Determination of Pesticide Multiresidues in Apple, Pear and Grape using modified QuEChERS and analysis by LC-QTOF MS

Application Note

Authors

Renato Zanella, Juliana S. Munaretto, and Manoel L. Martins
Federal University of Santa Maria, Chemistry Department, Laboratory of Pesticides Residues Analysis
LARP, 97105-900, Santa Maria RS, Brazil

Daniela Daniel
Agilent Technologies, Inc.

Abstract

This application note describes an analytical method for the determination of pesticide residues in fruits using a modified QuEChERS method for extraction and analysis by liquid chromatography electrospray quadrupole time-of-flight mass spectrometry (LC-QTOF MS) system operating in full scan mode with automatic identification based on the use of accurate-mass databases. A total of 96 pesticides were analyzed in three different matrices: apple, pear, and grape. The method was validated in terms of recovery and reproducibility and showed good linearity (R^2>0.99) in a concentration range of 1.0 to 100 µg/L for the analytical curves prepared in solvent and in the respective matrix extract. The spiking levels for the recovery experiments were 0.01, 0.04, and 0.1 mg/kg. Mean recoveries ranged between 66.2 and 121.7% (93.1% on average), with RSD below 15.7% (5.1% on average). Average mass accuracy error was 0.87 ppm.

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Introduction

Analysis of pesticide residues is very important for the protection of human health and for trade and official control purposes. Many compounds have been used in agriculture and most of these substances have regulatory guidelines set, for example, Maximum Residue Levels (MRLs) in food and analytical methods, usually based on GC/MS or LC/MS/MS [1]. However, due to the need to detect illegal or misused compounds, it is necessary to extend the scope of the methods available. Considering the diversity of pesticides in use in modern agriculture, the use of LC/QTOF/MS is very useful for fast evaluation of the degree of contamination of samples either directly, or as initial screening for further quantification [2,3].

This application note used 96 pesticides for the development of screening strategies based on the use of full scan LC/ESI/TOF/MS and automated library-based detection using accurate mass databases.

Experimental

LC conditions

Instrument	Agilent 1260 Infinity Quaternary LC
Mobile phases	(A) H_2O/methanol 98:2 (v/v) (B) methanol Both solutions with 0.1% formic acid and 5 mmoL/L of ammonium formate

Gradient

Time (min)	%B
0.00	20
0.25	20
4.00	80
9.00	80
10.0	20
15.0	20

Flow rate	0.3 mL/min
Column	Agilent ZORBAX Eclipse Plus C18, 2.1 × 100 mm, 1.8 µm
Temperature	35 °C
Injection	5 µL

MS conditions

Instrument	Agilent 6530 LC/MS/TOF
Ion mode	ESI/Agilent Jet Stream, positive ionization
Capillary voltage	3,500 V
Drying gas (nitrogen)	10 L/min
Drying gas temperature	300 °C
Nozzle voltage	1,000 V
Fragmentor	175 V
Skimmer	65 V

Sample Extraction

Extraction of the pesticides from apple, pear, and grape was performed using the modified QuEChERS method in which 10.0 g of the sample was placed in a 50-mL PP tube followed by extraction using 10.0 mL of acetonitrile (containing 1% v/v of acetic acid). The partition step was performed by adding 4.0 g of anhydrous magnesium sulphate ($MgSO_4$) and 1.7 g of anhydrous sodium acetate (NaAc) with consecutive hand shaking for 1 minute and centrifugation for 8 minutes at 3,400 rpm. For the clean-up, 4 mL of the supernatant was inserted into a 15-mL PP tube containing 200 mg of PSA sorbent and 600 mg of $MgSO_4$, vortexed for 1 minute, and centrifuged for 8 minutes at 3,500 rpm. Then, 0.5 mL of the extract was transferred to a vial and diluted with 0.5 mL of mobile phase (1:1, v/v).

Results and Discussion

The accurate mass of each compound was calculated and saved as an Excel spreadsheet, which was used by MassHunter software as the library. After the initial screening of the pesticides in the blank sample extracts, the next step was to add a known concentration of pesticides standards to measure both retention time and find the experimental mass, which are parameters used in automatic searching. Table 1 shows the list of 96 pesticides used in the database for the search of pesticides in fruit extracts.

Table 1. Qualitative Method for 96 Pesticides with the Respective Retention Time (min), Molecular Formula and Calculated Mass

Compound	Retention time (min)	Molecular formula	Ion selected	*m/z* calculated
Acrinathrin	9.6	$C_{26}H_{21}NO_5F_6$	$[M+NH_4]+$	559.1660
Aldicarb	6.2	$C_7H_{14}N_2O_2S$	[M+Na]+	213.0670
Allethrin	9	$C_{19}H_{26}O_3$	[M+H]+	303.1955
Ametryn	7.4	$C_9H_{17}N_5S$	[M+H]+	228.1277
Aramite	8.9	$C_{15}H_{23}O_4SCl$	$[M+NH_4]+$	352.1340
Atrazine	7.3	$C_8H_{14}N_5Cl$	[M+H]+	216.1011
Azaconazole	7.4	$C_{12}H_{11}N_3O_2Cl_2$	[M+H]+	300.0301
Azamethiphos	6.6	$C_9H_{10}N_2O_5PSCl$	[M+H]+	324.9809
Azimsulfurom	7.3	$C_{13}H_{16}N_{10}O_5S$	[M+H]+	425.1099
Azoxystrobin	7.5	$C_{22}H_{17}N_3O_5$	[M+H]+	404.1241
Benfuracarb	8.7	$C_{20}H_{30}N_2O_5S$	[M+H]+	411.1948
Boscalid	7.7	$C_{18}H_{12}N_2OCl_2$	[M+H]+	343.0399
Buprofezin	8.4	$C_{16}H_{23}N_3OS$	[M+H]+	306.1635
Carbendazim	3.2	$C_9H_9N_3O_2$	[M+H]+	192.0768
Carbophenothion	9.3	$C_{11}H_{16}O_2PS_3Cl$	[M+H]+	342.9811
Carbofuran	6.8	$C_{12}H_{15}NO_3$	[M+H]+	222.1125
Carbofuran-3-hidroxy	5.4	$C_{12}H_{15}NO_4$	[M+H]+	238.1074
Carboxin	7	$C_{12}H_{13}NO_2S$	[M+H]+	236.0740
Cyanazine	6.5	$C_9H_{13}N_6Cl$	[M+H]+	241.0963
Clomazone	7.5	$C_{12}H_{14}NO_2Cl$	[M+H]+	240.0786
Clothianidin	5	$C_6H_8N_5O_2SCl$	[M+H]+	250.0160
Deltamethrin	9.5	$C_{22}H_{19}NO_3Br_2$	$[M+NH_4]+$	521.0070
Desmedipham	7.4	$C_{16}H_{16}N_2O_4$	$[M+NH_4]+$	318.1450
Diazinon	8.3	$C_{12}H_{21}N_2O_3PS$	[M+H]+	305.1083
Dicrotophos	4.7	$C_8H_{16}NO_5P$	[M+H]+	238.0839
Difenoconazole	8.4	$C_{19}H_{17}N_3O_3Cl_2$	[M+H]+	406.0720

Table 1. Qualitative Method for 96 Pesticides with the Respective Retention Time (min), Molecular Formula and Calculated Mass (continued)

Compound	Retention time (min)	Molecular formula	Ion selected	*m/z* calculated
Diuron	7.4	$C_9H_{10}N_2OCl_2$	[M+H]+	233.0243
Dodemorph	7.3	$C_{18}H_{35}NO$	[M+H]+	282.2791
Epoxiconazole	8.0	$C_{17}H_{13}N_3OClF$	[M+H]+	330.0804
Ethion	9.0	$C_9H_{22}O_4P_2S_4$	[M+H]+	384.9949
Etofenprox	10.6	$C_{25}H_{28}O_3$	[M+NH_4]+	394.2380
Fenpyroximate-(E)	9.5	$C_{24}H_{27}N_3O_4$	[M+H]+	422.2074
Fenpropimorph	7.5	$C_{20}H_{33}NO$	[M+H]+	304.2635
Fenamidone	8.4	$C_{17}H_{17}N_3OS$	[M+NH_4]+	329.1430
Fenazaquin	9.9	$C_{20}H_{22}N_2O$	[M+H]+	307.1805
Fenthion-sulfoxide	6.9	$C_{10}H_{15}O_4PS_2$	[M+H]+	295.0222
Fluazifop-p-buthyl	8.7	$C_{19}H_{20}NO_4F_3$	[M+H]+	384.1417
Flutolanil	7.7	$C_{17}H_{16}NO_2F_3$	[M+H]+	324.1206
Phosmet	7.5	$C_{11}H_{12}NO_4PS_2$	[M+H]+	318.0018
Fosthiazate	7.1	$C_9H_{18}NO_3PS_2$	[M+H]+	284.0538
Furathiocarb	8.8	$C_{18}H_{26}N_2O_5S$	[M+H]+	383.1635
Hexythiazox	9.1	$C_{17}H_{21}N_2O_2SCl$	[M+H]+	353.1085
Imazalil	7.1	$C_{14}H_{14}N_2OCl_2$	[M+H]+	297.0556
Imidacloprid	5.0	$C_9H_{10}N_5O_2Cl$	[M+H]+	256.0596
Indoxacarb	8.4	$C_{22}H_{17}N_3O_7ClF_3$	[M+H]+	528.0780
Linurom	7.6	$C_9H_{10}N_2O_2Cl_2$	[M+H]+	249.0192
Malathion	7.8	$C_{10}H_{19}O_6PS_2$	[M+H]+	331.0433
Mecarbam	7.9	$C_{10}H_{20}NO_5PS_2$	[M+Na]+	352.0410
Mephosfolan	6.6	$C_8H_{16}NO_3PS_2$	[M+H]+	270.0382
Metalaxyl	7.3	$C_{15}H_{21}NO_4$	[M+H]+	280.1543
Methidathion	7.4	$C_6H_{11}N_2O_4PS_3$	[M+H]+	302.9691
Methiocarb sulfone	4.8	$C_{11}H_{15}NO_4S$	[M+H]+	258.0795
Methiocarb sulfoxide	5.2	$C_{11}H_{15}NO_3S$	[M+H]+	242.0845
Metobromuron	7.2	$C_9H_{11}N_2O_2Br$	[M+H]+	259.0077
Methomyl	7.0	$C_5H_{10}N_2O_2S$	[M+H]+	163.0536
Metoxuron	6.3	$C_{10}H_{13}N_2O_2Cl$	[M+H]+	229.0738
Monesine	10.5	$C_{36}H_{61}O_{11}$	[M+H]+	693.4184
Monocrotophos	4.1	$C_7H_{14}NO_5P$	[M+H]+	224.0682
Monolinuron	7.1	$C_9H_{11}N_2O_2Cl$	[M+H]+	215.0582
Omethoate	1.4	$C_5H_{12}NO_4PS$	[M+H]+	214.0297
Oxadixyl	6.4	$C_{14}H_{18}N_2O_4$	[M+H]+	279.1339

Table 1. Qualitative Method for 96 Pesticides with the Respective Retention Time (min), Molecular Formula and Calculated Mass (continued)

Compound	Retention time (min)	Molecular formula	Ion selected	*m/z* calculated
Oxamyl	2.1	$C_7H_{13}N_3O_3S$	[M+Na]+	242.0570
Oxyfluorfen	8.7	$C_{15}H_{11}NO_4ClF_3$	[M+H]+	362.0401
Paraoxon	7.2	$C_{10}H_{14}NO_6P$	[M+H]+	276.0632
Pencycuron	8.4	$C_{19}H_{21}N_2OCl$	[M+H]+	329.1415
Piperonyl butoxide	9.0	$C_{19}H_{30}O_5$	[M+NH_4]+	356.2430
Pyraclostrobin	8.3	$C_{19}H_{18}N_3O_4Cl$	[M+H]+	388.1059
Pyrazophos	8.4	$C_{14}H_{20}N_3O_5PS$	[M+H]+	374.0934
Pyrazosulfuron-ethyl	7.7	$C_{14}H_{18}N_6O_7S$	[M+H]+	415.1030
Pyridan	9.8	$C_{19}H_{25}N_2OSCl$	[M+H]+	365.1449
Pyridaphenthion	7.8	$C_{14}H_{17}N_2O_4PS$	[M+H]+	341.0719
Piridate	10.2	$C_{19}H_{23}N_2O_2SCl$	[M+H]+	379.1242
Pyrimethanil	7.5	$C_{12}H_{13}N_3$	[M+H]+	200.1182
Pyrimicarbe	6.4	$C_{11}H_{18}N_4O_2$	[M+H]+	239.1503
Pyrimiphos-ethyl	8.9	$C_{13}H_{24}N_3O_3PS$	[M+H]+	334.1349
Profenofos	8.8	$C_{11}H_{15}O_3PSClBr$	[M+H]+	372.9424
Profoxydim	8.6	$C_{24}H_{32}NO_4SCl$	[M+H]+	466.1813
Propanil	7.6	$C_9H_9NOCl_2$	[M+H]+	218.0134
Propargite	9.3	$C_{19}H_{26}O_4S$	[M+NH_4]+	368.1890
Prothiofos	9.9	$C_{11}H_{15}O_2PS_2Cl_2$	[M+H]+	344.9701
Quinoxyfen	9.1	$C_{15}H_8NOCl_2F$	[M+H]+	308.0040
Simazine	6.8	$C_7H_{12}N_5Cl$	[M+H]+	202.0854
Spinosad	8.2	$C_{41}H_{65}NO_{10}$	[M+H]+	732.4681
Tebufenpyrad	8.8	$C_{18}H_{24}N_3OCl$	[M+H]+	334.1681
Terbuthylazine	7.7	$C_9H_{16}N_5Cl$	[M+H]+	230.1167
Thiabendazole	4.7	$C_{10}H_7N_3S$	[M+H]+	202.0433
Thiacloprid	5.9	$C_{10}H_9N_4SCl$	[M+H]+	253.0309
Thiamethoxam	3.2	$C_8H_{10}N_5O_3SCl$	[M+H]+	292.0266
Thiodicarb	7.0	$C_{10}H_{18}N_4O_4S_3$	[M+H]+	355.0563
Thiophanate-methyl	6.7	$C_{12}H_{14}N_4O_4S_2$	[M+H]+	343.0529
Triasulfuron	6.6	$C_{14}H_{16}N_5O_5SCl$	[M+H]+	402.0633
Tricyclazole	6.1	$C_9H_7N_3S$	[M+H]+	190.0433
Trichlorphon	5.3	$C_4H_8O_4PCl_3$	[M+H]+	256.9299
Trifloxystrobin	8.5	$C_{20}H_{19}N_2O_4F_3$	[M+H]+	409.1370
Triflumuron	8.3	$C_{15}H_{10}N_2O_3ClF_3$	[M+H]+	359.0405
Vamidothion	5.4	$C_8H_{18}NO_4PS_2$	[M+H]+	288.0488

Figure 1 shows a chromatogram and spectrum obtained from this search using deltamethrin as an example. In Figure 2, it is possible to observe the chromatograms in full scan mode with the compounds identified by software identification.

The quantitative determination was performed by MassHunter Quantitative software B.05.01 for all 96 compounds in the full scan mode. The linearity of the analytical curve was studied using matrix-matched pesticide standard solutions in seven concentrations ranging between 1.0 to 100.0 µg/L. The response function was found to be linear with a coefficient of determination (R^2) values higher than 0.99. Figure 3 shows the example of the response for amethrine in pear. For some compounds, the more concentrated level was 50.0 µg/L due to the saturation of the detector at 100.0 µg/L caused by the high concentration of ions formed in the ion source. Figure 3 also shows the excellent mass accuracy during all the linear range, each is demonstrated by the number at the top of the peaks.

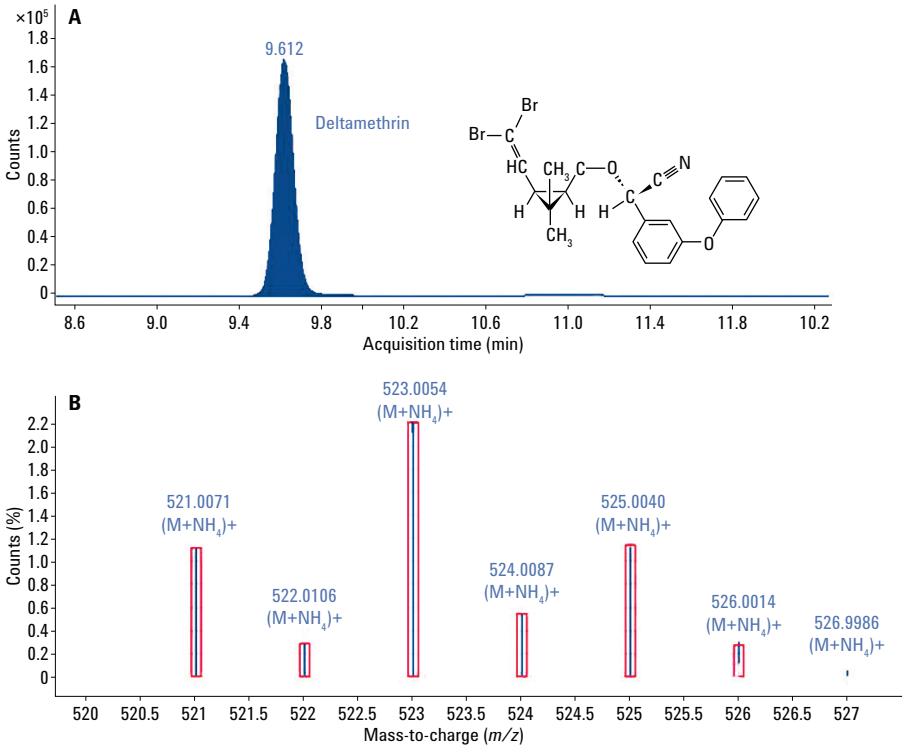

Figure 1. Chromatogram (A) and spectrum (B) of deltamethrin obtained by LC/QTOF/MS. The spectrum of the sample (blue) compared with the library (red).

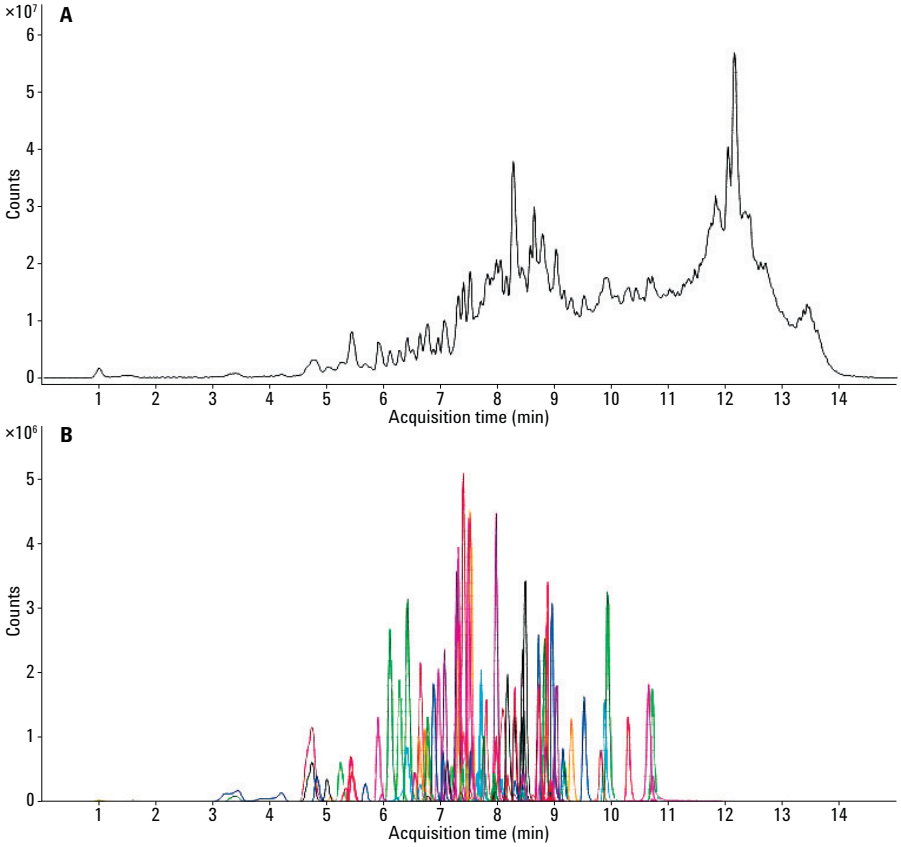

*Figure 2. (**A**) Full scan LC/QTOF/MS chromatogram of the 96 mixture compounds in acetonitrile and (**B**) chromatogram of all the compounds identified using the Qualitative MassHunter software.*

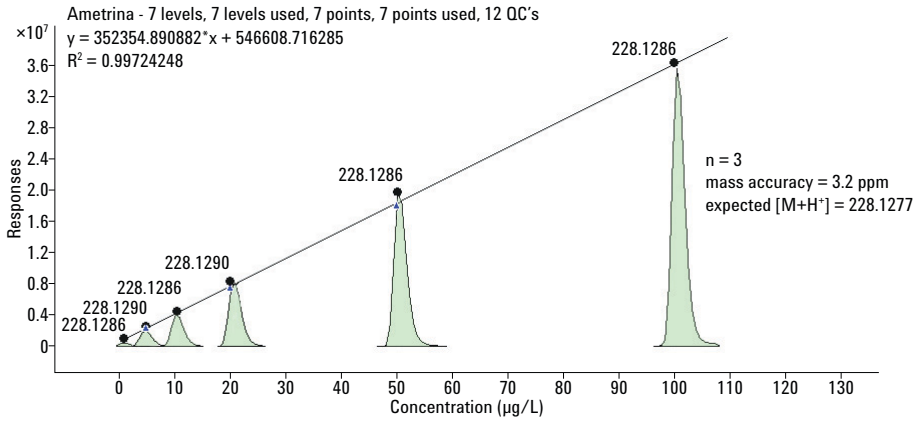

Figure 3. Linearity of the response for amethrine in pear using matrix-matched standard solutions.

Method accuracy and precision data were obtained for all pesticides spiked at concentrations of 0.01, 0.04, and 0.1 mg/kg in apple, pear, and grape. Table 2 summarizes the linear range in solvent, and in the matrix extract, method Limits of Quantification (LOQ) and the averages of the results.

The average mass accuracy error was 0.87 ppm. The LOQ were considered as being the lowest level of concentration spiked, with acceptable recovery and precision, of each compound in each matrix, with values between 0.01 and 0.04 mg/kg. Values of Limits of Detection (LOD) were calculated as the LOQ value divided by 3.33, resulting in the concentrations between 0.03 to 0.012 mg/kg. These obtained amounts were appropriate since they comply with the international legislation for the Maximum Residues Limit (MRL).

Table 2. Linear Range in Solvent and in the Matrix Extract, LOQ and the Averages (n=3) of Recovery (%), Relative Standard Deviations - RSD (%), Mass Accuracy Obtained by LC-QTOF-MS Analysis of Pear, Apple, and Grape

		Apple					Pear					Grape				
Pesticides	**Linear range (solvent) µg/L**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**
Acrinathrin	1 – 100	5 - 100	0.04	98.1	12.6	1.7	1 - 50	0.04	72.4	15.7	1.5	1 - 50	0.04	104.4	21.9	1.3
Aldicarb	1 – 100	1 - 100	0.01	92.8	2.2	2.3	1 - 100	0.01	93.0	4.0	1.2	2 - 100	0.01	93.6	4.8	3.9
Allethrin	1 – 100	5 - 100	0.01	99.0	6.6	3.3	1 - 100	0.01	97.1	10.2	2.0	1 - 100	0.01	95.5	11.2	0.8
Ametryn	1 – 100	2 - 100	0.01	95.0	1.4	1.8	1 - 100	0.01	93.9	3.3	1.4	1 - 100	0.01	92.8	3.3	0.7
Aramite	1 – 100	1 - 100	0.01	94.6	7.9	1.9	1 - 100	0.01	91.7	9.8	2.6	1 - 100	0.01	89.6	11.7	2.3
Atrazine	2 – 50	2 - 50	0.01	98.2	1.7	3.1	2 - 50	0.01	97.9	2.1	3.5	2 - 50	0.01	97.8	1.6	5.0
Azaconazole	1 – 50	1 - 50	0.01	96.3	2.4	1.9	1 - 50	0.01	98.3	2.5	1.3	1 - 50	0.01	106.8	2.7	0.9
Azamethiphos	1 – 100	1 - 100	0.01	93.5	2.8	-1.5	1 - 100	0.01	91.6	8.4	-3.6	1 - 100	0.01	92.2	3.6	-1.5
Azimsulfurom	1 – 100	2 - 100	0.04	66.8	1.3	-0.6	1 - 100	0.01	66.2	3.6	-3.8	1 - 100	0.01	93.1	5.6	-3.2
Azoxystrobin	1 – 100	1 - 100	0.01	97.0	2.4	-0.7	1 - 100	0.01	98.9	3.3	0.2	1 - 100	0.01	94.7	3.6	-0.2
Benfuracarb	1 – 100	1 - 100	0.01	77.5	2.0	2.4	1 - 100	0.01	76.3	2.8	2.6	1 - 100	0.01	76.6	12.7	3.5
Boscalid	1 – 100	2 - 100	0.01	94.7	1.7	0.9	1 - 100	0.01	96.1	5.2	2.5	1 - 100	0.01	94.3	4.5	2.8
Buprofezin	1 – 50	1 - 100	0.01	90.7	2.5	-0.4	1 - 100	0.01	91.4	5.1	-0.5	1 - 100	0.01	89.0	4.1	-0.6
Carbendazim	2 – 100	1 - 100	0.01	96.6	3.8	-0.8	1 - 50	0.04	106.3	3.1	-1.0	1 - 100	-----	-----	-----	-----
Carbophenothion	1 – 100	1 - 100	0.01	93.2	4.5	-0.1	1 - 100	0.01	89.0	14.4	0.3	1 - 50	0.01	81.3	6.3	0.7
Carbofuran	1 – 100	1 - 100	0.01	100.6	2.0	-0.3	1 - 100	0.01	96.0	4.6	-2.8	1 - 100	0.01	91.9	3.2	-0.4
Carbofuran-3-hidroxy	1 – 100	1 - 100	0.01	96.0	6.3	-0.6	1 - 100	0.01	96.5	11.4	-3.9	1 - 100	0.01	84.1	3.2	0.6
Carboxin	1 – 100	1 - 100	0.01	91.3	2.9	0.6	1 - 100	0.01	89.5	2.2	0.6	1 - 100	0.01	83.9	6.1	0.7
Cyanazine	1 – 100	1 - 100	0.01	100.5	0.6	1.9	1 - 100	0.01	105.2	4.4	-1.2	1 - 100	0.01	121.7	3.0	1.7
Clomazone	1 – 50	1 - 50	0.01	95.5	1.9	1.1	1 - 100	0.01	97.3	3.8	2.8	1 - 50	0.01	92.9	3.5	2.1
Clothianidin	1 – 100	1 - 100	0.01	96.6	2.3	-0.3	1 - 100	0.01	98.8	2.5	-1.5	1 - 100	0.01	98.0	4.1	-0.6
Deltamethrin	1 – 100	1 - 50	0.01	94.9	17.4	0.8	1 - 50	-----	-----	-----	-----	1 - 100	0.01	91.1	19.5	2.2
Desmedipham	1 – 100	1 - 100	0.01	93.5	2.8	2.7	1 - 100	0.01	91.3	2.6	0.4	1 - 100	0.01	96.1	4.0	1.3
Diazinon	1 – 100	2 - 100	0.04	102.7	11.1	4.8	2 - 100	0.01	87.2	13.6	4.3	1 - 100	0.04	99.4	9.4	3.5
Dicrotophos	1 – 100	1 - 100	0.01	93.4	1.2	0.7	1 - 100	0.01	77.7	14.6	0.3	1 - 100	0.01	93.6	3.2	2.3
Difenoconazole	1 – 100	1 - 50	0.04	91.0	7.7	2.7	1 - 100	0.01	111.3	5.3	4.3	1 - 50	0.01	89.5	7.1	5.7
Diuron	1 – 50	1 - 50	0.01	95.5	2.5	-0.5	1 - 50	0.01	93.1	3.1	-0.8	1 - 50	0.01	96.0	2.7	-1.3
Dodemorph	1 – 100	1 - 100	0.01	94.8	2.8	0.9	1 - 100	0.01	90.3	2.0	0.5	1 - 100	0.01	94.0	3.8	0.6

Table 2. Linear Range in Solvent and in the Matrix Extract, LOQ and the Averages (n=3) of Recovery (%), Relative Standard Deviations - RSD (%), Mass Accuracy Obtained by LC-QTOF-MS Analysis of Pear, Apple, and Grape (continued)

		Apple					Pear					Grape				
Pesticides	**Linear range (solvent) µg/L**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**
Epoxiconazole	1 – 100	1 - 50	0.01	94.7	8.3	-2.7	1 - 50	0.01	92.4	5.3	-2.3	1 - 50	0.01	98.7	4.0	-2.3
Ethion	1 – 100	1 - 100	0.01	95.7	2.6	1.0	1 - 100	0.01	88.4	4.0	0.9	1 - 100	0.01	89.8	4.7	0.8
Etofenprox	1 – 100	1 - 100	0.01	91.1	2.7	2.4	1 - 100	0.01	91.1	4.6	2.5	1 - 100	0.01	89.3	4.6	2.5
Fenpyroximate-(E)	1 – 100	2 - 100	0.01	98.1	2.4	4.3	1 - 100	0.01	91.9	1.7	3.8	1 - 100	0.01	95.0	2.8	3.7
Fenpropimorph	1 – 100	1 - 100	0.01	95.2	2.1	0.4	1 - 100	0.01	90.5	1.9	0.8	1 - 100	0.01	92.9	3.8	0.5
Fenamidone	1 – 50	1 - 50	0.04	92.5	7.7	-2.3	1 - 100	0.01	109.6	7.7	1.2	1 - 50	0.01	85.8	10.5	3.1
Fenazaquin	1 – 100	1 - 100	0.01	91.0	3.3	-1.3	1 - 100	0.01	87.5	3.9	0.3	1 - 100	0.01	88.0	4.5	0.1
Fenthion-sulfoxide	1 – 100	1 - 100	0.01	95.4	1.4	-1.0	1 - 100	0.01	93.7	2.5	-1.3	1 - 100	0.01	100.2	2.2	-1.0
Fluazifop-p-buthyl	1 – 100	1 - 100	0.01	97.4	5.2	-0.8	1 - 100	0.01	85.2	4.4	-1.2	1 - 100	0.01	90.7	5.4	-0.9
Flutolanil	1 – 100	1 - 50	0.01	98.3	1.3	1.5	1 - 50	0.01	92.5	2.1	1.7	1 - 100	0.01	94.3	3.3	1.2
Phosmet	1 – 100	1 - 50	0.01	95.1	2.4	2.2	1 - 50	0.01	92.0	4.3	3.8	1 - 50	0.01	94.5	4.4	3.7
Fosthiazate	1 – 100	1 - 100	0.01	96.4	1.8	1.5	1 - 100	0.01	91.9	1.3	2.3	1 - 100	0.01	95.5	4.2	1.8
Furathiocarb	1 – 100	1 - 100	0.01	95.3	2.6	-0.1	1 - 100	0.01	87.6	3.1	-0.1	1 - 100	0.01	89.8	3.0	0.0
Hexythiazox	1 – 100	2 - 100	0.01	93.0	3.7	3.3	2 - 100	0.01	93.7	5.6	3.9	1 - 100	0.01	91.0	3.5	3.3
Imazalil	1 – 100	1 - 100	0.01	99.0	4.0	-0.4	1 - 100	0.01	87.7	7.1	0.3	1 - 100	0.01	92.3	3.5	0.0
Imidacloprid	1 – 100	1 - 100	0.01	97.7	3.6	0.0	1 - 100	0.01	95.1	3.9	-0.9	1 - 100	0.01	97.7	3.2	-0.1
Indoxacarb	1 – 100	1 - 100	0.01	98.6	5.2	2.8	1 - 100	0.01	94.6	5.6	3.5	1 - 100	0.01	99.1	3.2	4.1
Linurom	1 – 100	1 - 50	-----	-----	-----	-----	1 - 100	0.01	93.3	13.4	4.2	1 - 50	0.04	89.4	11.5	4.2
Malathion	1 – 50	1 - 50	0.01	96.6	3.0	3.8	1 - 50	0.01	98.6	9.8	2.6	1 - 100	0.01	95.1	4.8	-0.1
Mecarbam	1 – 50	1 - 50	-----	-----	-----	-----	1 - 50	0.01	86.4	5.0	2.1	1 - 50	0.01	82.8	6.7	1.5
Mephosfolan	1 – 100	1 - 100	0.01	93.1	4.5	-0.9	1 - 100	0.01	83.3	12.3	-3.5	1 - 100	0.01	87.9	3.7	-1.1
Metalaxyl	1 – 100	1 - 50	0.01	97.1	2.5	2.7	1 - 50	0.01	95.7	6.2	3.2	1 - 100	0.01	96.8	3.5	2.9
Methidathion	1 – 100	1 - 50	0.01	86.2	4.0	2.3	1 - 50	0.01	93.1	8.3	1.6	1 - 100	0.01	94.7	5.3	1.3
Methiocarb sulfone	1 – 100	1 - 100	0.01	93.6	1.7	-0.2	1 - 100	0.01	89.9	1.1	-0.4	1 - 100	0.01	94.4	2.9	0.5
Methiocarb sulfoxide	1 – 100	1 - 100	0.01	92.8	2.3	-0.6	1 - 100	0.01	90.7	3.8	-3.5	1 - 100	0.01	93.5	2.7	-0.4
Metobromuron	1 – 100	1 - 100	0.01	91.6	3.0	1.6	1 - 100	0.01	93.2	5.6	1.5	1 - 100	0.01	96.3	4.3	1.2
Methomyl	2 – 100	5 - 100	0.04	105.48	2.76	2.52	1 - 100	0.01	100.4	4.6	2.2	1 - 100	0.01	105.3	3.6	2.2
Metoxuron	1 – 100	1 - 100	0.01	95.0	3.0	-2.8	1 - 100	0.01	92.5	4.3	-3.9	1 - 100	0.01	95.2	2.9	-1.0
Monesine	1 – 100	1 - 100	0.01	93.4	2.9	2.5	1 - 100	0.01	90.1	3.7	3.3	1 - 100	0.01	91.3	4.6	3.2
Monocrotophos	1 - 50	1 - 50	0.04	113.9	12.6	1.2	1 - 50	-----	-----	-----	-----	1 - 100	0.01	91.8	7.5	1.9
Monolinuron	1 – 100	1 - 50	0.01	99.0	3.0	1.6	1 - 50	0.01	94.7	5.3	1.6	1 - 100	0.01	96.0	2.7	1.1
Omethoate	1 – 100	1 - 100	0.01	95.3	2.8	-1.3	1 - 50	-----	-----	-----	-----	1 - 100	0.01	78.1	3.5	2.0
Oxadixyl	1 – 50	1 - 50	0.01	95.8	2.7	2.1	1 - 50	0.01	93.8	4.0	3.4	1 - 100	0.01	96.2	4.0	3.0
Oxamyl	1 – 100	1 - 100	0.04	96.0	3.4	0.3	1 - 100	0.01	91.6	5.9	3.1	1 - 100	0.01	83.7	6.7	3.0
Oxyfluorfen	5 – 50	20 - 100	0.04	117.5	8.5	-1.2	2 - 100	-----	-----	-----	-----	20 - 100	0.04	91.7	14.7	-1.4
Paraoxon	1 – 50	1 - 100	0.01	88.5	13.6	2.0	1 - 50	0.01	89.7	10.0	2.4	1 - 100	0.01	105.9	8.1	2.1
Pencycuron	1 – 50	1 - 50	0.01	92.0	11.9	1.5	1 - 100	0.01	109.5	7.9	4.6	1 - 50	0.01	85.9	10.5	6.0
Piperonyl butoxide	1 – 100	1 - 100	0.01	93.1	3.4	-0.1	1 - 100	0.01	91.1	7.0	0.0	1 - 100	0.01	89.8	3.8	0.1
Pyraclostrobin	1 – 100	1 - 100	0.01	105.9	8.1	5.1	1 - 100	0.01	89.3	14.1	5.1	1 - 100	0.01	95.3	10.0	5.4

Table 2. Linear Range in Solvent and in the Matrix Extract, LOQ and the Averages (n=3) of Recovery (%), Relative Standard Deviations - RSD (%), Mass Accuracy Obtained by LC-QTOF-MS Analysis of Pear, Apple, and Grape (continued)

		Apple					Pear					Grape				
Pesticides	**Linear range (solvent) µg/L**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**	**Linear range (matrix) µg/L**	**Method LOQ mg/kg**	**Recovery (%)**	**RSD (%)**	**Mass accuracy (ppm)**
Pyrazophos	1 – 50	1 - 50	0.01	94.4	7.7	-0.6	1 - 100	0.01	100.1	6.1	1.2	1 - 50	0.01	88.6	9.0	2.2
Pyrazosulfuron-ethyl	1 – 100	1 - 100	0.01	65.7	2.7	5.9	1 - 100	0.01	66.0	5.8	5.3	1 - 100	0.01	71.1	4.8	5.2
Pyridan	1 – 100	1 - 100	0.01	94.3	1.5	0.6	1 - 100	0.01	90.6	2.9	0.4	1 - 100	0.01	90.7	2.4	0.4
Pyridaphenthion	1 – 100	1 - 50	0.01	97.9	2.2	3.7	1 - 50	0.01	96.6	3.7	3.3	1 - 100	0.01	93.8	4.0	2.9
Piridate	1 – 100	1 - 100	0.01	81.4	3.2	-1.3	1 - 100	0.01	81.3	3.1	-0.7	1 - 100	0.01	81.9	3.7	0.0
Pyrimethanil	1 – 100	1 - 100	0.01	89.7	3.8	-0.5	1 - 100	0.01	90.1	3.9	3.5	1 - 100	0.01	90.4	5.9	3.4
Pyrimicarbe	1 – 50	1 - 50	0.01	98.8	1.4	-2.8	1 - 50	0.01	92.5	2.8	-5.4	1 - 50	0.01	94.4	6.0	-2.7
Pyrimiphos-ethyl	1 – 100	1 - 100	0.01	94.6	3.3	-0.3	1 - 100	0.01	87.7	4.1	0.0	1 - 100	0.01	89.1	4.3	-0.7
Profenofos	1 – 100	1 - 100	0.01	95.3	2.4	0.4	1 - 100	0.01	87.0	2.2	0.4	1 - 100	0.01	86.7	3.7	0.4
Profoxydim	1 – 100	1 - 100	0.01	94.5	3.2	-0.2	1 - 100	0.01	86.9	5.0	-0.3	1 - 100	0.01	86.9	3.0	0.4
Propanil	1 – 50	1 - 100	0.01	97.8	10.4	3.2	1 - 100	0.04	111.2	7.2	1.2	1 - 50	0.01	95.6	10.1	2.1
Propargite	1 – 100	1 - 100	0.01	93.8	2.5	-1.1	1 - 100	0.01	91.6	3.1	-1.0	1 - 100	0.01	89.3	4.8	-0.1
Prothiofos	1 – 100	1 - 100	0.01	94.6	8.8	0.7	1 - 100	0.01	89.6	12.4	0.2	1 - 100	0.04	96.6	4.8	0.1
Quinoxyfen	1 – 100	1 - 100	0.01	90.3	4.4	1.5	1 - 100	0.01	92.5	3.7	1.6	1 - 100	0.01	89.8	3.4	1.5
Simazine	1 – 50	1 - 50	0.01	94.9	3.1	0.8	1 - 50	0.01	95.1	4.2	-2.8	1 - 50	0.01	99.0	4.1	1.2
Spinosad	1 – 100	1 - 100	0.01	93.1	2.0	0.5	1 - 100	0.01	91.0	1.2	0.0	1 - 100	0.01	94.5	3.9	0.3
Tebufenpyrad	1 – 100	2 - 100	0.01	99.4	3.0	5.9	1 - 100	0.01	92.7	2.1	2.9	1 - 100	0.01	94.3	5.9	1.5
Terbuthylazine	1 – 100	1 - 50	0.01	96.2	3.2	-2.4	1 - 100	0.01	93.1	2.7	-2.1	1 - 50	0.01	98.1	3.3	-2.5
Thiabendazole	1 – 100	20 - 100	-----	-----	-----	-----	1 - 100	0.01	80.1	3.8	-1.4	1 - 100	0.01	85.5	2.5	-0.7
Thiacloprid	1 – 100	1 - 100	0.01	96.3	3.0	-1.5	1 - 100	0.01	96.2	2.6	-3.2	1 - 100	0.01	98.6	3.8	-2.1
Thiamethoxam	1 – 100	1 - 100	0.01	95.1	2.5	-0.1	1 - 100	0.01	87.6	7.1	0.0	1 - 100	0.01	96.0	4.5	-0.2
Thiodicarb	1 – 100	1 - 100	0.01	95.9	2.4	1.8	1 - 100	0.01	94.1	2.5	1.8	1 - 100	0.01	96.4	2.7	1.7
Thiophanate-methyl	1 – 50	1 - 50	0.01	83.4	4.6	-1.4	1 - 50	0.04	75.7	2.4	-3.0	1 - 50	-----	-----	-----	-----
Triasulfuron	1 – 100	1 - 100	0.01	82.7	4.2	1.0	1 - 100	0.01	81.6	7.4	-0.8	1 - 100	0.01	83.8	6.6	0.9
Tricyclazole	1 – 100	1 - 100	0.01	92.8	3.0	-2.9	1 - 100	0.01	86.1	5.7	-4.2	1 - 100	0.01	89.6	5.0	-2.4
Trichlorphon	1 – 100	1 - 100	0.01	91.4	3.1	-0.9	1 - 100	0.01	91.9	4.6	-4.1	1 - 100	0.01	96.3	2.6	-1.4
Trifloxystrobin	1 – 50	1 - 50	0.01	99.6	10.2	0.8	1 - 100	0.01	119.1	11.9	1.7	1 - 50	0.01	71.3	27.7	3.9
Triflumuron	1 – 100	1 - 100	0.04	102.1	16.6	5.3	1 - 50	0.01	87.9	25.7	4.9	1 - 100	0.04	118.9	14.8	3.6
Vamidothion	1 – 100	1 - 100	0.01	93.4	2.1	-1.8	1 - 100	0.01	91.2	1.6	-4.5	1 - 50	0.01	92.3	2.5	-1.8

Conclusion

The LC/QTOF/MS is a powerful tool for screening and identification of pesticides residues in food matrices. The proposed method proved to be adequate for the quantification of pesticide residues in apple, pear and grape by LC/QTOF/MS. This detection system proved to be very beneficial, because it allowed multiresidue determination of a wide quantity of analytes in a short time. The validation study demonstrated good recovery and precision for a wide number of compounds providing MRL values normally established by the different legislations.

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