Food Chemistry 176 (2015) 319–332

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Evaluation of QuEChERS sample preparation and liquid chromatography–triple-quadrupole mass spectrometry method for the determination of 109 pesticide residues in tomatoes

Ozgur Golge [a], Bulent Kabak [b,*]

[a] Ministry of Food, Agriculture and Livestock, General Directorate of Food and Control, Food Control Laboratory, Adana, Turkey
[b] Hitit University, Faculty of Engineering, Department of Food Engineering, TR-19030 Corum, Turkey

ARTICLE INFO

Article history:
Received 4 September 2014
Received in revised form 16 December 2014
Accepted 20 December 2014
Available online 29 December 2014

Keywords:
Pesticide residues
QuEChERS
LC–MS/MS
Screening
Tomato

ABSTRACT

A multiresidue method based on modified QuEChERS (quick, easy, cheap, effective, rugged and safe) sample preparation, followed by liquid chromatography tandem mass spectrometry (LC–MS/MS) was developed and validated for the determination of 109 selected multiclass pesticides in tomatoes. The recovery yields ranged from 77.1% to 113.2%, with repeatabilities of 4.4–19.2% and within-laboratory reproducibilities of 7.1–18.4%. The limit of detections (LODs) for target analytes in tomato extract were between 0.5 and 10.8 μg kg^{-1}, and the limit of quantifications (LOQs) were between 1.3 and 30.4 μg kg^{-1}. The expanded measurement uncertainty was not higher than 30% for all target analytes. The method has been successfully applied to the analysis of 345 tomato samples obtained from local markets and tomato traders. Residues of acetamiprid, azoxystrobin and triadimefon were identified and measured in 9.6% of tomato samples, ranging from 0.015 to 0.37 mg kg^{-1}.

1. Introduction

Tomato (*Solanum lycopersicum* L.) is one of the most important and widely grown vegetable plants in the world. According to FAO statistics, Turkey is fourth major producer with a production of 11.4 million metric tonnes, after China (50 million tonnes), India (17.5 million tonnes) and United States (13.2 million tonnes) (FAO, 2012). Tomato is one of the basic components of the Mediterranean, American, and Asian diets, which is consumed daily in diverse ways, including raw, cooked, or processed as a canned product, juice, or ketchup (Zhao et al., 2014). However, tomatoes are susceptible to several common abiotic disorders, as well as attack by fungal diseases, insects, nematodes and weeds that can significantly diminish yield or even destroy an entire crop (Pittenger, Garrison, Geisel, & Unruh, 2005). In order to achieve a high yield and good quality, the use of pesticide is considered to be a necessary, economic and conventional agricultural practice (Zhao et al., 2014).

Pesticides, which include insecticides, herbicides, fungicides, and others have been widely used in the cultivation and post-harvest storage of certain crops to control weeds, insect infestation and plant diseases and thus can improve yield as well as quality of the produce (Walorczyk et al., 2013; Wang, Wang, Zhang, Wang, & Guo, 2013). Despite their many merits and excessive use, pesticides are some of most toxic substances contaminating the environment. Their excessive use can have negative environmental impacts on water quality, terrestrial and aquatic biodiversity, while pesticide residues in foodstuffs can pose a risk to human health, varying from allergies to chronic diseases and cancer, depending on the intrinsic characteristics of their active substances and use patterns (Fenik, Tankiewicz, & Biziuk, 2011; Park et al., 2011). Additionally, the World Health Organisation (WHO) has reported that roughly three million pesticide

Abbreviations: ADI, acceptable daily intake; ARfD, acute reference dose; ASE, accelerated solvent extraction; CE, collision energy; CXP, collision cell exit potential; DP, declustering potential; EP, entrance potential; ESI, electrospray ionisation; GC–ECD, gas chromatography–electron capture detection; GC–MS, gas chromatography–mass spectrometry; GC–MS/MS, gas chromatography–tandem mass spectrometry; GPC, gel permeation chromatography; LC–MS/MS, liquid chromatography–tandem mass spectrometry; LOD, limit of detection; LOQ, limit of quantification; MAE, microwave-assisted extraction; MRL, maximum residue limit; MRM, multiple reaction monitoring; MSPD, matrix solid-phase dispersion; PSA, primary–secondary amine; RSD, relative standard deviation; SFE, supercritical fluid extraction; d-SPE, dispersive solid-phase extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction; SRM, selected reaction monitoring; QuEChERS, quick, easy, cheap, effective, rugged, and safe; *U*, expanded measurement uncertainty; u_c, combined uncertainty.

* Corresponding author. Tel.: +90 364 2274533; fax: +90 364 2274535.
E-mail address: bulentkabak@hitit.edu.tr (B. Kabak).

http://dx.doi.org/10.1016/j.foodchem.2014.12.083
0308-8146/

poisonings occur annually and result in 220,000 deaths worldwide (WHO, 1992). Therefore, pesticide residue determination in food products, especially in raw fruits and vegetables is a very demanding task in public health safety and trade.

In the European Union, a series of regulations and legislations have been issued in accordance with the appropriate use of pesticides. The core legislation regulating the approval of pesticides on the EU market is Regulation (EC) No. 1107/2009, directly applicable in Member States. Based on the predominance of health and environment protection over agricultural production, it sets EU-wide requirements for their registration (Commission Regulation, 2009). In order to protect consumer's health, maximum residue levels (MRLs) of pesticides in products of plant or animal origin have been established by various government agencies, European Union and Codex Alimentarius. Despite this fact, to our knowledge, no investigations of regular surveys and monitoring have been reported for the quantitation of pesticide residues in tomatoes consumed in Turkey. However, several studies have investigated and identified pesticide residues in tomatoes from China (Zhao et al., 2014), Portugal (Melo et al., 2012) and India (Kumari, Rao, Sahrawat, & Rajasekhar, 2012).

The development and validation of simple, rapid, robust, reproducible and cost-effective multiresidue analytical methods are of great importance to satisfy the demand for monitoring pesticides residues at low concentration levels in various agricultural crops, such as vegetables and fruits. Due to the wide variety of pesticides and complexity of food matrices the sample must be initially cleaned up using a compatible sample preparation technique before injection to the detection system. Traditional sample preparation procedures include solid-phase extraction (SPE) (Juan-García, Picó, & Font, 2005; Xie et al., 2011; Iwafune, Ogino, & Watanabe, 2014), solid-phase microextraction (SPME) (Correia, Delerue-Matos, & Matos, 2001), accelerated solvent extraction (ASE) (Adou, Bontoyan, & Sweeney, 2001), supercritical fluid extraction (SFE) (Rissato, Galhaine, Knoll, & Apon, 2004), matrix solid-phase dispersion (MSPD) (Valsamaki, Boti, Sakkas, & Albanis, 2006), microwave-assisted extraction (MAE) (Singh, Foster, & Khan, 2004) and gel permeation chromatography (GPC) (Ueno et al., 2004). However, the majority of these techniques are rather time-consuming, labour-intensive, complicated, expensive and produce considerable quantities of waste (Wilkowska & Biziuk, 2011). An alternative technique called QuEChERS (quick, easy, cheap, effective, rugged, and safe) was introduced first by Anastassiades, Lehotay, Stajnbaher, and Schenck (2003) and has been widely used for the multiclass, multiresidue analysis of a wide range of pesticides in different food matrix. Two more modified versions of this method were adopted by AOAC International (2007) and European Committee for Standardization/Technical Committee (2007). This method involves acetonitrile extraction, and followed by a dispersive SPE clean-up with a combination of primary–secondary amine (PSA) sorbent and $MgSO_4$. QuEChERS methodology is popular for more than 10 years since it requires fewer steps and minimal solvent requirement when compared to conventional sample preparation techniques.

The extract produced in QuEChERS multiresidue technique can be analysed by gas chromatography with electron capture detection (GC–ECD) (Herrero Martín, García Pinto, Pérez Pavón, & Moreno Cordero, 2010; Park et al., 2011), mass spectrometry (GC–MS) (Cieślik, Sadowska-Rociek, Molina Ruiz, & Surma-Zadora, 2011; Restrepo, Ortiz, Ossa, & Mesa, 2014) or tandem mass spectrometry (GC–MS/MS) (Chen et al., 2013; Zhao et al., 2014), and liquid chromatography–tandem mass spectrometry (LC–MS/MS) (Bakırcı & Hışıl, 2012; Iwafune et al., 2014). Liquid chromatography coupled to triple quadrupole mass spectrometry with electrospray ion (ESI) source, operated in selective reaction monitoring (SRM) mode has become the predominant analysis technique in the detection of multiresidue pesticides due to its outstanding selectivity and high sensitivity.

The aim of this study was to evaluate the utility of QuEChERS method in combination with LC–MS/MS for the identification and quantification of 109 multiclass pesticides in tomato. The validated method was also applied to the analysis of 345 tomato samples grown in Mersin and Antalya province during the months of January and December 2013.

2. Materials and methods

2.1. Reagents and chemicals

Methanol and acetonitrile were HPLC-grade and were both supplied by Sigma–Aldrich (St. Louis, MO, USA). Ammonium formate, $\geqslant$99% purity, was also from Sigma–Aldrich (Stenheim, Germany). The analytical reagent grade anhydrous magnesium sulfate (anh $MgSO_4$), anhydrous sodium acetate (99.9%, anh $C_2H_3NaO_2$) and glacial acetic acid were from Merck (Darmstadt, Germany). Primary–secondary amine (PSA, 50 μm) was from Supelco (Bellefonte, PA, USA). Ultrapure water of 18.2 Ω resistivity was produced on a Milli Q purification system (Millipore, Molsheim, France).

2.2. Standards

Individual certified pesticide standards (Table 1) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The purities of the certified pesticide standards were from 92% to 98%. Individual pesticide stock standard solutions (1000 mg L^{-1}) were prepared in acetonitrile and stored at −18 °C. From these individual stock solutions, a multistandard mixture, containing 10 mg L^{-1} of each pesticide was prepared in acetonitrile and stored at −18 °C less than 3 months. Mixed multistandard working solutions were prepared daily to avoid degradation of pesticides by diluting the multistandard solution with blank tomato (pesticide-free tomato) extract. The concentrations of the multistandard working solutions were 10, 25, 50, 100 and 250 μg kg^{-1}.

2.3. Samples

A total of 345 tomato samples were collected in the provinces of Mersin and Antalya, Turkey. The samples were taken from various local markets and tomato traders in the period of January–December 2013. Representative portion of 1 kg tomato sample was taken, shipped to laboratory in an insulated container and stored at 4 °C until analysis.

2.4. Sample preparation

Tomato samples were analysed based on QuEChERS method described by Anastassiades et al. (2003), with some modifications. All samples were analysed unwashed. Approximately 1 kg of tomato samples were homogenised with a blender (Waring Products Co., Torrington, CT, USA) for 1 min at room temperature. A portion of 15 g ground and homogenised sample was weighed into 50 ml Teflon centrifuge tube and covered by 15 ml of acetonitrile–acetic acid (99:1, v/v), 6 g $MgSO_4$ and 1.5 g sodium acetate. Next, the mixture was shaken by the vortex mixer (Nüve NM-110, Ankara, Turkey) for 1 min. The sample extract was centrifuged (Eppendorf 5804, Hamburg, Germany) at 5000 rpm for 1 min. 4 ml of upper layer extract was then transferred to a 15 ml centrifuge tube containing 0.6 g MgSO4 and 0.2 g PSA. The mixture was vortexed for 1 min and centrifuged at 5000 rpm for 1 min. After centrifugation, the supernatant was transferred to an autosampler vial for analysis by LC–MS/MS.

Table 1
MS/MS parameters for the analysis of target analytes in the MRM ESI mode.

Pesticide	Type of pesticide[a]	Chemical group	Molecular formula	Retention time (min)	Precursor ion (*m/z*)	Product ions (*m/z*)	CE (V)	DP (V)	EP (V)	CEP (V)	CXP (V)
2,4-D	H/GR	Phenoxy	$C_8H_6Cl_2O_3$	2.9	219.0	160.8	−18	−30	−11	−14	−6
						124.9	−34	−30	−11	−14	−6
Abamectin	I/A/N	Macrocyclic lactone	$C_{48}H_{72}O_{14}$	9.5	890.5	305.1	39	31	7	38	4
						113.3	79	31	7	38	4
Acetamiprid	I	Neonicotinoid	$C_{10}H_{11}ClN_4$	5.8	223.1	126.2	31	46	6	12	4
						99.2	53	46	6	12	6
Alachlor	H	Aniline	$C_{14}H_{20}ClNO_2$	8.1	270.1	238.0	15	21	9	16	4
						161.9	27	21	9	16	4
Atrazine	H	Triazine	$C_8H_{14}ClN_5$	7.4	216.1	174.1	29	51	10	14	4
						68.1	51	51	10	14	4
Azinphos methyl	I	Organophosphate	$C_{10}H_{12}N_3O_3PS_2$	7.7	318.0	132.1	23	21	8	18	4
						160.1	15	21	8	18	4
Azoxystrobin	F	Strobilurin	$C_{22}H_{17}N_3O_5$	8.0	404.1	371.9	21	31	7	28	4
						344.2	33	31	7	28	4
Bifenthrin	I	Pyrethroid	$C_{23}H_{22}ClF_3O_2$	9.9	440.0	181.2	27	26	5	26	4
						166.2	53	26	5	26	6
Boscalid	F	Carboxamide aka analide	$C_{18}H_{12}Cl_2N_2O$	7.8	343.1	307.2	27	61	5	22	6
						140.2	29	61	5	22	4
Bromuconazole	F	Triazole	$C_{13}H_{12}BrCl_2N_3O$	8.1	378.0	159.0	45	51	4	16	4
						161.0	43	51	4	16	4
Bupirimate	F	Pyrimidine	$C_{13}H_{24}N_4O_3S$	8.1	317.2	166.0	37	56	5	14	4
						108.2	39	56	5	14	4
Buprofezin	I	Thiadiazine	$C_{16}H_{23}N_3OS$	8.6	306.2	201.2	19	26	5	14	4
						116.1	23	26	5	14	2
Carbaryl	I	Carbamate	$C_{12}H_{11}NO_2$	7.3	202.1	145.0	17	26	9	18	4
						117.1	37	26	9	18	4
Carbendazim	F	Benzimidazole	$C_9H_9N_3O_2$	6.3	192.3	160.1	27	41	10	12	6
						132.2	41	41	10	12	4
Carbofuran	I	Carbamate	$C_{12}H_{15}NO_3$	7.0	222.1	165.3	19	36	7	14	4
						77.3	61	36	7	14	4
Carboxin	F	Carboxamide	$C_{12}H_{13}NO_2S$	7.2	236.1	143.1	23	31	11	14	4
						86.8	35	31	11	14	4
Chlorfluazuron	I	Benzoylurea	$C_{20}H_9Cl_3F_5N_3O_3$	9.0	540.2	383.0	31	61	9	28	8
						158.1	29	61	9	28	4
Chlorpropham	H/GR	Carbamate	$C_{10}H_{12}ClNO_2$	7.9	214.1	172.1	13	21	10	12	4
						154.0	27	21	10	12	4
Chlorpyrifos ethyl	I	Organophosphate	$C_9H_{11}Cl_3NO_3PS$	8.7	350.0	197.8	29	36	7	16	4
						97.1	49	36	7	16	6
Chlorpyrifos methyl	I	Organophosphate	$C_7H_7Cl_3NO_3PS$	7.7	322.1	125.1	27	41	7	20	4
						290.0	25	41	7	20	10
Clofentezine	A	Tetrazine	$C_{14}H_8Cl_2N_4$	8.3	303.2	138.2	23	31	6	22	4
						102.1	53	31	6	22	4
Cycloate	H	Carbamate	$C_{11}H_{21}NOS$	8.4	216.3	134.2	19	31	10	14	4
						154.3	19	31	10	14	4
Cymoxanil	F	Acetamide	$C_7H_{10}N_4O_3$	6.1	199.1	128.0	13	21	10	12	2
						111.2	29	21	10	12	4
Cypermethrin	I	Pyrethroid	$C_{22}H_{19}Cl_2NO_3$	9.0	433.1	190.9	23	26	5	18	4
						127.2	45	26	5	18	4
Cyproconazole	F	Triazole	$C_{15}H_{18}ClN_3O$	7.9	292.1	70.0	37	41	5	14	2
						125.2	45	41	5	14	4
Cyprodinil	F	Pyrimidinamines	$C_{14}H_{15}N_3$	8.3	226.3	93.1	49	61	11	16	4
						77.2	65	61	11	16	10
Deltamethrin	I	Pyrethroid	$C_{22}H_{19}Br_2NO_3$	9.0	523.0	280.8	25	26	6	22	4
						181.1	57	26	6	22	4
Diafenthiuron	I/A	Thiourea	$C_{23}H_{32}N_2OS$	8.8	385.2	329.2	25	56	8	16	4

(*continued on next page*)

Table 1 (*continued*)

Pesticide	Type of pesticide[a]	Chemical group	Molecular formula	Retention time (min)	Precursor ion (*m/z*)	Product ions (*m/z*)	CE (V)	DP (V)	EP (V)	CEP (V)	CXP (V)
						278.2	49	56	8	16	4
Diazinon	I	Organophosphate	$C_{12}H_{21}N_2O_3PS$	8.2	305.1	169.0	29	41	5	14	4
						153.2	31	41	5	14	4
Dichlofluanid	F/A	Sulphamide	$C_9H_{11}Cl_2FN_2O_2S_2$	8.0	350.2	224.1	23	26	4	16	6
						123.1	41	26	4	16	6
Dichlorvos	I	Organophosphate	$C_4H_7Cl_2O_4P$	6.9	221.2	109.1	25	41	8	14	4
						127.0	29	41	8	14	4
Diethofencarb	F	Carbamate	$C_{14}H_{21}NO_4$	7.7	268.2	226.2	17	26	10	16	6
						180.3	25	26	10	16	4
Difenoconazole	F	Triazole	$C_{19}H_{17}Cl_2N_3O_3$	8.4	406.0	251.0	43	56	8	20	4
						187.9	63	56	8	20	4
Diflubenzuron	I	Benzamide	$C_{14}H_9ClF_2N_2O_2$	3.3	309.1	156.1	−12	−25	−9	−30	−6
						289.1	−10	−25	−9	−30	−12
Dimethoate	I	Organophosphate	$C_5H_{12}NO_3PS_2$	5.4	230.0	199.0	15	26	8	12	4
						125.0	33	26	8	12	4
Dimethomorph	F	Morpholine	$C_{21}H_{22}ClNO_4$	7.8	388.1	301.1	27	51	5	16	4
						164.9	47	51	5	16	4
Diniconazole	F	Triazole	$C_{15}H_{17}Cl_2N_3O$	8.4	326.0	70.0	51	51	6	18	4
						159.1	43	51	6	18	6
Dinocap	F/A	Dinitrophenol	$C_{18}H_{24}N_2O_6$	3.3	295.1	209.0	−42	−50	−6	−28	−10
						134.2	−74	−50	−6	−28	−8
Diphenamid	H	Amide	$C_{16}H_{17}NO$	7.6	240.2	134.1	33	51	11	16	4
						165.1	61	51	11	16	4
Dithianon	F	Quinone	$C_{14}H_4N_2O_2S_2$	3.3	296.2	208.9	−40	−60	−4	−24	−10
						210.1	−36	−60	−4	−24	−20
Diuron	H	Phenylurea	$C_9H_{10}Cl_2N_2O$	7.5	233.0	72.0	35	41	5	14	2
						160.0	37	41	5	14	4
Epoxiconazole	F	Triazole	$C_{17}H_{13}ClFN_3O$	8.1	330.4	121.1	27	46	9	26	4
						101.2	69	46	9	26	6
Ethiofencarb	I	Carbamate	$C_{11}H_{15}NO_2S$	7.3	226.1	106.9	23	26	10	14	4
						78.9	51	26	10	14	4
Ethofumesate	H	Benzofuran	$C_{13}H_{18}O_5S$	4.7	304.2	241.0	17	21	4	18	4
						121.0	31	21	4	18	4
Ethoprophos	I/N	Organophosphate	$C_8H_{19}O_2PS_2$	5.0	243.2	96.9	43	31	8	14	4
						131.0	27	31	8	14	4
Famoxadone	F	Oxazole	$C_{22}H_{18}N_2O_4$	5.3	392.3	331.2	19	21	5	20	10
						238.2	25	21	5	20	6
Fenamiphos	I	Organophosphate	$C_{13}H_{22}NO_3PS$	5.1	304.2	217.1	31	41	5	18	6
						202.2	47	41	5	18	6
Fenarimol	F	Pyrimidine	$C_{17}H_{12}Cl_2N_2O$	5.0	331.0	268.1	29	61	4	14	6
						139.2	51	61	4	14	4
Fenazaquin	I/A	Quinazoline	$C_{20}H_{22}N_2O$	6.1	307.4	161.2	23	46	8	20	4
						147.1	27	46	8	20	4
Fenoxycarb	IGR	Carbamate	$C_{17}H_{19}NO_4$	8.2	302.4	88.1	27	36	10	20	6
						115.9	17	36	10	20	6
Fenpropathrin	I/A	Pyrethroid	$C_{22}H_{23}NO_3$	8.8	350.4	125.3	21	26	10	26	4
						97.0	43	26	10	26	6
Fenpyroximate	I/A	Pyrazole	$C_{24}H_{27}N_3O_4$	9.0	422.2	366.1	23	46	5	18	4
						135.1	47	46	5	18	4
Fenthion	I	Organophosphate	$C_{10}H_{15}O_3PS_2$	8.1	279.3	169.2	27	36	7	20	4
						247.1	23	36	7	20	18
Fluazifop-p-butyl	H	Phenoxy	$C_{19}H_{20}F_3NO_4$	5.6	384.2	282.2	27	51	10	14	4
						328.0	23	51	10	14	4
Flutriafol	F	Triazole	$C_{16}H_{13}F_2N_3O$	4.4	302.1	70.2	37	36	5	16	4
						123	43	36	5	16	4
Formetanate	I/A	Formamidine	$C_{11}H_{15}N_3O_2$	3.0	222.3	165.2	21	31	8	12	4

						93.0	47	31	8	12	4
Furathiocarb	I	Carbamate	C18H26	9.4	383.4	195.3	25	41	9	18	2
						252.1	21	41	9	18	6
Hexaconazole	F	Triazole	$C_{14}H_{17}Cl_2N_3O$	5.3	314.3	70.0	39	36	5	22	4
						159.1	43	36	5	22	6
Hexaflumuron	I	Benzoylurea	$C_{16}H_8Cl_2F_6N_2O_3$	3.4	459.0	438.9	−14	−25	−5	−26	−12
						275.9	−24	−25	−5	−26	−8
Hexythiazox	A	Carboxamide	$C_{17}H_{21}ClN_2O_2S$	5.7	353.1	228.0	21	41	4	14	4
						168.2	39	41	4	14	4
Imazalil	F	Imidazole	$C_{14}H_{14}Cl_2N_2O$	5.3	297.3	159.0	33	41	8	24	6
						255.1	25	41	8	24	6
Imidacloprid	I	Neonicotinoid	$C_9H_{10}ClN_5O_2$	3.1	256.1	175.1	29	41	5	18	4
						209.4	27	41	5	18	4
Iprodione	F	Dicarboximide	$C_{13}H_{13}Cl_2N_3O_3$	1.5	330.0	140.9	−18	−15	−7	−20	0
						161.7	−44	−15	−7	−20	0
Kresoxim methyl	F	Strobilurin	$C_{18}H_{19}NO_4$	5.2	314.1	116.1	23	26	7	16	2
						131.1	33	26	7	16	4
Lufenuron	I/A	Benzoylurea	$C_{17}H_8Cl_2F_8N_2O_3$	5.8	511.1	141.1	71	51	6	24	6
						158.2	27	51	6	24	4
Malathion	I	Organophosphate	$C_{10}H_{19}O_6PS_2$	4.9	331.0	127.0	19	36	8	18	2
						99.0	33	36	8	18	2
Metalaxyl	F	Phenylamide	$C_{15}H_{21}NO_4$	4.5	280.4	220.3	17	41	6	20	4
						160.2	33	41	6	20	4
Methidathion	I	Organophosphate	$C_6H_{11}N_2O_4PS3$	4.5	303.0	145.1	17	26	10	18	4
						85.0	31	26	10	18	4
Methomyl	I	Carbamate	$C_5H_{10}N_2O_2S$	2.3	163.1	88.0	15	21	7	12	0
						106.1	17	21	7	12	2
Metolachlor	H	Chloroacetamide	$C_{15}H_{22}ClNO_2$	5.1	285.1	253.1	23	31	6	20	6
						177.2	35	31	6	20	4
Metribuzin	H	Triazinone	$C_8H_{14}N_4OS$	4.1	215.2	84.0	23	41	10	14	6
						126.0	29	41	10	14	4
Monocrotophos	I	Organophosphate	$C_7H_{14}NO_5P$	0.4	224.3	127.2	23	26	10	14	4
						98.1	19	26	10	14	4
Monolinuron	H	Urea	$C_9H_{11}ClN_2O_2$	7.2	215.1	125.9	27	36	10	14	4
						99.0	45	36	10	14	4
Myclobutanil	F	Triazole	$C_{15}H_{17}ClN_4$	7.9	289.2	70.0	35	41	8	22	4
						125.1	45	41	8	22	4
Omethoate	I/A	Organophosphate	$C_5H_{12}NO_4PS$	0.7	214.2	125.0	29	26	10	14	4
						183.1	15	26	10	14	6
Oxadixyl	F	Phenylamide	$C_{14}H_{18}N_2O_4$	3.9	279.2	218.9	17	31	8	16	4
						132.0	45	31	8	16	4
Oxamyl	I	Carbamate	$C_7H_{13}N_3O_3S$	0.7	237.1	72.2	25	11	4	16	4
						90.0	13	11	4	16	2
Oxyfluorfen	H	Diphenyl ether	$C_{15}H_{11}ClF_3NO_4$	5.7	379.0	315.9	25	11	3	32	4
						237.0	39	11	3	32	4
Parathion methyl	I	Organophosphate	$C_8H_{10}NO_5PS$	11.5	264.0	125.1	23	46	8	14	4
						109.0	39	46	8	14	4
Penconazole	F	Triazole	$C_{13}H_{15}Cl_2N_3$	8.2	284.3	159.1	41	41	6	18	6
						70.1	33	41	6	18	6
Pendimethalin	H	Dinitroaniline	$C_{13}H_{19}N_3O_4$	8.8	282.4	212.1	17	16	6	18	6
						194.2	27	16	6	18	8
Phenmedipham	H	Bis-carbamate	$C_{16}H_{16}N_2O_4$	5.6	301.1	257.2	35	16	3	12	4
						192.1	51	16	3	12	4
Phenthoate	I	Organophosphate	$C_{12}H_{17}O_4PS_2$	5.2	321.2	79.2	59	31	10	20	4
						135.2	27	31	10	20	4
Phosalone	I/A	Organophosphate	$C_{12}H_{15}ClNO_4PS_2$	5.3	368.2	182.0	27	31	10	20	10
						11.0	55	31	10	20	6
Pirimicarb	I	Carbamate	$C_{11}H_{18}N_4O_2$	7.4	239.4	71.9	29	36	9	16	4
						182.3	23	36	9	16	6

(*continued on next page*)

Table 1 (*continued*)

Pesticide	Type of pesticide[a]	Chemical group	Molecular formula	Retention time (min)	Precursor ion (*m/z*)	Product ions (*m/z*)	CE (V)	DP (V)	EP (V)	CEP (V)	CXP (V)
Pirimiphos methyl	I/A	Organophosphate	$C_{11}H_{20}N_3O_3PS$	8.3	306.2	164.1	33	61	8	12	4
						108.2	45	61	8	12	4
Prochloraz	F	Imidazole	$C_{15}H_{16}Cl_3N_3O_2$	8.3	377.0	308.0	19	21	3	20	10
						70.0	43	21	3	20	4
Profenofos	I/A	Organophosphate	$C_{11}H_{15}BrClO_3PS$	8.6	373.1	302.9	25	41	9	24	4
						96.9	49	41	9	24	4
Propiconazole	F	Triazole	$C_{15}H_{17}Cl_2N_3O_2$	8.3	342.1	159.0	47	56	5	14	4
						69.3	37	56	5	14	2
Propyzamide	H	Benzamide	$C_{12}H_{11}Cl_2NO$	7.9	256.1	190.0	19	41	7	16	4
						173.0	35	41	7	16	4
Prothiofos	I	Organophosphate	$C_{11}H_{15}Cl_2O_2PS_2$	9.2	345.0	240.9	29	36	7	16	4
						133.2	73	36	7	16	4
Pyraclostrobin	F	Strobilurin	$C_{19}H_{18}ClN_3O_4$	8.3	388.2	194.1	19	26	8	18	6
						163.1	31	26	8	18	4
Pyrazophos	F	Phosphorothiolate	$C_{14}H_{20}N_3O_5PS$	8.4	374.1	222.1	31	61	6	24	4
						193.9	49	61	6	24	4
Pyridaben	I/A	Pyridazinone	$C_{19}H_{25}ClN_2OS$	9.1	365.2	174.4	37	36	10	16	4
						309.3	19	36	10	16	4
Pyridafenthion	I	Organophosphate	$C_{14}H_{17}N_2O_4PS$	7.9	341.1	92.0	53	56	9	14	4
						65.0	91	56	9	14	4
Pyriproxyfen	IGR	Unclassified	$C_{20}H_{19}NO_3$	8.7	322.2	96.1	25	36	5	14	2
						77.9	79	36	5	14	4
Teflubenzuron	I	Benzoylurea	$C_{14}H_6Cl_2F_4N_2O_2$	3.5	378.9	195.9	−26	−25	−4	−38	−8
						338.9	−14	−25	−4	−38	−10
Thiabendazole	F	Benzimidazole	$C_{10}H_7N_3S$	7.0	202.3	175.1	37	61	12	12	6
						131.2	45	61	12	12	4
Thiacloprid	I	Neonicotinoid	$C_{10}H_9ClN_4S$	6.5	253.1	126.0	33	51	9	14	4
						98.9	59	51	9	14	4
Thiamethoxam	I	Neonicotinoid	$C_8H_{10}ClN_5O_3S$	0.6	292.2	211.2	21	31	12	18	8
						181.2	31	31	12	18	6
Thiometon	I/A	Organophosphate	$C_6H_{15}O_2PS_3$	7.4	246.9	89.2	19	21	8	14	0
						88.3	17	21	8	14	52
Thiophanate methyl	F	Benzimidazole	$C_{12}H_{14}N_4O_4S_2$	7.1	343.1	151.2	33	41	8	22	4
						117.9	75	41	8	22	4
Tolylfluanid	F	Sulphamide	$C_{10}H_{13}Cl_2FN_2O_2S_2$	8.2	364.2	238.0	21	46	3	20	6
						137.2	43	46	3	20	4
Triadimefon	F	Triazole	$C_{14}H_{16}ClN_3O_2$	7.9	294.3	197.2	21	36	9	24	6
						70.1	35	36	9	24	4
Triadimenol	F	Triazole	$C_{14}H_{18}ClN_3O_2$	7.9	296.3	70.1	25	21	5	20	2
						69.4	33	21	5	20	58
Triallate	H	Thiocarbamate	$C_{10}H_{16}Cl_3NOS$	8.7	304.0	142.8	39	36	8	14	4
						83.1	71	36	8	14	4
Trichlorfon	I	Organophosphate	$C_4H_8Cl_3O_4P$	4.4	256.9	108.9	25	36	9	14	4
						220.9	17	36	9	14	4
Trifloxystrobin	F	Strobilurin	$C_{20}H_{19}F_3N_2O_4$	8.3	409.1	185.9	27	36	8	22	4
						144.9	65	36	8	22	4
Triflumizole	F	Imidazole	$C_{15}H_{15}ClF_3N_3O$	8.4	347.0	278.7	17	21	5	20	12
						73.1	27	21	5	20	4

[a] A: acaricide; F: fungicide; GR: growth regulator; H: herbicide; IGR: insect growth regulator; I: insecticide; N: nematicide.

2.5. LC–MS/MS analysis

The LC–MS/MS system consisted of a Shimadzu Prominence/20 series (Shimadzu, Tokyo, Japan) apparatus (a LC-20 AD binary pump, a SIL-20 AHT autosampler, a DGU-20A3 online degasser and a CTO-10AS VPI column oven) coupled to an Applied Biosystems (Foster City, CA, USA) 3200 triple quadrupole tandem mass spectrometer equipped with a Turbo V electrospray ionisation (ESI) interface source. Nitrogen gas of 99% purity generated from a Peak Scientific nitrogen generator (Billerica, MA, USA) was used in the ESI source and the collision cell.

Chromatographic separation was performed at 30 °C on an Inertsil ODS-4 column (50 mm × 2.1 mm i.d., 3 μm particle size) supplied by GL Sciences Inc. (Tokyo, Japan) connected to a Fusion-RP guard column (4 mm × 2.0 mm i.d., 4 μm particle size) from Phenomenex (Torrance, CA, USA). Aliquots of 15 μl of sample extract or standards were injected into the column. A mobile phase consisting of eluants A (5 mM ammonium formate in water) and eluents B (5 mM ammonium formate in methanol) was used at a flow rate of 0.5 ml min^{-1}. A gradient elution was performed as follows: 0–8 min: 95% B; 8–12 min: 5% B.

The mass analyses were performed using an ESI source either in positive or negative mode. The following general MS parameters were employed: ion spray voltage 4.5 kV, source temperature 500 °C, curtain gas (nitrogen) 30 psi, ion source gas 1 40 psi, ion source gas 2 60 psi, collision gas (nitrogen) 5 psi. ESI-MS/MS was operated in scheduled multiple reaction monitoring mode (MRM) with monitoring of two precursor/products ion transitions for each target analyte. Both transitions were used for quantification and confirmation purposes. Analyst software version 1.6.1. (Concord, Ontario, Canada) was used for data acquisition and processing. Table 1 shows the retention times of pesticide residues and their fragments quantitatively and qualitatively used in MRM mode.

2.6. Method validation and quality control

The analytical method was validated on the basis of DG SANCO Guidelines (European Commission, 2011). The performance characteristics of the developed LC–MS/MS method including specificity and selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), method repeatability, within-laboratory reproducibility, uncertainity and method trueness in terms of recovery were evaluated by spiking experiments using pesticide-free tomato extract.

2.6.1. Specificity and selectivity

The specificity and selectivity of the method was tested through the analysis of fortified and non-fortified blank samples to evaluate possible interferences.

2.6.2. Linearity

Blank tomatoes were pretreated according to the optimised extraction and clean-up procedures described previously. To assess the linearity of the method, the tomato extracts from blank materials were spiked with multistandard solutions containing the 109 pesticides over a concentration range of 10–250 μg kg^{-1}. In total, 5 different concentrations were included and the analytical procedure was performed in triplicate at each concentration. The calibration curves were constructed by using the peak area of analytes at five different concentrations (10, 25, 50, 100 and 250 μg kg^{-1}) versus the corresponding concentrations in the matrix solution. Least-squares regression analysis was applied to determine equation of each calibration graph. The equation describing the calibration curve was $y = A(x) + B$, where y is the peak area of standard solution and x is the concentration of standard solution expressed in μg kg^{-1}. The coefficient of determination (R^2) value of >0.99 for each target analytes was acceptable.

2.6.3. LOD and LOQ

The LODs and LOQs of the analytical method were determined according to EURACHEM Guide as the minimum concentration of analyte in the spiked blank samples including SRM traces with a signal-to noise (S/N) ratio of 3 and 10, respectively (EURACHEM., 1998). Blank tomato extract were spiked with 10 μg kg^{-1} for each pesticides except for abamectin, alachlor, chlorfluazuron, chlorpyriphos methyl, clofentezine, diafenthiuron, dinocap, dithianon, hexaflumuron, iprodione, parathion methyl, phenthoate, tolyfluanid (25 μg kg^{-1}), and diflubenzuron and thiometon (50 μg kg^{-1}) and measured in 10 independent replicates. The LODs and LOQs were calculated using the following relations:

$$\mathrm{LOD} = X + 3s$$

$$\mathrm{LOQ} = X + 10s$$

in which, "X" is the mean concentration of spiked sample blank values, and "s" is the sample standard deviation.

2.6.4. Trueness

The closeness of an average to a true value, trueness, referred to as apparent recovery was evaluated by recovery experiment. Since tomato certified reference materials for the analysis of target pesticide residues are not available, artificially fortified pesticides-free ground tomato samples were analysed and the percent recovery was assessed. In detail, the recovery was calculated by the analysis of six representative blank samples spiked with target analytes at two concentration levels of 10 and 100 μg kg^{-1}. The observed signal was plotted against the actual concentration. The measured concentration was determined using the calibration curves and the recovery value was calculated by the following equation:

$$\%\ \text{recovery} = \frac{\text{measured concentration}}{\text{spiked(added)concentration}} \times 100 \quad (1)$$

2.6.5. Precision

The precision of the method refers to a combination of repeatability and reproducibility. The repeatability of the method was evaluated by six-replicated analysis of blank samples fortified with target analytes at two concentration levels (10 and 100 μg kg^{-1}) by single operator in one day. For the determination of within-laboratory reproducibility, two replicates at two different concentrations were analysed in 10 consecutive days by different operators. The precision was expressed as relative standard deviation (RSD) of replicate measurements.

2.6.6. Measurement uncertainty

The evaluation of uncertainty of analytical results is compulsory for laboratories accredited according to ISO/IEC17025 (ISO, 2005). While there are several proposed methods to calculate uncertainty of analytical methods, the expanded measurement uncertainty (U) was determined for all target analytes, according to procedures recommended by EURACHEM/CITAC Guide CG4 (Ellison, Rosselin, & Williams, 2000). The combined uncertainty (u_c) was determined taking into account the following uncertainty sources: mass (u_m), the volumetric equipments used ($\sum u_{vi}$), purity of standards (u_p), calibration curve (u_M) and mean recovery (u_R). The root sum squared method was used to calculate the combined uncertainty as shown in follows (Eq. (2)):

$$u_c = \sqrt{u_m^2 + \sum u_{vi}^2 + u_p^2 + u_M^2 + u_R^2} \quad (2)$$

Table 2
Method validation parameters of QuEChERS-LC–MS/MS method for determination of 109 target analytes in tomato.

Analyte	Linearity (μg kg^{-1})	Linear regression equation	R^2	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	Apparent recovery (%, n = 6)		Repeatability, %RSD, n = 6		Within-laboratory reproducibility, %RSD, n = 20		U, %
						10 μg kg^{-1}	100 μg kg^{-1}	10 μg kg^{-1}	100 μg kg^{-1}	10 μg kg^{-1}	100 μg kg^{-1}	
2,4-D	10–250	$y = 65672x - 9.1$	0.9998	1.9	4.9	85.8	89.6	11.0	11.1	9.6	12.4	18.2
Abamectin	10–250	$y = 49258x - 246.1$	0.9970	4.7	14.5	93.7	89.3	18.7	11.3	12.9	12.3	24.6
Acetamiprid	10–250	$y = 506.1x + 4423.2$	0.9998	1.0	2.6	98.0	88.8	13.4	13.0	19.6	15.6	23.4
Alachlor	10–250	$y = 61.1x + 128$	0.9997	4.8	14.5	104.5	88.8	11.0	9.6	12.3	11.6	23.7
Atrazine	10–250	$y = 197.4x + 276.3$	0.9982	1.4	3.8	91.8	96.6	10.7	10.8	9.6	12.0	23.5
Azinphos methyl	10–250	$y = 41.4x + 197.9$	0.9980	1.3	3.7	83.0	90.7	9.6	13.6	8.9	9.3	21.0
Azoxystrobin	10–250	$y = 828167x - 237.5$	0.9999	1.0	2.9	96.3	90.3	14.0	14.1	15.5	18.2	27.4
Bifenthrin	10–250	$y = 28656x - 191.4$	0.9909	1.9	5.5	92.8	85.4	16.7	14.1	9.6	11.8	24.6
Boscalid	10–250	$y = 133.2x + 323.8$	0.9999	1.5	4.6	101.8	83.1	8.5	13.3	12.4	11.5	21.6
Bromuconazole	10–250	$y = 76225x - 59.0$	0.9992	1.3	3.8	93.3	82.7	15.3	10.1	13.1	15.0	25.1
Bupirimate	10–250	$y = 369.8x - 1143.6$	0.9989	1.0	3.0	94.2	93.2	17.5	11.2	15.5	16.1	24.9
Buprofezin	10–250	$y = 988983x - 1327$	0.9976	1.6	4.5	85.8	90.4	14.6	4.4	9.8	11.2	18.1
Carbaryl	10–250	$y = 182x + 498.1$	0.9982	0.7	1.9	84.5	88.3	13.4	10.2	8.5	13.5	20.2
Carbendazim	10–250	$y = 300000x - 17450$	0.9952	1.2	3.3	103.3	90.9	18.7	11.0	9.6	19.2	30.4
Carbofuran	10–250	$y = 602621x - 220.8$	0.9998	1.1	3.2	97.5	87.2	10.0	13.8	8.9	11.9	22.2
Carboxin	10–250	$y = 668768x - 3260.2$	0.9916	0.9	2.6	98.5	93.9	16.2	13.9	8.5	11.5	25.3
Chlorfluazuron	10–250	$y = 55.5x - 427.9$	0.9928	5.6	17.0	102.2	90.2	13.0	14.0	8.3	13.5	24.8
Chlorpropham	10–250	$y = 30862x - 103.3$	0.9923	2.2	6.3	97.8	90.2	14.0	14.3	12.0	11.5	25.5
Chlorpyrifos ethyl	10–250	$y = 53.2x + 168.3$	0.9997	0.8	2.1	93.7	80.4	15.0	13.5	10.4	17.0	23.5
Chlorpyriphos methyl	10–250	$y = 81.9x + 237.7$	0.9999	5.0	14.5	92.7	81.7	17.1	9.8	13.7	11.3	23.1
Clofentezine	10–250	$y = 94191x - 242.6$	0.9992	5.0	15.0	86.8	83.9	16.3	10.0	16.8	11.8	22.5
Cycloate	10–250	$y = 106822x - 131$	0.9998	1.3	3.8	103.8	91.4	7.8	11.7	10.8	11.0	17.5
Cymoxanil	10–250	$y = 120.3x + 417.2$	0.9999	2.3	6.3	97.5	88.3	8.7	13.9	12.8	12.6	21.1
Cypermethrin	10–250	$y = 84882x - 81.1$	0.9998	3.0	8.6	103.5	89.9	12.5	14.2	7.9	10.5	23.7
Cyproconazole	10–250	$y = 165480x - 169.8$	0.9928	1.8	5.4	91.5	87.6	12.1	10.6	9.5	12.8	21.3
Cyprodinil	10–250	$y = 103805x - 394.4$	0.9983	1.3	4.1	91.0	94.0	15.7	7.3	11.5	14.6	25.5
Deltamethrin	10–250	$y = 17185x - 13.3$	0.9988	2.9	8.5	112.0	84.4	14.2	14.2	10.9	18.4	23.5
Diafenthiuron	10–250	$y = 98947x + 170$	0.9922	5.1	15.0	99.0	91.4	18.6	12.8	19.4	10.6	26.4
Diazinon	10–250	$y = 456575x - 552$	0.9998	0.8	2.5	98.5	90.4	13.3	13.5	10.2	12.3	20.5
Dichlofluanid	10–250	$y = 8.5x + 2.8$	0.9998	1.2	3.7	94.0	87.7	16.8	13.4	8.7	11.8	22.2
Dichlorvos	10–250	$y = 33124x - 4.2$	0.9983	1.3	3.8	103.3	90.1	9.9	13.5	7.5	10.2	25.8
Diethofencarb	10–250	$y = 250.9x + 1207.6$	0.9979	0.7	2.0	101.3	96.2	12.5	12.2	11.1	10.8	27.0
Difenoconazole	10–250	$y = 298542x - 211.4$	0.9999	1.7	5.0	94.7	92.4	16.9	11.2	13.0	13.5	28.0
Diflubenzuron	10–250	$y = 5562.5x - 37.4$	0.9947	10.1	28.8	83.3	82.4	17.7	9.0	13.4	12.2	18.5
Dimethoate	10–250	$y = 202.2x + 531.9$	0.9980	1.9	5.1	104.5	100.8	7.0	9.4	8.2	13.3	24.4
Dimethomorph	10–250	$y = 97x - 112.9$	0.9984	1.7	5.0	97.8	91.1	12.6	12.7	9.5	12.8	25.1
Diniconazole	10–250	$y = 175x - 110.4$	0.9999	1.5	4.2	92.7	88.1	17.7	12.2	11.7	11.5	23.0
Dinocap	10–250	$y = 2.8x + 3.1$	0.9999	5.8	17.0	87.5	90.3	19.2	13.6	9.1	12.2	32.7
Diphenamid	10–250	$y = 8607.1x - 41.5$	0.9973	3.1	8.1	95.5	84.4	15.4	14.8	16.0	13.0	24.5
Dithianon	10–250	$y = 65672x - 9.1$	0.9998	7.8	19.3	96.0	92.7	12.0	13.1	15.7	11.3	23.1
Diuron	10–250	$y = 76430x - 13.6$	0.9998	1.3	3.5	106.3	77.1	5.7	5.7	9.6	9.9	20.3
Epoxiconazole	10–250	$y = 215.8x + 627.8$	0.9999	2.2	6.3	101.3	89.2	12.2	11.8	11.5	10.9	22.5
Ethiofencarb	10–250	$y = 138.5x - 121.3$	0.9999	1.2	3.3	101.3	86.7	17.7	9.8	7.6	10.1	23.0
Ethofumesate	10–250	$y = 93294x - 310.6$	0.9913	1.4	4.2	99.2	91.6	14.1	13.4	7.1	12.6	26.5
Ethoprophos	10–250	$y = 216.9x + 285$	0.9981	1.7	5.0	106.0	93.0	14.1	13.1	11.9	14.0	28.6
Famoxadone	10–250	$y = 62293x - 79.6$	0.9997	2.3	6.7	88.3	86.7	17.0	12.0	11.2	11.1	26.4
Fenamiphos	10–250	$y = 622.4x + 509.3$	0.9997	0.6	1.9	92.2	92.8	11.0	7.8	12.6	11.8	14.7
Fenarimol	10–250	$y = 51953x - 306.5$	0.9961	2.6	7.9	92.3	86.7	15.8	5.8	13.1	10.6	21.8
Fenazaquin	10–250	$y = 100000x - 1646$	0.9996	0.9	3.0	108.8	89.8	8.2	9.5	11.0	9.9	19.7
Fenoxycarb	10–250	$y = 247.6x + 864.8$	0.9973	1.4	4.0	97.8	90.0	12.1	7.9	11.1	9.2	18.0
Fenpropathrin	10–250	$y = 127518x - 226.7$	0.9982	2.0	5.7	102.5	84.4	15.5	14.3	8.5	11.5	21.4
Fenpyroximate	10–250	$y = 260.8x + 1273.8$	0.9987	1.7	4.8	98.0	87.4	14.5	14.5	9.3	10.4	23.5

Fenthion	10–250	$y = 106246x - 454.8$	0.9909	2.0	6.0	93.2	89.4	18.9	9.2	10.2	17.0	24.8
Fluazifop-p-butyl	10–250	$y = 828.2x + 2055.4$	0.9997	0.8	2.2	99.0	89.5	16.7	9.0	9.6	11.2	23.9
Flutriafol	10–250	$y = 194.7x + 584.1$	0.9999	1.9	5.2	104.0	92.7	13.0	12.5	11.3	14.6	25.4
Formetanate	10–250	$y = 65672x - 9.1$	0.9998	1.3	3.8	93.3	89.0	15.4	5.4	7.5	11.4	20.1
Furathiocarb	10–250	$y = 808147x - 653.3$	0.9982	1.2	3.0	104.2	94.7	13.1	12.1	10.4	14.3	24.6
Hexaconazole	10–250	$y = 240x + 423.1$	0.9981	1.7	5.0	106.2	94.0	11.1	6.6	9.9	12.4	16.7
Hexaflumuron	10–250	$y = 22.8x + 12.8$	0.9999	5.4	16.4	99.7	89.1	19.0	10.3	11.4	11.9	26.4
Hexythiazox	10–250	$y = 105.1x + 319.6$	0.9997	0.8	2.3	100.5	83.3	14.9	14.3	10.0	10.2	21.2
Imazalil	10–250	$y = 261.2x + 52.6$	0.9998	1.9	5.5	102.3	92.5	14.8	5.9	12.5	10.9	22.2
Imidacloprid	10–250	$y = 50.2x + 39.5$	0.9985	1.0	2.7	107.2	91.5	13.0	13.0	14.0	13.0	25.4
Iprodione	10–250	$y = 26.1x - 34.1$	0.9986	6.2	18.1	101.8	85.3	18.2	9.0	10.0	9.4	24.8
Kresoxim methyl	10–250	$y = 112.5x - 125.6$	0.9998	0.9	2.8	104.3	87.9	14.2	10.9	14.3	10.5	20.9
Lufenuron	10–250	$y = 24.3x + 38.9$	0.9996	1.2	3.4	97.8	89.6	14.0	14.0	11.3	14.5	25.4
Malathion	10–250	$y = 235738x - 72$	0.9998	1.8	5.5	98.7	92.0	15.5	12.2	9.0	11.2	25.7
Metalaxyl	10–250	$y = 1128.3x - 81.5$	0.9999	0.5	1.3	93.7	89.8	12.5	12.8	13.4	16.0	23.1
Methidathion	10–250	$y = 224.5x + 486.2$	0.9979	1.8	5.1	101.5	89.9	12.5	12.3	10.3	13.0	21.2
Methomyl	10–250	$y = 88.9x + 253.6$	0.9979	1.2	3.0	103.5	93.3	12.0	12.4	13.1	12.8	26.3
Metolachlor	10–250	$y = 609.7x + 1275.9$	0.9985	0.7	2.1	89.0	85.2	15.1	11.4	11.6	10.9	18.4
Metribuzin	10–250	$y = 41.2x + 135$	0.9998	1.2	3.3	93.5	97.2	14.3	11.4	9.9	13.1	23.3
Monocrotophos	10–250	$y = 374.1x + 1396.8$	0.9938	1.8	4.6	108.7	90.0	11.9	10.2	11.3	9.7	19.2
Monolinuron	10–250	$y = 100.8x + 113.8$	0.9980	2.2	6.2	106.0	97.9	16.2	14.9	9.4	12.5	22.8
Myclobutanil	10–250	$y = 296825x - 450.1$	0.9986	1.3	3.8	101.7	86.5	14.3	14.3	9.4	10.6	19.2
Omethoate	10–250	$y = 128.8x - 518.3$	0.9959	1.4	3.7	104.8	86.3	16.3	7.3	10.8	10.7	22.5
Oxadixyl	10–250	$y = 65672x - 9.1$	0.9998	0.9	2.0	93.0	93.0	11.0	14.0	9.1	9.6	20.7
Oxamyl	10–250	$y = 899.3x - 890.9$	0,9994	2.3	6.3	104.3	87.3	8.7	11.5	10.9	12.0	20.4
Oxyfluorfen	10–250	$y = 25597x - 29.1$	0.9998	2.0	5.6	100.8	90.1	16.2	12.0	10.3	16.5	27.5
Parathion methyl	10–250	$y = 100000x - 149$	0.9979	5.6	16.1	99.8	90.8	12.0	12.0	9.0	12.1	29.6
Penconazole	10–250	$y = 388194x - 461$	0.9985	1.0	2.9	95.8	91.3	18.6	4.4	10.3	13.0	24.3
Pendimethalin	10–250	$y = 128284x + 247$	0.9996	2.3	6.7	100.7	90.5	10.9	8.3	10.9	10.3	19.1
Phenmedipham	10–250	$y = 391.8x + 1432$	0.9989	0.8	2.5	84.8	91.1	7.6	14.4	10.6	13.1	24.8
Phenthoate	10–250	$y = 198x + 273.4$	0.9994	4.9	14.7	95.0	86.3	15.7	13.6	14.9	11.1	23.4
Phosalone	10–250	$y = 124746x - 232$	0.9995	1.4	4.3	96.5	89.4	18.2	13.8	10.0	13.6	26.5
Pirimicarb	10–250	$y = 724644x - 659.2$	0.9996	1.1	2.9	106.2	95.5	14.2	12.1	8.7	13.0	25.4
Pirimiphos methyl	10–250	$y = 495853x - 798.6$	0.9996	1.3	4.1	92.8	93.8	18.8	6.4	13.5	11.1	23.6
Prochloraz	10–250	$y = 89.4x - 78.6$	0.9998	1.0	3.0	99.3	88.3	10.8	13.2	10.4	13.0	21.1
Profenofos	10–250	$y = 142.6x + 491.2$	0.9974	0.8	2.2	93.8	94.9	16.8	10.1	10.7	10.0	25.8
Propiconazole	10–250	$y = 393.4x + 87.7$	0.9998	1.9	5.5	97.0	94.9	13.3	5.4	15.2	15.1	20.2
Propyzamide	10–250	$y = 87460x - 212.2$	0.9958	2.1	6.1	101.2	91.2	13.9	12.6	9.5	11.4	23.2
Prothiofos	10–250	$y = 28078x - 55.9$	0.9984	1.7	5.2	113.2	88.6	12.2	14.1	9.6	15.2	20.2
Pyraclostrobin	10–250	$y = 600048x - 1784$	0.9957	0.8	2.6	94.3	86.2	13.5	10.6	11.5	15.3	18.3
Pyrazophos	10–250	$y = 861050x - 1096.9$	0.9993	0.8	2.2	101.7	87.4	11.4	9.5	15.2	15.5	20.9
Pyridaben	10–250	$y = 735188x - 931.4$	0.9990	1.4	4.5	104.2	94.3	9.3	9.7	10.1	11.8	18.8
Pyridafenthion	10–250	$y = 707.5x + 183.6$	0.9995	1.3	3.9	92.2	92.6	13.2	5.6	10.7	11.0	24.0
Pyriproxyfen	10–250	$y = 935771x + 3225.9$	0.9929	1.2	3.4	100.8	90.5	14.9	13.1	7.3	13.7	20.7
Teflubenzuron	10–250	$y = 31.9x + 387.5$	0.9970	1.3	4.0	81.8	95.0	13.4	12.7	10.0	9.8	24.9
Thiabendazole	10–250	$y = 774125x - 1097.6$	0.9983	0.6	1.8	100.2	84.9	11.1	13.5	12.1	14.8	22.6
Thiacloprid	10–250	$y = 546.4x + 2341.6$	0.9998	1.6	4.3	89.7	91.1	12.1	13.4	10.5	10.6	20.9
Thiamethoxam	10–250	$y = 138.4x + 1125$	0.9979	1.4	4.2	103.5	91.7	9.6	12.1	11.1	9.5	20.5
Thiometon	10–250	$y = 54130x - 231$	0.9957	10.8	30.4	92.5	86.1	17.6	14.0	12.5	11.4	24.9
Thiophanate methyl	10–250	$y = 340632x - 150.7$	0.9996	1.2	3.4	106.3	93.2	9.5	12.8	11.2	7.6	27.1
Tolylfluanid	10–250	$y = 17348x - 73.3$	0.9972	4.9	14.7	102.5	90.9	16.6	9.4	10.0	12.5	24.7
Triadimefon	10–250	$y = 271.8x + 359$	0.9999	1.3	3.7	106.2	81.9	14.5	10.8	8.5	11.1	19.7
Triadimenol	10–250	$y = 159.9x + 414$	0.9989	1.9	5.6	96.3	85.5	16.5	8.0	13.3	15.8	21.6
Triallate	10–250	$y = 43.2x - 55.4$	0.9997	1.1	3.2	96.5	95.2	18.2	12.8	9.6	9.3	27.0
Trichlorfon	10–250	$y = 187.2x + 2767.3$	0.9999	2.3	6.0	103.0	90.5	17.1	13.3	9.5	14.6	24.6
Trifloxystrobin	10–250	$y = 798x + 4074.9$	0.9995	0.7	2.0	93.8	91.5	12.4	12.4	14.7	14.0	21.2
Triflumizole	10–250	$y = 40.1x + 171.3$	0.9959	1.3	3.5	106.2	91.0	11.0	6.5	10.8	13.3	20.6

The expanded measurement uncertainty, U, was calculated by multiplying the combined uncertainty (u_c) by a coverage factor of $k = 2$, based on an approximate level of confidence of 95% (Eq. (3)).

$$U = 2 \times u_c \quad (3)$$

3. Results and discussion

3.1. Optimization of LC–MS/MS conditions

Optimization of triple-quadrupole MS/MS was performed via direct infusion of 100 μg kg^{-1} of each analyte in the mass spectrometer via a syringe pump at a flow rate of 10 μl min^{-1}, with a dwell time of 1 ms. The mass spectrometer was initially operated in full scan mode for selection of the parent ions (precursor ions), taking into account a compromise between selectivity and sensitivity. Two specific MRM transitions were selected for each pesticide after checking the fragmentation of each parent ion and the collision energy (CE) voltages were optimised for each selected transition. The optimization of the mass spectrometry parameters including CE, declustering potential (DP), entrance potential (EP), collision cell entrance potential (CEP), collision cell exit potential (CXP) values and the characteristic ion transition for each compound during MRM monitoring along with the chemical information for 109 pesticides are listed in Table 1.

3.2. Method validation

The QuEChERS-LC–MS/MS method used in this study was initially validated for the simultaneous determination of 109 pesticides in tomatoes according to DG SANCO Guidelines (European Commission, 2011). The validation parameters of the analytical method established from fortified blank tomato samples are summarised in Table 2.

The use of a triple quadrupole facilitates the correct identification of the analytes and leads to a further improvement of selectivity and specificity. The monitoring of two MRM transitions per analyte improves specificity. For a positive identification, the relative abundance of the MRM transitions signals were within 20–50% of the ratio obtained for the standards. In addition, the retention time of the analytes in the sample were below 2.5% of retention time in the standard. The specificity of the method was further confirmed by analysing many representative blank tomato samples (more than 20) over a 1 year period.

The linearity of the chromatographic response was evaluated by constructing calibration curves with standard solutions at five concentrations (10–250 μg kg^{-1}) in tomato extract. The calibration curves showed good linearity for all the analytes in related concentration ranges, with coefficient of determination (R^2) greater than 0.99.

Low LODs and LOQs were obtained for all target analytes in tomato matrix. The LODs were ranged from 0.5 to 10.8 μg kg^{-1}, whereas the LOQs were ranged from 1.3 to 30.4 μg kg^{-1}. The lowest LOD and LOQ corresponded to metalaxyl, while to highest to thiometon. These values are much smaller than MRLs established by the European Union for tomatoes.

Zhao et al. (2014) analysed 186 pesticide residues in tomato with GC–MS/MS after extraction with the QuEChERS method, and obtained LOD and LOQ values ranging from 0.2 to 3 μg kg^{-1} and from 1 to 10 μg kg^{-1}, respectively. In another study, Bakırcı and Hışıl (2012) used QuEChERS and LC–MS/MS method for the determination of 71 pesticides in vegetables and fruits, and obtained LOD and LOQ values in the range 0.12–2.16 μg kg^{-1}, and 0.40–7.21 μg kg^{-1}, respectively. Several methods for the analysis of pesticide residues in various food matrices have been used. However, no method has been previously reported for simultaneous analysis of all pesticides monitored in this study. Therefore, an LC–MS/MS method was validated for the determination of more than a hundred multiclass pesticides in matrix with high water content. The

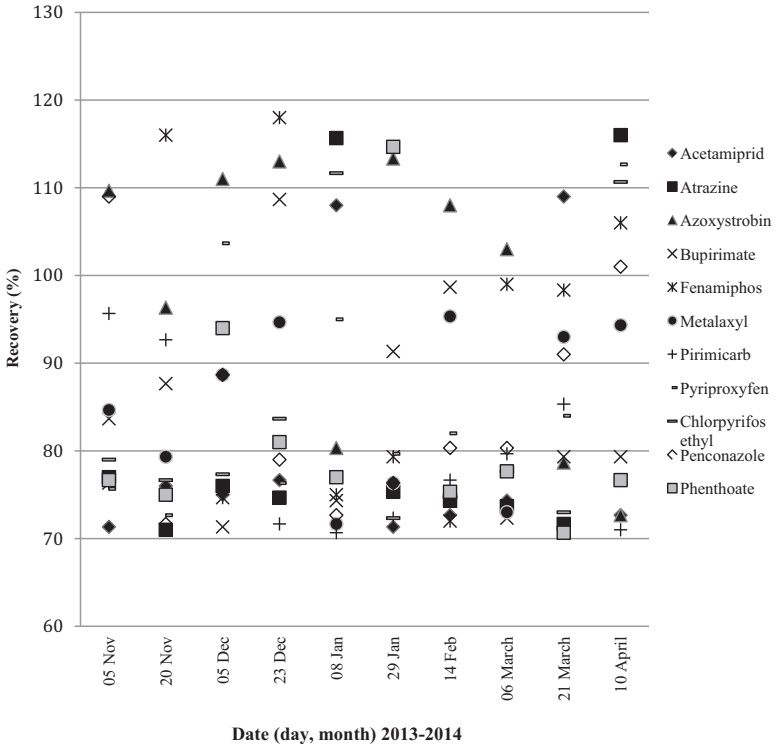


Fig. 1. Quality control chart, showing the recoveries of 11 target analytes from the control fortified samples. Each spot represents one data point.

MS parameters were initially performed by full-scan for the different class of compounds. The developed scan mode allowed determination of 109 pesticide residues in run time as short as 12 min.

Since there is no available reference material of target pesticides in tomatoes, the trueness and precision of the proposed method were carried out using fortified blank samples at two different levels. As shown in Table 2, the method gave satisfactory mean recoveries and precision for all target analytes. The apparent recoveries varied from 77.1% (for diuron) to 113.2% (for prothiofos). The RSD_r values under repeatability conditions (intraday, $n = 6$) were ranging from 4.4% to 19.2%, whereas the RSD_R under within-laboratory reproducibility conditions were ranging from 7.1 to 19.4%. These values fulfill the requirement of the DG-SANCO guideline. It is stated that recovery rate of 70–120%, and repeatability RSD_r and within-laboratory reproducibility $RSD_R \leqslant 20\%$ for pesticides is acceptable. In the original QuEChERS method, the amount of PSA sorbent was 25 mg per 1 ml of aliquot of acetonitrile layer. In our experiment, 50 mg of PSA was used per 1 ml of acetonitrile and good recoveries (more than 77%) could be obtained for different class of pesticides.

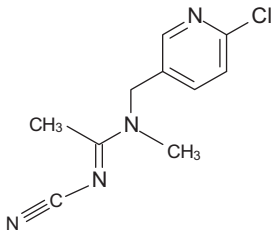
The uncertainty of measurements represents a quantitative indicator of the reliability of the analytical data and describes the range around a reported or experimental result within which the true value can be expected to lie within a defined probability (European Commission, 2011). The expanded measurement uncertainities were for all the pesticides between 14.7% and 30.4%. The recovery was the largest contribution to the measurement uncertainty. Other sources including mass, volumetric equipments, purity of standards and calibration curve provide small contribution in the uncertainty values.

The performance of the analytical method was also monitored for 11 pesticide residues (10% of target analytes) (acetamiprid, atrazine, azoxystrobin, bupirimate, chlorpyrifos ethyl, fenamiphos, metalaxyl, penconazole, phenthoate, pirimicarb, pyriproxyfen) over 6 months by means of quality control chart, representing the results obtained from the analysis of the control spiked samples (Fig. 1). The number of representative analytes fulfill the requirement of the DG-SANCO guideline. It is stated that the choice must include at least 10% of the representative analytes. As can be seen in Fig. 1, the analytical method was under control within the period of analysis and recoveries for 11 selected pesticides were within 70–120%.

3.3. Application of the method for the analysis of tomato samples

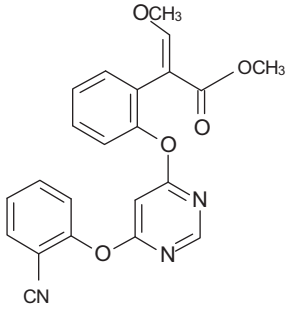
The optimised and validated method was applied to the analysis of real samples belong to the group of high water content commodities. Between January and December 2013, 345 tomato samples collected from local markets and tomato traders in the provinces of Mersin and Antalya, Turkey were analysed to assess 109 target analytes. In 312 out of 345 tomato samples (90.4%), none of the target analytes was detected at a level equal to or above the LODs. Of the 109 target analytes monitored, only three pesticides (acetamiprid, azoxystrobin and triadimefon) were detected at least once in samples in the concentration range 0.015–0.37 mg kg^{-1}. Chemical structures of the detected pesticides in tomato samples are illustrated in Fig. 2.

Acetamiprid was the most frequently detected pesticide (23 out of 345 samples, 6.7%) in tomato samples analysed, with levels ranging from 0.015 to 0.37 mg kg^{-1}. As the EU MRL and Codex MRL (CXL) for acetamiprid in tomatoes during the period investigated is 0.2 mg kg^{-1}, five samples exceeded the limit. Fig. 3 illustrates a LC–MS/MS chromatogram of the extract of tomato sample containing acetamiprid at a level of 0.23 μg kg^{-1}. Acetamiprid, which belongs to the group of neonicotinoid compounds, is used as insecticide to control *Hemiptera*, *Lepidoptera*, *Thysanoptera* and *Coleoptera*. It is applied in various fruiting vegetables including tomatoes, leafy vegetables, various fruits such as apricot, grapes, citrus fruits, pome fruits, and cotton and tree nuts etc. In mammals, acetamiprid caused generalised, nonspecific toxicity and did not appear to have specific target organ toxicity. The acceptable daily intake (ADI) and acute reference dose (ARfD) for acetamiprid is 0.07 and 0.1 mg kg^{-1} b.w, respectively (EFSA, 2013). Since tomato consumption in Turkey is 115 kg per year (i.e. 0.315 kg of tomato per day) (TUIK, 2012), and the average acetamiprid level is 0.008 mg kg^{-1}, the estimated daily intake of acetamiprid through tomatoes is 0.04 μg kg^{-1} b.w., which is well below (1750-fold) the value of ADI.



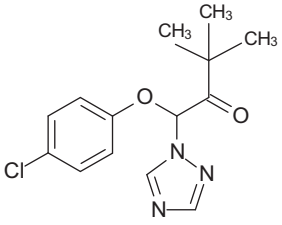
N-[(6-chloro-3-pyridyl)methyl]-N'-cyano-N-methyl-acetamidine

(A) Acetamiprid



(E)-4-hydroxy-3-[2-[6-(2-methylphenoxy)pyrimidin-4-yl]oxyphenyl]but-3-en-2-one

(B) Azoxystrobin



1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-one

(C) Triadimefon

Fig. 2. Structures of the detected pesticides in tomato samples.

Triadimefon was also simultaneously found in three samples (0.023–0.21 mg kg^{-1}), while the residue levels were below the EU MRL and CXL of 1 mg kg^{-1}. Triadimefon, systematic fungicide, is used to control rusts and powdery mildew on cereals, fruits and vegetables. It is classified by WHO as moderately toxic (Class III). According to the recent evaluation by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) in 2004, the ADI for triadimefon is 0–0.3 mg kg^{-1} b.w., while ARfD is 0.08 mg kg^{-1} b.w. (FAO, 2011).

Azoxystrobin was detected in 13 tomato samples (3.8%) at the concentrations ranged from 0.021 to 0.34 mg kg^{-1}. All samples showed levels of azoxystrobin below the EU MRL and CXL of

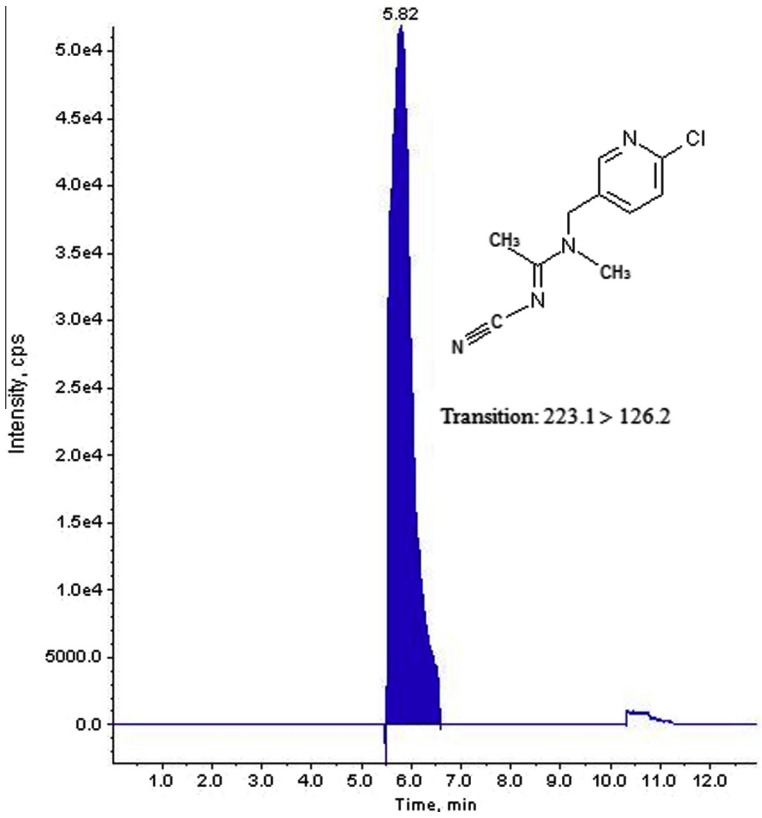


Fig. 3. LC–MS/MS chromatograms of the extract of tomato sample containing acetamiprid at a level of 0.23 μg kg^{-1}.

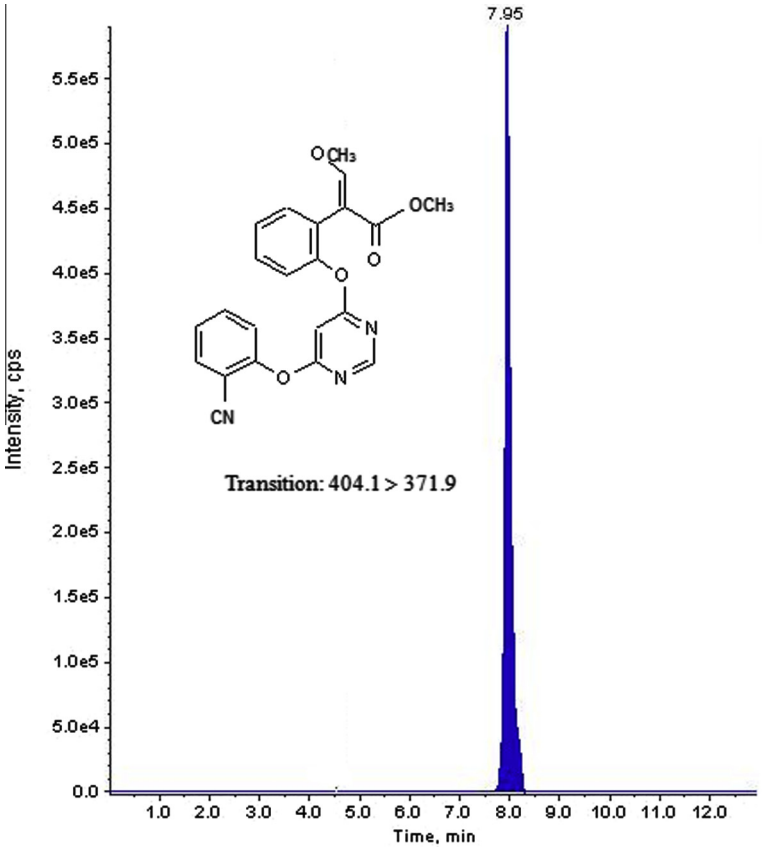


Fig. 4. LC–MS/MS chromatograms of the extract of tomato sample containing azoxystrobin at a level of 0.15 μg kg^{-1}.

3 mg kg^{-1} in tomatoes during the period of investigation. Fig. 4 shows a LC–MS/MS chromatogram of the extract of tomato sample containing azoxystrobin at a level of 0.15 μg kg^{-1}. Our data also showed that 3 samples simultaneously contained acetamiprid and azoxystrobin. Azoxystrobin is systematic, broad-spectrum fungicide belonging to the class of methoxyacrylates, which is used for the control of variety fungal diseases in agriculture/horticulture and viticulture. The major target organs in mammals are the liver and bile duct as shown by changes in body weights, histopathology and clinical chemistry parameters. The ADI of azoxystrobin is set at 0.2 mg kg^{-1} b.w., applying an assessment factor of 100, while no ARfD is allocated (EFSA, 2010). Based on the results obtained present study, the estimated daily intake of 0.02 μg kg^{-1} b.w. of azoxystrobin through the consumption of tomatoes is ten-thousand-fold below the ADI.

The results obtained present study are much lower than the previous observation by Kumari et al. (2012), who found several insecticides in 26 out of 75 tomato samples (35%) commercialised in India. In Portugal, twenty tomato samples were analysed for the monitoring 30 pesticide residues including azoxystrobin with dispersive liquid–liquid microextraction followed by GC–MS method. Six pesticides including azoxystrobin, trifloxystrobin, λ-cyhalothrin, fenhexamid, tolyfluanid and cyprodinil were detected in 23% of samples, but all values were below the EU MRLs (Melo et al., 2012). In a recent study by Zhao et al. (2014), 186 pesticides (including triadimefon) were monitored in tomato and tomato products (10 tomato, 5 tomato juice, and 5 ketchup samples) from China by GC–MS/MS method after multiplug filtration cleanup procedure. From the analytical results, triadimefon was not detected in none of the samples, while chlorpyrifos (1.6–8.1 μg kg^{-1}), procymidone (17–51 μg kg^{-1}), flucythrinate (5.6–8.7 μg kg^{-1}), and metalaxyl (2.3–11.2 μg kg^{-1}) were detected in six tomato samples.

4. Conclusions

A rapid and sensitive analytical method for the simultaneous determination of multiple pesticides in tomato was developed and validated. The modified QuEChERS-based sample preparation and subsequent quantification by LC–MS/MS method showed satisfactory specificity, linearity (R^2 > 0.99) and LOD/LOQ for selected 109 pesticides in tomato, with high precision (RSD < 20%, in all cases) and trueness values (77–113% in all cases). A total of 345 tomato samples were monitored using this validated method. While 106 pesticides were not detected in tomato samples analysed, acetamiprid was the most frequently detected (6.7%) pesticide, followed by azoxystrobin (3.8%). The developed method should potentially be applicable in other food matrixes belonging to the commodity group of high water content fruits and vegetables.

Acknowledgements

The authors have declared no conflict of interest.

References

Adou, K., Bontoyan, W. R., & Sweeney, P. J. (2001). Multiresidue method for the analysis of pesticide residues in fruits and vegetables by accelerated solvent extraction and capillary gas chromatography. *Journal of Agricultural and Food Chemistry, 49*, 4153–4160.

Anastassiades, M., Lehotay, S. J., Stajnbaher, D., & Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *Journal of AOAC International, 86*, 412–431.

AOAC International (Association of Official Analytical Chemists). (2007). Pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulphate. AOAC Official method 2007.01.

Bakırcı, G. T., & Hışıl, Y. (2012). Fast and simple extraction of pesticide residues in selected fruits and vegetables using tetrafluorethane and toluene followed by ultrahigh-performance liquid chromatography/tandem mass spectrometry. *Food Chemistry, 135*, 1901–1913.

Chen, X., Bian, Z., Hou, H., Yang, F., Liu, S., & Tang, G. (2013). Development and validation of a method for the determination of 159 pesticide residues in tobacco by gas chromatography–tandem mass spectrometry. *Journal of Agricultural and Food Chemistry, 61*, 5746–5757.

Cieślik, E., Sadowska-Rociek, A., Molina Ruiz, J. M., & Surma-Zadora, M. (2011). Evaluation of QuEChERS method for the determination of organochloride pesticide residues in selected groups of fruits. *Food Chemistry, 125*, 773–778.

Commission Regulation. (2009). Regulation No 1107/2009 of the European Parliament and of the Council of 21 October 2009. *Official Journal of the European Union, L309*, 1–49.

Correia, M., Delerue-Matos, C., & Alves, A. (2001). Development of a SPME-GC–ECD methodology for selected pesticides in must and wine samples. *Fresenius' Journal of Analytical Chemistry, 369*, 647–651.

EFSA. (2010). Conclusion on the peer review of the pesticide risk assessment of the active substance azoxystrobin. *The EFSA Journal, 8*, 1542.

EFSA. (2013). Reasoned opinion on the modification of the existing maximum residue level (MRL) for acetamiprid in apricots and tree nuts. *The EFSA Journal, 11*, 1–30.

Ellison, S. L. R., Rosselin, M., & Williams, A. (2000). Quantifying uncertainty in analytical measurement. EURACHEM/CITAC Guide CG 4, 1–120.

EURACHEM. (1998). *The fitness for purpose of analytical methods. A laboratory guide to method validation and related topics*. Middlesex, TW11 OLY. United Kingdom: EURACHEM Working Group.

European Commission. (2011). *Method validation and quality control procedures for pesticide residues analysis in food and feed*. Document No. SANCO/12495/2011. Available from <http://ec.europa.eu/food/plant/protection/pesticides/docs/qualcontrol_en.pdf> (cited 2014 Jan 13).

European Committee for Standardization/Technical Committee CEN/TC 275. (2007). *Determination of pesticides using GC–MS and/or LC–MS/MS following acetonitrile extraction/partitioning and cleanup by dispersive SPE-QuEChERS method*. European Committee for Standardization 2007, Brussels.

FAO. (2011). *FAO specifications and evaluations for triadimefon*. FAO specification 352/TC (p. 39).

FAO. (2012). *FAO statistical databases and data sets*. Available from <http://faostat.fao.org> (cited 2013 Dec 3).

Fenik, J., Tankiewicz, M., & Biziuk, M. (2011). Properties and determination of pesticides in fruits and vegetables. *Trends in Analytical Chemistry, 30*, 814–826.

Herrero Martín, S., García Pinto, C., Pérez Pavón, J. L., & Moreno Cordero, B. (2010). Determination of trihalomethanes in soil matrices by simplified quick, easy, cheap, effective, rugged and safe extraction and fast gas chromatography with electron capture detection. *Journal of Chromatography A, 1217*, 4883–4889.

ISO/IEC 17025:2005. (2005). *General requirements for the competence of testing and calibration laboratories*. Available from <http://www.iso.org> (cited 2013 Dec 11).

Iwafune, T., Ogino, T., & Watanabe, E. (2014). Water-based extraction and liquid chromatography–tandem mass spectrometry analysis of neonicotinoid insecticides and their metabolites in green pepper/tomato samples. *Journal of Agricultural and Food Chemistry, 62*, 2790–2796.

Juan-García, A., Picó, Y., & Font, G. (2005). Capillary electrophoresis for analyzing pesticides in fruits and vegetables using solid-phase extraction and stir-bar sorptive extraction. *Journal of Chromatography A, 1073*, 229–236.

Kumari, B. R., Rao, G. V. R., Sahrawat, K. L., & Rajasekhar, P. (2012). Occurrence of insecticide residues in selected crops and natural resources. *Bulletin of Environmental Contamination and Toxicology, 89*, 187–192.

Melo, A., Cunha, S. C., Mansilha, C., Aguiar, A., Pinho, O., & Ferreira, I. M. P. L. V. O. (2012). Monitoring pesticide residues in greenhouse tomato by combining acetonitrile-based extraction with dispersive liquid–liquid microextraction followed by gas-chromatography–mass spectrometry. *Food Chemistry, 135*, 1071–1077.

Park, J.-Y., Choi, J.-H., El-Aty, A. M. A., Kim, B. M., Oh, J.-H., Do, J.-A., et al. (2011). Simultaneous multiresidue analysis of 41 pesticide residues in cooked foodstuff using QuEChERS: Comparison with classical method. *Food Chemistry, 128*, 241–253.

Pittenger, D. R., Garrison, N. F., Geisel, P. M., & Unruh, C. L. (2005). *Growing tomatoes in the home garden* (vol. 8159). University of California Division of Agriculture and Natural Resources, ANR Publication, pp. 1–10.

Restrepo, A. R., Ortiz, A. F. G., Ossa, D. E. H., & Mesa, G. A. P. (2014). QuEChERS GC–MS validation and monitoring of pesticide residues in different foods in the tomato classification group. *Food Chemistry, 158*, 153–161.

Rissato, S. R., Galhaine, M. S., Knoll, F. R., & Apon, P. M. (2004). Supercritical fluid extraction for pesticide multiresidue analysis in honey: Determination by gas chromatography with electron-capture and mass spectrometry detection. *Journal of Chromatography A, 1048*, 153–159.

Singh, S. B., Foster, G. D., & Khan, S. U. (2004). Microwave-assisted extraction for the simultaneous determination of thiamethoxam, imidacloprid, and carbendazim residues in fresh and cooked vegetable samples. *Journal of Agricultural and Food Chemistry, 52*, 105–109.

TUIK (Turkish Statistical Institute). (2012). *The summary of agricultural statistics*. Available from <http://tuik.gov.tr> (cited 2014 Jan 23).

Ueno, E., Oshima, H., Saito, I., Matsumoto, H., Yoshimura, Y., & Nakazawa, H. (2004). Multiresidue analysis of pesticides in vegetables and fruits by gas chromatography/mass spectrometry after gel permeation chromatography and graphitized carbon column clean-up. *Journal of AOAC International, 87*, 1003–1015.

Valsamaki, V. I., Boti, V. I., Sakkas, V. A., & Albanis, T. A. (2006). Determination of organochlorine pesticides and polychlorinated biphenyls in chicken eggs by matrix solid phase dispersion. *Analytica Chimica Acta, 573–574*, 195–201.

Walorczyk, S., Drożdżyński, D., Kowalska, J., Remlein-Starosta, D., Ziółkowski, A., Przewoźniak, M., et al. (2013). Pesticide residues determination in Polish organic crops in 2007–2010 applying gas chromatography–tandem quadrupole mass spectrometry. *Food Chemistry, 139*, 482–487.

Wang, S., Wang, Z., Zhang, Y., Wang, J., & Guo, R. (2013). Pesticide residues in market foods in Shaanxi province of China in 2010. *Food Chemistry, 138*, 2016–2025.

WHO. (1992). *Our planet, our health*. Report of the WHO Commission on Health and Environment. Geneva, Switzerland: World Health Organisation

Wilkowska, A., & Biziuk, M. (2011). Determination of pesticide residues in food matrices using the QuEChERS methodology. *Food Chemistry, 125*, 803–812.

Xie, W., Han, C., Qian, Y., Ding, H., Chen, X., & Xi, J. (2011). Determination of neonicotinoid pesticide residues in agricultural samples by solid-phase extraction combined with liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A, 1218*, 4426–4433.

Zhao, P., Huang, B., Li, Y., Han, Y., Zou, N., Gu, K., et al. (2014). Rapid multiplug filtration cleanup with multiple-walled carbon nanotubes and gas chromatography–triple–quadrupole mass spectrometry detection for 186 pesticide residues in tomato and tomato products. *Journal of Agricultural and Food Chemistry, 62*, 3710–3725.