.05	105.06	6.40	98.49	11.81	93.48	15.76	106.77	1.94	26.51	−1.65
Fenthion	1.72	5.73	0.999	107.27	9.29	108.33	10.26	103.95	8.47	110.24	8.76	103.02	12.95	106.02	12.77	28.28	−3.24
Fenthion-sulfone	1.96	6.54	0.992	81.42	5.38	112.61	11.91	108.46	2.52	76.22	16.93	112.43	5.53	107.26	2.77	43.51	−9.64
Fenthion-sulfoxide	1.96	6.55	0.999	103.56	8.75	108.21	14.18	104.14	12.49	101.82	10.52	109.12	3.82	107.62	2.07	24.44	3.38
Fluazifop-p-butyl	2.60	8.66	0.999	111.29	7.73	110.86	13.69	104.66	14.33	87.05	16.20	85.13	14.86	113.24	1.85	33.60	−12.48
Flufenoxuron	1.02	3.40	0.999	107.93	9.42	107.98	6.77	115.65	15.31	98.08	13.88	80.93	17.36	90.70	15.33	35.02	11.34
Fluopicolide	1.33	4.42	0.993	76.06	15.18	115.38	2.16	100.30	17.69	78.68	7.77	104.81	12.54	119.82	6.20	39.77	−1.62
Fluopyram	1.06	3.52	0.999	110.23	9.17	108.65	9.62	81.71	13.22	115.39	2.15	107.82	5.59	106.47	3.70	29.43	−1.64
Fluquinconazole	1.73	5.77	0.999	84.87	11.77	92.57	12.22	82.16	11.50	85.32	7.96	109.36	8.49	110.63	4.36	33.11	−2.68
Flusilazole	2.19	7.30	0.997	87.40	16.80	94.27	16.53	87.01	16.00	94.13	6.71	100.84	10.62	90.89	12.82	29.49	−20.22
Flutriafol	1.10	3.66	0.994	76.57	7.50	110.81	15.09	104.20	2.92	78.59	15.22	98.00	9.72	90.36	11.77	35.41	−13.02
Fonofos*	0.28	0.92	0.990	116.04	3.34	98.92	2.17	103.51	3.67	100.52	1.77	94.92	2.65	99.62	2.25	15.82	182.09
Forchlorfenuron	1.08	3.59	0.992	74.42	9.06	103.02	17.94	105.76	7.35	80.21	14.17	97.71	11.80	115.72	9.86	37.93	−22.15
Formetanete hydrochloride	2.19	7.30	0.998	100.13	12.68	112.19	5.20	106.19	6.05	94.70	12.11	111.18	3.12	115.31	16.12	29.99	−14.01
Fosthiazate	2.94	9.80	0.998	75.35	12.89	100.79	8.53	97.42	12.01	78.56	8.87	111.77	5.47	114.91	6.65	36.12	1.72
Furathiocarb	0.61	2.04	0.999	102.44	10.02	105.18	9.41	106.58	8.17	99.83	11.87	94.42	4.27	89.62	11.15	24.48	−1.24
Haloxyfop-R-methyl	0.92	3.08	0.996	86.33	16.69	106.71	3.86	94.66	9.00	82.04	8.19	96.31	18.26	102.58	12.23	34.04	−0.82
Heptachlor*	1.22	4.05	0.990	104.11	7.08	82.29	6.40	93.24	5.51	116.08	3.93	83.62	6.90	90.68	6.50	27.94	327.73
Heptachlor endo epoxide*	1.03	3.42	0.991	115.34	9.19	84.82	6.02	96.09	8.67	91.52	6.17	82.46	3.80	94.35	9.77	29.41	112.32
Heptachlor exo epoxide*	1.03	3.45	0.991	109.20	9.83	83.04	5.72	94.29	8.70	105.02	12.40	83.34	5.68	93.94	7.14	29.00	108.77
Heptenophos	1.99	6.65	0.998	76.92	10.80	105.86	11.81	96.50	8.83	81.35	10.49	92.52	10.75	86.01	6.88	33.58	−9.62
Hexaconazole	0.81	2.72	0.998	88.21	14.20	110.09	9.39	101.54	10.80	91.35	14.95	96.18	13.70	100.03	14.28	30.17	−3.97
Hexythiazox	0.88	2.93	0.999	117.06	6.47	112.15	6.23	105.21	13.85	98.44	12.54	81.09	10.12	96.73	10.65	32.98	12.25
Imazalil sulfate	2.77	9.24	0.989	100.81	12.10	87.01	12.31	89.18	13.83	96.22	6.78	94.00	10.78	85.38	16.43	39.81	16.47
Imidacloprid	1.69	5.62	0.993	107.89	16.80	114.38	4.33	115.59	9.16	87.84	13.04	109.90	4.64	111.35	9.75	32.93	−16.63
Indoxacarb	1.45	4.84	0.999	96.69	12.93	109.18	8.57	97.82	8.91	106.03	6.90	105.59	9.91	114.07	9.79	28.00	17.00
Iodosulfuron-methyl-sodium	2.01	6.70	0.995	90.48	15.15	116.56	5.50	117.97	7.77	96.45	8.27	104.80	11.67	113.43	6.19	31.34	−33.17
Isocarbofos	1.70	5.66	0.995	97.07	15.84	108.13	12.61	96.79	10.96	74.49	14.63	104.89	6.36	95.70	5.42	31.53	−8.17
Kresoxim Methyl	1.19	3.98	0.991	92.33	16.36	108.72	11.00	106.35	9.12	88.51	15.52	106.39	8.34	117.86	6.72	34.77	−4.21
Lenacil	1.14	3.81	0.997	77.79	6.24	114.23	7.34	104.88	11.90	93.99	6.45	106.41	8.27	96.41	12.59	29.74	−16.79
Linuron	1.62	5.39	0.996	116.17	5.66	115.05	11.14	101.87	15.56	103.16	13.29	98.66	7.69	113.07	10.33	30.84	−8.07
Lufenuron	2.20	7.33	0.999	108.38	9.69	106.93	15.81	97.58	10.43	83.99	12.68	97.04	10.74	88.34	4.39	28.05	2.41
Malaoxon	2.90	9.65	0.999	86.52	10.11	113.88	9.91	105.37	9.84	80.57	7.02	96.08	5.84	98.85	4.40	28.60	−0.05
Malathion	1.03	3.43	0.999	103.01	13.81	110.94	7.24	94.24	18.06	108.02	9.42	108.53	5.34	114.36	11.93	30.35	4.11
Mandipropamid	2.66	8.86	0.998	81.17	9.61	114.53	7.97	95.95	18.58	94.61	4.08	101.32	11.06	101.59	7.97	28.77	−21.33
MCPA	1.60	5.34	0.999	81.28	15.97	102.57	6.70	92.63	13.19	92.64	6.29	99.18	12.98	92.00	13.77	28.96	−14.24
Mecarbam	2.45	8.17	0.999	102.93	12.20	105.06	11.65	93.27	13.37	95.39	12.45	111.97	2.85	117.12	13.85	30.58	−8.09

(*continued on next page*)

Table 2 (*continued*)

Analyte	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	R^2	Repeatibility ($n = 10$)						Reproductibility ($n = 10$)						U'%	ME%
				10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}		10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}			
				Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
Mepanipyrim-hyroxypropyl	1.54	5.13	0.998	95.61	12.42	93.27	17.42	97.19	10.09	106.96	4.33	102.18	7.68	84.35	9.96	27.07	−16.49
Metaflumizone	0.74	2.46	0.999	109.96	9.02	104.66	9.29	105.15	6.08	115.65	3.49	96.50	11.00	118.92	4.38	28.96	11.03
Metalaxyl-M	2.80	9.34	0.998	94.67	14.42	112.63	11.75	109.17	9.06	109.67	4.35	104.06	10.01	103.69	9.21	26.55	4.03
Metamitron	2.40	8.01	0.996	76.47	14.17	112.94	8.32	106.13	8.29	78.88	6.37	104.79	8.40	102.65	11.68	34.29	−1.11
Methacrifos-poz	1.01	3.37	0.999	78.38	17.58	101.41	7.48	98.06	7.35	79.00	8.94	100.23	14.38	93.45	6.28	31.77	−8.60
Methamidophos	1.77	5.91	0.999	80.21	4.82	88.70	9.48	88.44	10.60	77.49	3.33	89.79	3.75	88.63	4.25	32.72	−74.42
Methidathion	2.25	7.50	0.999	90.96	16.73	95.55	16.95	86.12	18.08	97.19	8.22	102.79	5.50	87.85	8.09	28.86	−26.66
Methiocarb	2.84	9.48	0.994	78.21	12.82	115.94	11.52	97.20	15.65	100.07	5.19	101.83	7.40	105.89	7.00	30.84	−15.68
Methiocarb-sulfone	2.05	6.84	0.992	77.62	3.84	113.52	6.02	103.58	6.20	70.91	10.37	105.74	4.45	109.99	5.20	35.82	−6.62
Methiocarb-sulfoxide	1.48	4.94	0.991	75.41	5.46	115.49	9.51	100.86	11.37	79.71	11.59	108.78	9.91	110.38	5.67	37.50	−0.36
Methomyl	2.92	9.74	0.999	102.15	7.43	103.54	10.39	104.01	8.27	95.32	7.18	99.99	6.54	98.11	8.09	18.20	−8.42
Methoxyfenozide	0.76	2.52	0.998	95.32	14.77	100.19	14.38	80.83	17.74	112.28	4.40	113.11	5.36	97.70	5.61	30.73	15.64
Metolachlor-S	2.34	7.80	0.998	115.16	9.48	100.32	7.46	98.24	12.48	115.34	3.15	111.80	9.83	116.66	7.61	31.76	−8.75
Metosulam	2.97	9.90	0.995	100.30	13.07	118.60	7.27	111.94	10.14	97.75	12.55	115.20	3.27	115.05	9.76	32.71	−6.38
Metrafenone	1.29	4.29	0.995	93.88	16.24	107.05	5.46	109.93	7.37	76.47	15.43	110.15	8.04	113.48	10.34	34.84	−1.74
Metribuzin	2.99	9.98	0.999	95.32	12.62	115.52	12.44	103.97	8.95	88.58	12.45	100.95	8.04	97.62	9.02	27.12	−9.49
Molinate	1.32	4.40	0.998	84.33	12.94	95.61	6.95	87.57	6.55	88.52	13.83	98.81	9.47	87.79	8.97	28.10	−15.67
Monocrotophos	1.38	4.60	0.999	88.03	5.81	100.10	7.21	96.66	4.97	83.71	12.10	86.05	4.42	86.22	8.02	26.94	−1.11
Monolinuron	2.69	8.97	0.998	81.87	11.46	107.81	9.59	98.78	9.67	86.13	10.42	96.09	11.73	90.31	8.35	28.96	−9.42
Myclobutanil	0.90	3.00	0.998	111.75	8.47	112.40	13.73	88.46	13.66	114.29	3.17	98.78	8.53	93.48	5.37	28.67	−5.74
Nicosulfuron	2.20	7.33	0.993	79.53	10.88	114.54	11.71	114.18	7.39	75.34	12.80	111.09	5.34	109.92	11.40	46.18	−30.10
Novaluron	1.57	5.23	0.995	99.11	13.80	110.17	5.46	90.26	12.54	87.67	10.08	104.41	13.94	118.29	9.82	32.32	2.84
Nuarimol	1.50	5.00	0.995	71.95	18.87	115.12	6.36	102.19	5.25	82.88	8.63	97.16	12.71	98.15	4.68	34.53	−13.01
o.p DDD*	1.96	6.54	0.991	110.08	5.33	82.29	7.60	97.40	9.57	111.69	5.41	79.31	6.50	90.71	8.55	30.25	337.39
o.p DDE*	1.04	3.47	0.991	111.35	2.68	89.00	3.17	98.05	3.27	105.31	4.00	83.22	3.79	93.04	4.25	22.13	59.16
o.p DDT*	2.54	8.47	0.997	84.07	6.33	80.42	10.90	101.83	9.07	75.85	5.05	76.36	12.09	96.18	10.20	38.04	508.07
Omethoate	1.16	3.85	0.999	104.19	7.13	93.89	7.93	85.94	7.89	113.72	3.88	87.38	10.51	81.76	12.03	29.10	−66.83
Oxadixyl	1.54	5.12	0.993	80.82	12.36	117.01	9.88	118.29	4.05	78.93	9.88	109.03	8.17	116.53	6.11	39.45	−8.51
Oxamyl	2.89	9.65	0.993	75.89	7.40	102.61	10.30	107.09	12.04	75.36	15.84	95.31	13.40	104.36	9.98	36.09	5.45
Oxycarboxin	2.70	9.00	0.995	80.69	16.89	110.22	6.05	95.07	13.23	78.80	11.95	105.63	6.30	110.14	4.98	32.59	−12.11
Oxydemeton-methyl	2.81	9.37	0.999	94.30	10.08	112.19	3.50	107.77	11.27	107.92	6.32	111.40	7.41	101.67	9.08	25.39	−1.76
p.p DDD*	2.61	8.72	0.991	116.02	5.54	103.17	9.11	107.03	7.94	111.86	5.12	89.36	9.69	109.35	10.26	27.66	306.25
p.p DDE*	0.86	2.86	0.992	102.82	3.23	88.58	2.84	96.86	2.70	106.40	2.89	79.44	3.28	90.84	4.52	22.99	49.46
Paclobutrazol	1.92	6.41	0.998	105.91	16.06	112.95	6.43	100.40	14.35	97.97	7.10	100.60	10.82	93.32	7.42	26.56	11.05
Paraoxon-ethyl	1.65	5.51	0.995	107.55	5.64	111.87	7.08	105.05	3.64	97.77	13.52	103.21	8.13	94.01	6.22	21.00	−0.06
Paraoxon-methyl	1.52	5.07	0.996	74.99	12.13	102.43	6.88	93.67	5.11	81.62	8.51	101.18	4.67	101.87	5.30	28.98	−15.34
Parathion-ethyl*	0.84	2.80	0.994	110.95	4.87	89.12	1.96	96.68	1.65	107.61	6.76	80.26	7.84	86.92	10.31	27.01	139.78
Parathion-ethyl	2.12	7.05	0.996	112.67	13.15	102.59	15.80	91.69	9.17	113.53	5.72	78.29	11.84	97.93	15.64	35.58	35.29
Penconazole	0.65	2.15	0.994	85.33	10.08	105.46	11.16	106.38	11.19	87.99	13.92	100.41	13.28	117.92	11.59	35.06	−17.67
Pencycuron	2.06	6.86	0.997	100.09	12.53	104.33	3.81	102.07	5.01	100.77	16.38	106.29	13.04	115.41	11.32	28.51	14.16
Pendimenthalin	2.52	8.41	0.999	112.49	3.85	107.13	3.63	106.21	4.57	89.49	13.47	81.02	10.22	106.08	8.19	27.97	−3.87
Pentachloroaniline*	0.91	3.03	0.991	103.79	1.83	84.07	3.34	98.14	5.12	113.30	2.22	83.61	2.99	88.64	3.96	24.96	46.56
Phenmedipham	1.31	4.36	0.999	80.44	15.14	86.35	10.30	74.29	6.10	87.80	3.08	83.46	6.76	98.86	14.89	39.79	−30.11
Phenthoate	1.02	3.39	0.994	101.87	17.43	110.61	10.01	101.29	10.93	96.68	13.35	107.29	9.68	118.42	10.11	31.79	−8.24
Phorate	0.92	3.07	0.999	105.47	10.82	107.02	7.33	98.48	13.04	104.04	7.94	97.10	11.96	89.94	11.58	23.55	−1.24
Phorate-sulfone	2.04	6.80	0.992	91.33	15.57	112.91	7.06	108.88	5.82	89.32	17.08	112.16	4.51	106.30	7.54	38.22	−7.64
Phorate-sulfoxide	1.60	5.32	0.991	79.82	9.68	101.45	11.27	105.94	6.05	76.72	8.66	104.14	11.94	100.40	7.20	31.32	−13.41
Phosalone	1.13	3.76	0.998	101.51	14.41	105.75	5.54	106.19	8.31	108.07	10.37	106.70	7.39	108.24	13.84	27.85	23.56
Phosphamidon	2.87	9.55	0.999	99.93	10.39	114.04	9.51	116.26	11.08	94.65	7.32	111.55	6.06	117.51	14.02	33.28	9.11
Pirimicarb-Desmethyl	2.53	8.45	0.997	86.46	7.41	111.64	12.31	101.13	6.27	84.92	5.03	100.66	9.62	93.17	9.22	27.29	−12.98

(*continued on next page*)

Table 2 (*continued*)

Analyte	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	R^2	Repeatability ($n = 10$)						Reproductibility ($n = 10$)						U'%	ME%
				10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}		10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}			
				Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
Primicarb	2.02	6.72	0.995	104.43	18.02	116.97	5.75	118.59	3.04	101.63	8.25	111.03	7.98	109.94	13.07	32.02	4.56
Primiphos -ethyl	1.25	4.16	0.999	116.97	5.63	99.85	12.59	97.75	11.25	98.53	11.08	81.27	12.44	95.88	18.95	32.86	5.53
Primiphos -methyl	0.89	2.96	0.990	80.38	13.41	104.23	8.27	110.03	10.10	85.27	8.45	93.84	11.95	98.26	8.19	33.06	−4.60
Prochloraz	1.00	3.33	0.999	97.24	15.18	104.43	4.85	111.90	12.87	92.86	13.93	112.97	13.27	111.92	14.52	32.45	8.14
Procymidone*	2.74	9.13	0.990	78.38	8.41	75.77	4.27	91.94	8.93	77.62	8.92	79.24	7.30	96.13	10.12	40.03	322.55
Profenefos	1.08	3.60	0.996	96.99	14.18	107.23	6.20	104.08	7.70	78.33	7.95	102.41	6.03	99.11	7.13	25.91	−0.78
Profoxydim-lithium	1.63	5.43	0.996	98.88	14.71	107.70	6.12	100.82	10.07	94.80	10.67	105.71	8.51	111.39	10.85	28.34	50.31
Promecarb	1.01	3.35	0.996	75.36	5.65	102.18	9.75	84.52	15.72	85.66	6.90	95.65	11.63	92.76	7.13	32.63	−16.61
Prometryn	0.64	2.13	0.999	84.59	10.10	103.69	13.77	102.46	10.82	95.56	13.07	104.86	4.90	115.23	9.49	31.19	−20.62
Propaquizafob	0.92	3.05	0.999	100.59	17.39	112.21	14.37	112.01	5.83	82.81	14.31	97.85	8.59	90.02	8.88	31.68	−1.51
Propargite	1.60	5.32	0.999	111.23	7.04	113.90	5.28	109.65	8.67	92.73	13.27	93.44	2.49	94.60	8.24	26.55	5.11
Propazine	2.81	9.38	0.999	106.36	12.84	115.28	13.44	109.75	14.01	110.56	8.01	111.10	5.97	115.86	14.85	35.70	7.65
Propiconazole	1.08	3.60	0.999	95.22	11.36	96.68	11.26	88.49	12.36	109.13	4.54	100.79	7.78	92.95	18.23	25.82	3.27
Propoxur	0.87	2.89	0.995	73.83	7.84	115.29	7.26	113.39	4.87	78.64	6.59	104.70	6.36	105.55	9.31	35.73	−4.45
Propyzamide	1.29	4.31	0.999	100.90	9.14	107.93	6.89	96.04	11.41	95.93	13.27	107.66	7.31	112.52	9.10	25.06	−3.74
Prothiophos	1.43	4.78	0.998	87.62	10.69	92.15	11.39	94.18	15.17	72.54	14.90	89.64	9.90	77.86	13.43	41.99	−45.20
Pymetrozine	2.50	8.35	0.996	92.85	12.86	116.31	4.20	116.14	6.50	85.78	11.60	110.58	6.22	112.55	10.92	32.47	−24.54
Pyraclostrobin	1.56	5.21	0.998	110.58	5.06	102.46	18.48	109.05	8.93	100.63	13.28	109.23	5.45	103.03	4.59	28.00	−9.62
Pyrazophos	1.77	5.91	0.996	94.87	17.67	111.91	10.45	100.10	10.99	84.35	10.41	104.28	13.98	116.51	10.45	33.44	13.91
Pyridaben	1.30	4.35	0.999	111.23	5.42	96.20	8.36	94.67	10.12	92.77	12.05	87.34	17.54	82.72	17.47	33.18	−8.23
Pyridaphenthion	1.66	5.53	0.998	108.39	11.19	107.05	12.35	84.92	14.79	100.49	12.39	109.49	8.08	113.14	3.81	29.93	−19.59
Pyridate	0.81	2.71	0.999	93.35	9.32	94.53	7.40	94.90	13.73	77.28	8.86	89.13	8.65	78.21	13.23	37.10	−17.28
Pyrimethanil	1.42	4.75	0.999	93.02	17.99	91.21	13.17	83.90	8.17	83.47	6.12	92.98	10.41	87.13	8.87	31.95	−21.26
Pyriproxyfen	0.63	2.08	0.999	107.84	7.88	108.43	4.40	103.66	8.66	79.20	5.74	75.59	6.93	81.69	10.21	37.24	−9.16
Quinalphos	1.01	3.35	0.993	94.43	12.84	113.47	6.94	101.83	13.11	97.22	12.76	100.87	8.39	115.17	13.83	30.44	−4.66
Quinoxyfen*	1.39	4.63	0.990	93.21	5.08	78.54	6.77	87.92	9.34	96.60	3.85	78.00	3.57	98.34	5.16	30.21	180.59
Quintozene*	2.95	9.84	0.993	108.41	8.27	90.26	14.16	104.85	8.26	110.89	10.73	84.22	14.81	101.36	9.36	28.93	435.36
Quizalofop-ethyl	1.21	4.04	0.999	104.73	16.84	100.93	9.77	101.02	7.00	84.32	11.99	91.19	13.80	110.05	4.59	28.50	−10.20
Rimsulfuron	2.66	8.85	0.994	76.22	6.34	113.08	13.63	101.39	11.72	74.95	3.36	106.65	9.10	103.27	8.47	36.35	−31.51
Sethoxydim	1.56	5.20	0.994	111.98	13.54	107.60	4.65	95.71	15.04	115.97	5.64	110.48	4.43	114.91	9.46	31.93	3.17
Simazine	2.02	6.74	0.995	80.71	11.15	105.43	15.04	104.76	3.85	78.19	4.63	101.18	6.72	91.44	5.95	30.27	−7.89
Spinosyn A	1.67	5.57	0.998	114.71	9.11	100.52	12.63	89.11	12.61	92.72	14.13	77.35	9.83	91.40	13.60	34.58	−1.48
Spinosyn D	1.55	5.17	0.999	90.33	13.86	98.70	7.36	86.93	5.76	79.22	6.96	89.66	11.47	83.70	18.60	37.22	−20.54
Spirodiclofen	1.36	4.54	0.997	109.44	7.61	98.95	6.27	90.17	11.81	94.73	7.89	73.74	2.89	95.70	15.29	31.75	−0.13
Spiroxamine	0.95	3.17	0.999	103.82	16.83	103.07	7.56	98.68	12.06	90.01	12.73	105.48	6.78	105.48	15.33	27.20	−16.49
Sulfoxaflor	1.47	4.91	0.996	102.56	14.79	118.42	8.10	116.25	12.23	98.75	4.11	96.80	5.42	103.09	2.68	28.36	−11.67
Tebuconazole	1.05	3.48	0.993	94.84	14.28	107.65	9.70	114.58	14.48	88.97	12.91	103.22	11.25	94.08	4.61	29.50	−13.63
Tebufenpyrad	0.54	1.82	0.999	91.30	12.80	112.64	10.28	105.23	10.87	82.02	9.96	89.74	14.35	95.67	6.16	31.72	−9.89
Tecnazene*	2.64	8.82	0.994	111.60	8.59	78.58	7.78	90.76	8.19	108.74	9.05	81.54	8.94	93.57	4.31	31.14	264.03
Tefluthrin*	1.43	4.75	0.992	113.81	3.59	80.05	7.96	95.78	7.17	105.83	5.18	79.93	6.46	91.75	8.05	29.73	418.32
Tepraloxydim	1.57	5.23	0.998	87.15	11.33	81.55	9.86	76.32	6.92	77.16	6.04	116.54	13.37	80.67	15.83	46.10	27.16
Terbutryn	1.66	5.53	0.999	91.97	16.78	98.02	13.33	96.33	13.96	102.29	4.52	100.52	7.00	96.55	7.96	24.17	−17.31
Terbutylazine	1.69	5.64	0.998	110.94	4.10	106.80	15.49	112.50	13.33	107.85	6.29	107.71	10.61	107.95	10.70	30.71	−3.98
Tetrachlorvinphos*	1.51	5.05	0.993	112.94	3.57	75.75	7.06	85.39	6.86	102.82	4.66	78.15	9.68	83.85	8.60	35.73	407.52
Tetraconazole	1.80	5.99	0.997	98.59	11.02	103.44	14.12	88.38	11.09	97.16	9.84	106.97	8.71	114.26	11.06	27.29	−8.39
Tetradifon*	2.94	9.79	0.992	109.47	4.46	74.15	6.91	91.29	15.48	109.51	5.00	78.34	7.24	86.54	11.63	37.38	381.73
Tetramethrin	1.14	3.79	0.997	102.15	11.47	109.33	11.85	101.86	14.12	89.90	16.90	95.42	9.34	115.39	8.48	30.73	2.25
Tetrasul*	1.26	4.19	0.993	92.75	5.22	85.96	8.71	108.23	3.58	92.01	8.08	83.14	5.88	92.30	5.54	25.41	113.76
Thiabendazole	1.59	5.30	0.999	107.46	11.28	99.45	15.96	100.62	15.78	104.47	12.49	100.00	11.20	108.54	10.13	27.71	25.73
Thiacloprid	1.38	4.61	0.996	79.00	7.30	105.23	7.31	103.46	6.53	76.34	10.39	98.53	5.99	92.42	7.15	31.31	−32.09
Thiamethoxam	2.30	7.66	0.991	96.73	15.82	116.04	7.26	118.62	5.45	85.85	10.40	115.80	5.77	114.69	12.80	35.99	−10.67

(*continued on next page*)

Table 2 (*continued*)

Analyte	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	R^2	Repeatability ($n = 10$)						Reproductibility ($n = 10$)						U'%	ME%
				10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}		10 μg kg^{-1}		50 μg kg^{-1}		100 μg kg^{-1}			
				Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
Thifensulfuron-methyl	2.30	7.66	0.997	81.20	13.51	116.39	7.96	113.49	5.09	89.90	11.79	108.45	4.85	116.11	8.88	33.88	−19.06
Thiobencarb	0.87	2.91	0.991	82.39	9.90	112.23	2.45	107.94	11.17	72.42	15.83	98.87	13.29	114.00	17.59	40.76	−9.85
Thiodicarb	2.02	6.72	0.992	110.92	5.23	116.49	11.58	115.71	5.20	94.36	9.90	97.71	7.12	102.70	14.85	29.99	−7.78
Thiophanate-methyl	2.64	8.80	0.997	94.55	7.02	86.55	10.12	77.76	5.11	88.75	8.42	112.54	4.00	116.26	5.63	34.05	−1.80
Tolclofos-methyl	1.24	4.13	0.996	76.41	13.90	95.78	12.09	92.60	14.29	82.85	12.85	81.14	9.96	84.10	12.14	39.97	5.76
Tolfenpyrad	0.97	3.23	0.998	96.97	13.73	91.58	11.96	85.44	9.29	81.74	7.86	87.19	10.33	84.81	10.32	34.14	4.00
Tolyfluanid	0.95	3.17	0.997	88.79	12.62	109.21	13.77	101.34	10.41	113.17	9.14	110.43	7.08	117.22	8.26	31.83	6.47
Tralkoxydim	1.54	5.15	0.992	112.99	12.33	106.66	8.22	101.77	12.20	113.60	6.34	111.01	5.31	112.59	7.57	30.08	7.95
Trans chlordane*	0.75	2.48	0.991	111.83	2.63	82.42	2.10	91.64	3.32	102.37	4.84	79.41	2.13	88.09	3.73	28.09	85.58
Triadimefon	0.55	1.82	0.997	102.37	14.75	113.13	9.36	91.98	13.12	106.71	7.42	105.73	9.92	97.95	6.58	27.01	−0.99
Triadimenol	2.33	7.76	0.998	90.00	3.67	101.99	3.67	76.51	3.67	90.00	3.67	92.62	3.67	92.59	3.67	35.71	−53.19
Triallate*	1.48	4.94	0.991	119.39	3.18	84.85	7.40	97.64	8.43	111.75	9.90	82.21	8.09	88.66	6.13	31.47	122.80
Triasulfuron	2.32	7.73	0.994	94.26	14.69	116.65	6.24	117.91	2.36	90.53	14.35	114.38	9.30	98.54	4.65	31.74	−21.04
Triazophos	2.79	9.31	0.998	99.92	13.43	100.46	17.99	84.76	15.16	96.14	12.71	85.98	5.41	84.58	5.59	31.58	−16.66
Tribenuron methyl	2.99	9.97	0.991	73.60	5.17	107.83	6.55	102.12	7.79	78.72	4.33	91.99	8.31	84.98	5.71	34.15	−18.21
Trichlorfon	2.09	6.98	0.991	82.02	8.96	115.84	6.72	111.41	10.49	78.52	2.69	111.14	4.66	103.40	5.96	33.48	−14.37
Trifloxystrobin	0.93	3.08	0.999	111.95	12.05	108.17	6.64	101.63	9.78	99.43	13.44	108.12	10.23	93.85	9.84	28.70	0.09
Triflumizole	1.33	4.45	0.998	106.89	9.26	106.24	4.71	114.23	5.41	107.69	7.46	107.03	10.89	117.06	5.90	29.17	−3.70
Triflumuron	1.33	4.43	0.999	109.62	9.32	111.26	4.90	104.08	5.79	96.12	13.09	107.96	11.04	117.60	8.44	30.87	−0.77
Trifluralin*	1.32	4.41	0.991	114.57	2.66	85.71	6.56	101.02	5.77	108.58	3.07	82.65	6.88	97.86	5.15	24.83	334.62
Triticonazole	1.04	3.47	0.998	84.00	12.84	101.78	9.72	77.21	10.51	87.28	10.87	90.54	6.69	85.91	6.27	33.96	−19.50
Vinclozoline	2.44	8.12	0.995	108.02	4.63	93.17	8.77	103.86	11.98	107.64	8.59	92.02	11.04	102.14	8.52	22.32	499.91

* GC-MS– amenable pesticides.

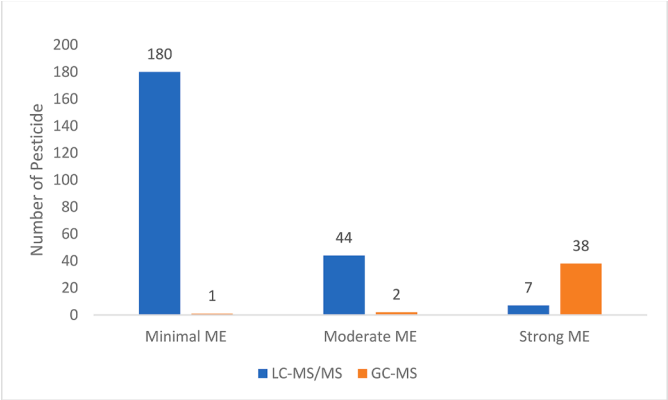

Fig. 3. The number of pesticides showed minimal, moderate, or strong matrix effect in almond.

LOQ were within the range of 0.54–3.00 mg kg^{-1} and 1.82–9.98 mg kg^{-1} respectively. The linearity was evaluated for LC-MS/MS and GC–MS by grape matrix-matched calibration at 5, 10, 25, 50, 100 and 200 μg kg^{-1}. The linearity of the calibration curve was determined with an R^2 value greater than 0.99 for pesticides for both GC and LC amenable. The recovery values for GC amenable pesticides obtained under repeatability (RSD_r) and reproducibility (RSD_{wR}) conditions ranged from 71.94 to 119.39 % and 75.12–116.08 %, respectively. The RSD_r values ranged from 1.65 to 15.48 %, whereas the RSD_{wR} ranged from 1.77 to 14.81 %. The expanded measurement uncertainties for GC amenable pesticides were between 15.82 and 40.03 %. The recovery values for LC amenable pesticides obtained under repeatability (RSD_r) and reproducibility (RSD_{wR}) conditions ranged from 71.95 to 118.62 % and 70.91–119.82 %, respectively. The RSD_r values ranged from 2.16 to 19.15 %, whereas the RSD_{wR} ranged from 1.85 to 19.42 %. The expanded measurement uncertainties for LC amenable pesticides were between 18.20 and 46.58 %. The method validation data for the almond matrix across the 230 LC-amenable and 40 GC-amenable pesticides are given in Table 2. The values accomplished the requirements of Document SANTE/11312/2021. Our study has some advantages over other studies. Liu et al. (2016), Wang et al. (2017), Mahdavi et al. (2019), Taghizadeh et al. (2019), Arabameri et al. (2020), Mahdavi et al. (2020), Cebi et al. (2021), and Taghizadeh et al. (2021) validated 36, 106, 11, 2, 77 and 18 pesticides in various nuts, respectively. While 270 pesticides were validated on almonds in this study, much fewer pesticides were validated in published studies. Wang et al. (2017) determined 106 pesticides in 15 min by LC-MS/MS. In our study, more than 2 times (240) pesticides were detected in the same minute. Liu et al. (2016) determined organophosphates at 32.93 min in GC-FPD, and organochlorines and pyrethroids at 40 min in GC-ECD. In this study, the pesticide groups mentioned in GC-MS were determined in a single injection in 22.89 min, thus saving time and energy.

Matrix effect (ME)

MEs were determined for all pesticides in almond (Table 2). In the study, both signal suppression and enhancement were determined depending on the analyte and matrix combination. MEs greater than 20 % or less than −20 % indicate an increased or suppressed peak signal, respectively. In Fig. 2, MEs are classified into three types: minimal signal suppression or enhancement effects (ME range −20 % to 20 %), moderate effects (ME range - 50 % to −20 % or 20 % to 50 %) and strong matrix effects (less than 50 % or more than 50 %) (Szarka et al., 2022).

In LC-MS/MS analysis, minimal ME was observed in almond matrix (Fig. 3). MEs were found in the range of −99 % to 50 %. In GC-MS analysis, a strong matrix effect was detected in almond matrix. Only a pesticide showed minimal ME in our study. Signal suppression is generally less common in GG analyzes (Szarka et al., 2022). In this study, signal enhancement was observed in all pesticides.

Different rates of ME were detected in all samples in both GG-MS and LC-MS/MS. In order to eliminate this effect, matrix compatible standard solutions should be used or other recommended approaches should be used. The use of matrix-matched calibration curves provides more precise and accurate analysis results. The SANTE document considers the

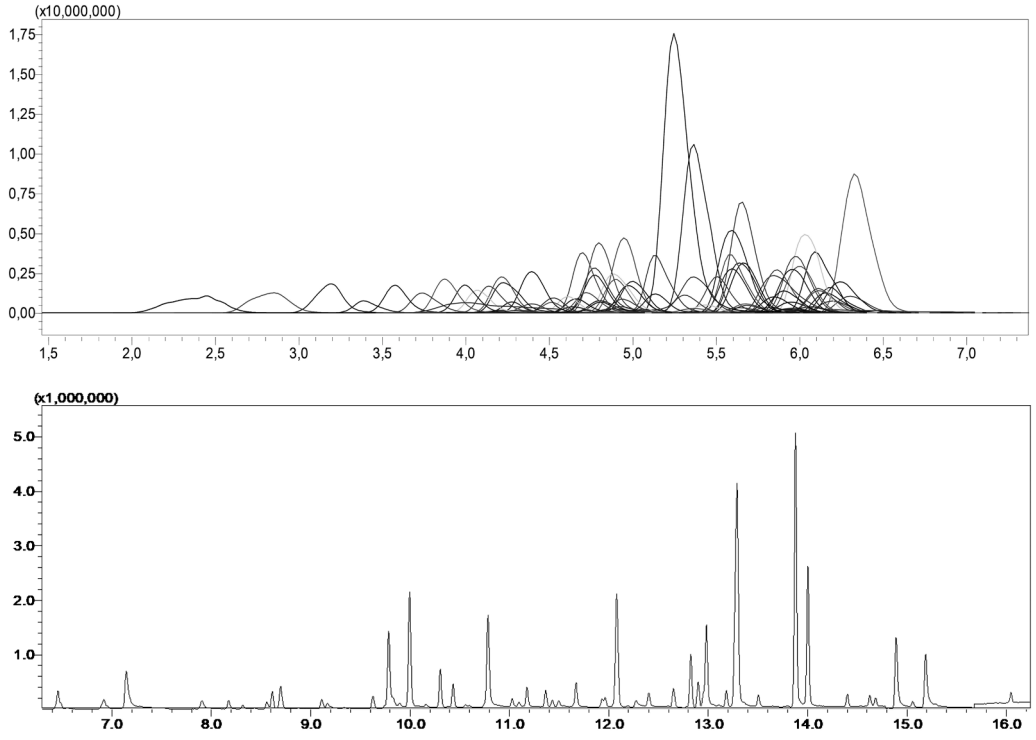

Fig. 4. LC-MS/MS total ion chromatogram (upper) of 230 pesticides and GC-MS total ion chromatogram (lower) of 40 pesticides.

matrix effect an important component of method validation and generally recommends the use of matrix calibration to enable method validation in pesticide analysis (SANTE, 2021). The results of the study confirm what is stated in the above.

Pesticide residues analyses in almonds

The method was used to the analysis of 90 almond samples. Any of 90 almond samples, pesticides were not determined at levels equal to or higher than LODs. Total ion chromatograms of the 270 pesticides scanned are given in Fig. 4.

Residue studies on almonds are very limited. Reviewing the residue studies in other nuts can give some information about the subject. Özkan (2015), detected dichlorvos in two peanut samples and acetamiprid in one peanut sample. These values were higher than the MRL. Liu et al. (2016) investigated pesticide residue levels in chestnuts, walnuts and pine nuts collected from seven production regions of China. 20.5 % of the samples had values above the EU-MRL. Wang et al. (2017) examined 180 samples to determine residue levels in walnuts, almonds and sweet almonds purchased from local market and traders in Urumqi, China. They determined acetamiprid, chlordimeform, ethirimol, myclobutanil and tebufenozide. Only chlordimeform residue in a walnut sample was exceeded the MRL (50 μg/kg) level in China. Arabameri et al. (2020), determined 11 different pesticides in Iran. Two types of neonicotinoids including imidacloprid and acetamiprid exceeded the EU-MRL. Mahdavi et al. (2020) reported that acetamiprid and imidacloprid residues in pistachios did not exceed the MRL. Cebi et al. (2021) determined acetochlor, boscalid, carbendazim, chlorantraniliprole, chloridazon, diflubenzuron, fenarimol and fluopyram in hazelnut. They noted that the pesticide values were significantly lower than the EU-MRL. Taghizadeh et. al (2021), reported concentrations of 18 pesticides in walnuts (Iran) exceeded the EU-MRLs.

While no pesticides were detected in almonds in our study, pesticides at different concentrations were detected in the above-mentioned studies on various nuts. The PHI of the insecticides/acaricide used in almonds in Turkey is 3–14 days, and the fungicides are 21 days. The reason why pesticides are not detected in almonds in Turkey may be the application of the last spraying 30 days before the harvest.

Conclusions

In this study, the QuEChERS method for quantitative analysis of 230 pesticides in LC–MS/MS and 40 pesticides in GC-MS was validated according to SANTE 11312/2021 guidelines. Almond samples were subjected to two different sorbents combinations during the clean-up phase: (1) PSA and C18, (2) PSA, C18 and GCB sorbents. The combination of PSA and C18 demonstrated better recovery and clean-up efficiency. The method showed satisfactory recovery and accuracy, low LOQs for 270 target analytes, and demonstrated a high suitability for the multi-residue pesticide analysis in almonds for routine residue monitoring purposes. A total of 90 almond samples were analyzed using the method. Any of 90 almond samples, pesticides were not determined at levels equal to or higher than LODs.

CRediT authorship contribution statement

Tarık Balkan: Conceptualization, Validation, Investigation, Writing – original draft, Writing – review & editing. **Kenan Kara:** Conceptualization, Investigation, Writing – original draft. **Özlem Yılmaz:** Validation, Investigation. **Mehmet Kızılarslan:** Investigation. **Ömer Faruk Özbek:** Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This study was presented as an oral presentation at Workshop on Pesticide Residues and Risks (15 June 2022, Aydın, Turkey).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.focha.2023.100442.

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