Analysis of Pesticide Residues in Mango by GC/MS/MS With Bond Elut QuEChERS EN Kits

Application Note

Food Testing and Agriculture

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Abstract

This application note describes the quantitative analysis of 19 of the 40 regulated pesticides with maximum residue limits (MRLs) established by the Brazilian Health Surveillance Agency (ANVISA). We also analyzed nine pesticides found in mango during the monitoring programs developed in the Pesticide Residues Laboratory (LRP/IB)/São Paulo State and by governmental programs. The samples were also analyzed with a qualitative multiresidue method for 258 pesticides, extending the analytical scope to analytes with low probability of being present, as recommended in SANCO/12571/2013 guidelines [1]. The extraction was performed using an Agilent Bond Elut QuEChERS EN kit. Target pesticides were analyzed by GC/MS/MS using an Agilent 7890A GC and an Agilent 7000B Triple Quadrupole GC/MS in a constant pressure/postcolumn backflush configuration (Pesticide Analyzer 411). The method was validated in terms of recovery and reproducibility. The limits of detection (LOD) ranged between 0.0006 and 0.0607 mg/kg and limits of quantitation (LOQ) were between 0.0025 and 0.5 mg/kg. LOQs were established as ¼ of MRL. Recoveries for all compounds were 70 to 120%, and RSDs were below 20% for five replicates. LODs were calculated as three times the RSDs at LOQ levels.

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Introduction

Mango is one of the most consumed fresh fruits in the world, and Brazil is one of the main exporters. It is a fruit with a large range of varieties (Palmer, Tommy Atkins, Edward, Peter, Haden, Keith, Mummy, Julie, Saigon, Dabsha, Hindi, Van Dyke, Benisha, Kesar, and Lick). Each one has its own characteristics in terms of pulp quality, taste, color, and so on. In general, mango is consumed fresh and unprocessed. However, it is possible to find it in different forms, such as purée, juice, sliced, chutney, and flakes. World market demand for mangoes has been rapidly growing. For example, growth averaged nine percent per year from 2006 to 2010 [2].

The international market varies considerably and depends on the preference of the consumer. To be exported, the fruit must exhibit a brilliant red color, have short fibers, and weigh around 250 to 600 g. In general, Tommy Atkins is the variety with a large market due mainly to its intense color and durability in long-distance transport [3]. For this reason, Tommy Atkins was chosen for this study.

Increasing the scope of the quantitative method was considered an illogical expense in terms of the cost of further standards and their application. However, to assess the presence of pesticides with low probability, the samples were also screened qualitatively with the same chromatographic method but with MRM transitions for 258 pesticides, including isomers and metabolites.

The Brazilian Health Surveillance Agency (ANVISA) regulates and lists maximum residue limits (MRLs) for about 40 pesticides for use on mango [4]. Of these regulated pesticides, 19 were selected on the basis of amenability to GC, and availability of standards. In addition, nine other pesticides found in mango during the national monitoring programs were included in the list, 28 compounds were analyzed quantitatively.

Two Brazilian national monitoring programs have begun, namely Pesticide Residues Analysis Program (PARA) on Food, developed by ANVISA, and National Plan for Control of Residues and Contaminants in Products of Plant Origin (PNCRC), developed by the Ministry of Agriculture. These initiatives are based on programs initially set up at the Instituto Biologico's Laboratório de Resíduos de Pesticidas (LRP) pesticide residues laboratory and São Paulo General Warehousing and Centers Company (CEAGESP) in 1978, with LRP participating in the PNCRC program. National programs were created to establish a service to evaluate and promote food quality regarding the use of pesticides and similar compounds [4]. The high quantity of pesticides not allowed for specific crops was also verified in PARA and PNCRC monitoring programs, and from LRP analysis [4,9,10,11].

The programs list some commodities that may or may not be included in the annual sampling plan; mango is one of them. The others are rice, zucchini, pineapple, lettuce, banana, potato, beet, onion, carrot, cabbage, bean, orange, apple, papaya, corn, strawberry, cucumber, green pepper, cabbage, tomato, and grape [4].

Materials and Methods

Acetonitrile, isooctane, and acetone were pesticide-residue grade. Pure standards from AccuStandard, around 99% pure, were used to prepare stock solutions at 1,000 ng/µL and working solutions that varied in concentration. Triphenyl phosphate at 0.5 mg/kg was prepared in isooctane and used as internal standard.

We performed extractions using the Agilent QuEChERS Extraction Kit for EN method 15662EN (p/n 5982-5650CH), in which 10 g of mango sample was extracted using premixed sachets of 4 g $MgSO_4$, 1 g NaCl, 1 g Na citrate, and 0.5 g disodium citrate sesquihydrate. More details are shown in Figure 1. Mango is a highly pigmented fruit, so the GC components should be kept free from pigments and nonvolatiles [8]. We chose a subsequent dispersive cleanup designed to include pigment removal (Agilent Bond Elut QuEChERS SPE Dispersive Kit for Pigmented Fruits and Vegetables, EN method, p/n 5982-5256CH). This included premixed sachets containing 150 mg PSA, 15 mg graphitized carbon (GCB), and 885 mg $MgSO_4$. Cleanup removed polar organic acids, some sugars and lipids, and carotenoids and chlorophyll. It is known that the use of GCB can affect planar pesticides such as quintozene and thiabendazole in our target list for quantitation [5]. However, the relatively low level of GCB in the Agilent formulation was a key criterion in its choice, and the good RSDs and recoveries we found (see Table 2) supported this approach.

A calibration in matrix extract was prepared daily and injected before and after the sample set to check calibration curve integrity. TPP was added after cleanup to avoid its retention by GCB [8]. The Agilent 7000B Triple Quadrupole GC/MS System was configured according to the Agilent Pesticide Analyzer 411 configuration, featuring a 30 m analytical column with postcolumn backflush.

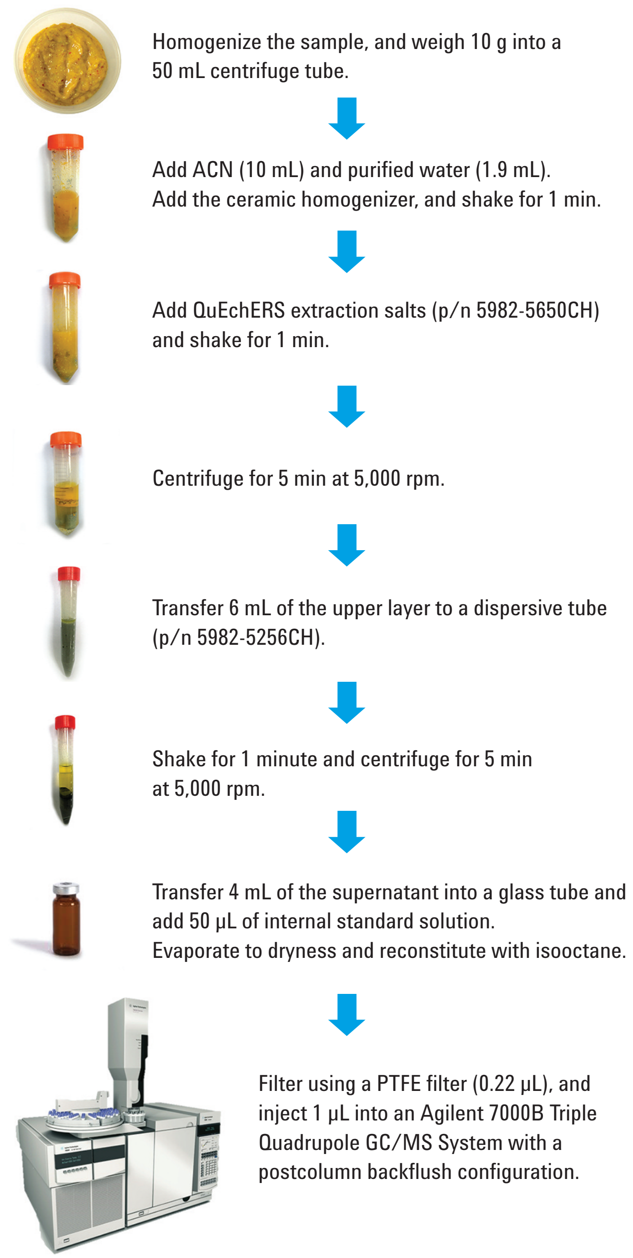

Figure 1. Mango sample preparation process.

Instrumental conditions

GC conditions

Column:	Agilent J&W DB-5ms, 30 m × 0.25 mm, 0.25 µm (p/n 122-5532)
Inlet:	Split/splitless
Inlet liner:	Splitless, single taper, Ultra Inert liner with glass wool (p/n 5190-3167)
Carrier:	Helium
Inlet pressure:	36 psi (constant pressure mode) during run, 1 psi during backflush
Inlet temp:	280 °C
Inj vol:	1 µL
Purge flow to split vent:	30 mL/min at 0.75 min
Gas saver:	On (20 mL/min at 2.0 min)
Oven temp :	70 °C (1 min), 50 °C/min to 150 °C (0 min), 6 °C/min to 200 °C (0 min), 16 °C/min to 280 °C (5.5 min)
Capillary flow technology:	Agilent Purged Ultimate Union (p/n G3186) used for backflushing the column and retention gap
Restrictor:	Deactivated capillary tubing, 0.7 m × 0.15 mm
Retention time locking:	Chlorpyrifos-methyl locked at 16.59 min
GC:	Agilent 7890A series (G3440A)
Autosampler:	Agilent 7693A Automatic Liquid Sampler injector and sample tray

MS conditions

Spectrometer:	Agilent 7000B Triple Quadrupole GC/MS System
Mode:	Electron Impact
Transfer line temp:	280 °C
Solvent delay:	2.3 min
Source temp:	300 °C
Quadrupole temp:	Q1 and Q2 = 180 °C

Results and Discussion

Performance evaluation, quantitative method

Blank samples were spiked with concentrations of 1 MRL, ½ MRL, and ¼ MRL. Calibration curves were prepared at five levels in concentrations of ¼, ½, 1, 2.5, and 5x MRL, all above $R^2 = 0.99$ linearity. Recoveries ranged from 70 to 120% at ¼ MRL for the pesticides listed in Table 1.

In an effort to increase the low recovery of carbosulfan, 600 µL of 5 N NaOH were added after the addition of salts into the sample [6]. The addition of NaOH increased the pH from 4 to 6. Carbosulfan is an acid-sensitive pesticide; therefore, at pH 4 it may be hydrolyzed and converted into carbofuran. Carbosulfan exhibited increased recovery after pH adjustment from 59 to 113% when spiking at 0.0125 mg/kg. However, due to their sensitiveness to basic solutions [7], this addition affected the recoveries of vinclozolin, cyhalothrin, and cypermethrin, lowering them to about 50%. Therefore, it is recommended to prepare both solutions to have better recoveries for all pesticides.

Table 1. Pesticides analyzed with limits of detection (LOD), limits of quantitation (LOQ), RSD, recovery (REC), and MRM transitions.

No.	Pesticide	MRL	RT (min)	LOD	LOQ	RSD (%)	REC (%)	Quant	CE (V)	Qual	CE (V)
1	Azoxystrobin	0.3	36.6	0.0287	0.0750	13.1	97	344.1 → 329.0	15	344.1 → 182.9	25
										344.1 → 171.9	40
2	BHC-*alpha*	0.01*	12.3	0.0007	0.0025	9.4	95	218.8 → 183.0	5	218.8 → 145.0	20
										181.0 → 145.0	15
3	Bifenthrin	0.1	29.0	0.0088	0.0250	13.8	85	181.2 → 165.2	25	166.2 → 165.2	20
										181.2 → 166.2	10
4	Carbosulfan	0.05	28.7	0.0016	0.0125	7.1	59/113*	118.0 → 76.0	5	164.0 → 103.1	25
										164.0 → 149.0	10
5	Chlorpyrifos	0.05*	19.1	0.0047	0.0125	15.1	83	313.8 → 257.8	15	196.9 → 107.0	40
6	Cyhalothrin (λ)	0.1	30.5	0.0089	0.0250	12.6	94	208.0 → 181.0	7	197.0 → 161.0	5
										197.0 → 141.0	10
7	Cypermethrin I	0.7	33.1	0.0480	0.1750	10.9	84	163.0 → 127.0	5	209.0 → 116.0	15
										181.0 → 127.0	30
										165.0 → 127.0	5
8	Diazinon	0.05*	14.4	0.0052	0.0125	12.4	112	137.1 → 84.0	10	137.1 → 54.0	20
										199.1 → 93.0	15
9	Difenoconazole I	0.2	35.5	0.0170	0.0500	15.6	72	322.8 → 264.8	15	264.9 → 202.0	20
										324.8 → 266.8	15
10	Endosulfan I	0.01*	23.1	0.0010	0.0025	13.1	100	239.0 → 204.0	15	339.0 → 267.0	2
										207.0 → 172.0	15
										241.0 → 136.0	20
										241.0 → 206.0	20
11	Endosulfan II	0.01*	25.7	0.0010	0.0025	17.3	81	241.0 → 206.0	15	339.0 → 267.0	2
										241.0 → 136.0	40
										239.0 → 204.0	15
										207.0 → 172.0	15
12	Endosulfan sulfate	0.01*	27.1	0.0011	0.0025	17.0	85	271.8 → 237.0	15	387.0 → 253.0	10
										271.8 → 235.0	15
13	Ethion	0.05*	26.1	0.0049	0.0125	13.1	100	152.9 → 96.9	10	124.9 → 96.9	0
										230.9 → 175.0	10
14	Etofenprox	0.3	33.5	0.0219	0.0750	12.7	77	163.0 → 107.1	20	135.0 → 107.0	10
										163.0 → 135.1	10
15	Famoxadone	0.2	37.1	0.0163	0.0500	10.9	100	223.9 → 196.2	10	197.0 → 141.1	15
										197.0 → 115.0	30
16	Fenthion	0.05	19.1	0.0047	0.0125	13.9	90	278.0 → 109.0	15	278.0 → 169.0	15
17	Imazalil	1	24.1	0.0607	0.2500	9.4	86	214.9 → 173.0	5	216.8 → 175.0	5
										172.9 → 145.0	15

No.	Pesticide	MRL	RT (min)	LOD	LOQ	RSD (%)	REC (%)	Quant	CE (V)	Qual	CE (V)
18	Kresoxim-methyl	0.2	25.0	0.0184	0.0500	13.9	88	116.0 → 89.0	15	131.0 → 89.0	30
										116.0 → 63.0	30
19	Methidathion	0.05*	22.6	0.0056	0.0125	14.7	102	144.9 → 85.0	5	144.9 → 58.1	15
										85.0 → 58.0	5
20	Prochloraz	0.2	31.9	0.0134	0.0500	10.6	85	180.0 → 138.0	10	310.0 → 70.0	15
										308.0 → 70.0	15
21	Pyraclostrobin	0.1	34.7	0.0094	0.0250	12.2	102	132.0 → 77.1	20	132.0 → 104.0	15
										164.0 → 132.1	10
22	Quintozene	0.3	13.4	0.0006	0.0025	8.6	95	294.9 → 236.8	15	294.9 → 142.9	45
										236.8 → 143.0	30
23	Tebuconazole	0.1	27.8	0.0084	0.0250	10.3	108	250.0 → 125.0	20	125.0 → 99.0	20
										125.0 → 89.0	15
24	Tetraconazole	0.1	19.9	0.0101	0.0250	12.6	106	336.0 → 217.9	20	336.0 → 203.8	30
										170.9 → 136.0	10
25	Thiabendazole	2	21.8	0.0199	0.5000	1.5	87	201.0 → 174.0	15	201.9 → 175.0	15
										173.9 → 65.0	30
26	Tiametoxam	0.05	20.7	0.0018	0.0125	4.2	112	212.0 → 139.0	15	247.0 → 182.0	15
										247.0 → 212.0	5
27	Trifloxystrobin	0.05	27.3	0.0051	0.0125	14.4	95	116.0 → 89.0	15	172.0 → 145.1	15
										116.0 → 63.0	30
IS	Triphenyl phosphate	–	28.0	–	–	–	–	325.0 → 169.0	20	326.0 → 233.0	10
28	Vinclozolin	0.05*	16.8	0.0044	0.0125	13.6	86	187.0 → 124.0	20	211.9 → 172.0	15
										284.9 → 212.0	15

Note: * Pesticide not permitted on this crop (NPC)

The recovery study was carried out to determine method accuracy and precision. For each blank matrix, three levels at 1 MRL, ½ MRL, and ¼ MRL were prepared. For the pesticides that do not have an established MRL, it was set as 0.01 mg/kg, with 0.05 mg/kg for the compounds that have MRLs set by the European Union, as shown on Table 1.

MRMs of the compounds were selected based on the Agilent Pesticide and Environmental Pollutants MRM Database (G9250AA) and Agilent Pesticide Analysis Reference Guide [5].

The LOQs for the pesticides were determined based on the recovery and RSD results, and defined as the selected lowest-validated spiked level meeting the requirement described in SANCO/12571/2013 [1], where recovery should be 70 to 120% and RSD below 20%. Five replicates were used. The LODs were calculated as three times the RSD of the spiked samples at their assigned LOQ levels.

Real world sample analysis, quantitative method

Tommy Atkins mangoes were purchased at local groceries. Twenty lots of samples (from different stores) were analyzed. Three mangoes from each lot were extracted. The samples were chopped (including peel), blended, homogenized, and extracted soon after.

Using the quantitative method, it was possible to verify the presence of azoxystrobin, cyhalothrin, cypermethrin, difenoconazole, imazalil, prochloraz, pyraclostrobin, tebuconazole, tetraconazole, and thiabendazole below MRL. We also found chlorpyrifos, thiamethoxam, trifloxystrobin, and vinclozolin, none of which are permitted on mango. Two samples had concentrations of prochloraz above the MRL established by ANVISA, showing levels of 0.85 and 0.92 mg/kg (MRL = 0.2 mg/kg). The full list of pesticides is in Table 2.

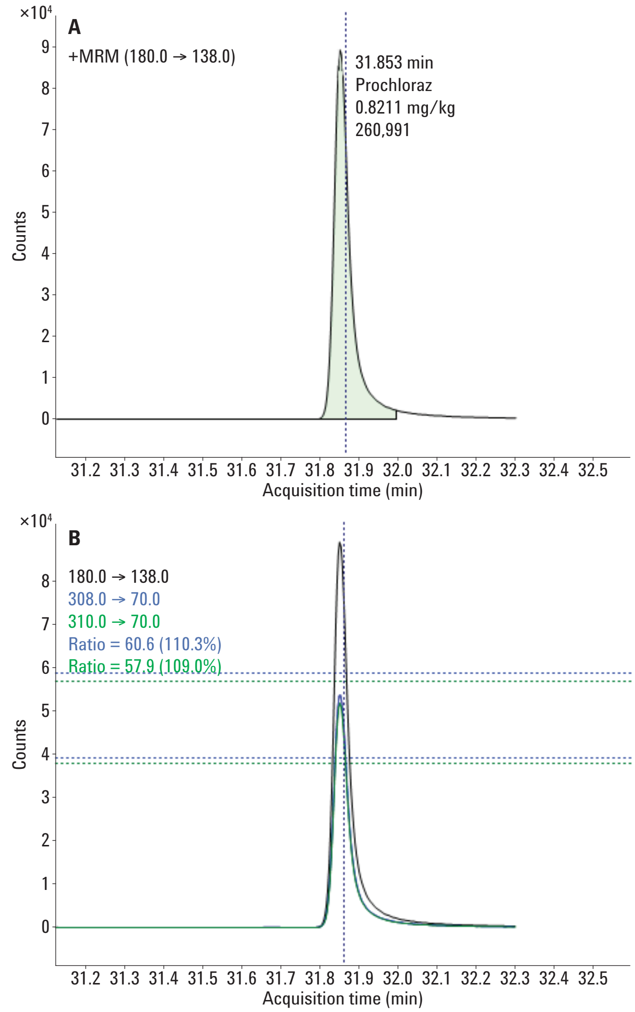

Figure 2. Prochloraz peak detected in a mango sample purchased at São Paulo supermarket.

Table 2. Pesticides detected in mango using the quantitative method.

		Sample no.																			
	Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	BHC-*alpha*	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2	Quintozene	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
3	Diazinon	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4	Vinclozolin	–	–	–	–	–	–	–	<LOD	<LOQ	–	<LOQ	<LOQ	–	–	–	–	–	–	–	–
5	Chlorpyrifos	–	–	–	–	–	–	–	<LOQ	–	–	–	–	–	–	–	<LOQ	–	–	–	–
6	Fenthion	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	Tetraconazole	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	<LOQ	–
8	Tiametoxam	–	–	–	–	–	–	–	–	–	–	0.049	–	–	–	0.023	–	–	–	–	–
9	Thiabendazole	<LOQ		–	–	–	–	<LOQ	–	–	–	–	–	–	–	–	–	–	–	–	–
10	Methidathion	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
11	Endosulfan I	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
12	Imazalil	<LOQ	–	–	–	<LOQ	<LOQ	<LOQ	<LOQ	–	–	<LOQ	<LOQ	–	–	<LOQ	–	–	–	–	
13	Kresoxim-methyl	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
14	Endosulfan II	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
15	Ethion	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
16	Endosulfan sulfate	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
17	Trifloxystrobin	–	–	–	–	–	–	–	–	–	–	–	<LOQ	–	<LOQ	<LOQ	–	–		–	–
18	Tebuconazole	–	–	0.0817	<LOQ	<LOQ	–	–	–	–	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	–	
19	Carbosulfan	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
20	Bifenthrin	–	–	–	–	–	–	–	–	–	–	–	–	–	–	<LOQ	<LOQ	–	–	–	–
21	Cyhalothrin (λ)	–	–	–	–	–	–	<LOQ	<LOQ	–	–	<LOQ	–	–	<LOQ	<LOQ	–	–	<LOQ	<LOQ	<LOQ
22	Prochloraz	–	–	–	–	–	–	<LOQ	0.92	–	–	–	–	–	–	–	0.8501	<LOQ	0.114	–	–
23	Cypermethrin I	–	–	–	<LOQ	–	–	–	–	–	–	–	<LOQ	–	<LOQ	<LOQ	–	–	–	<LOQ	–
24	Etofenprox	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
25	Pyraclostrobin	–	0.0212	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	<LOQ	–	–
26	Difenoconazole I	–	–	–	–	–	–	–	–	–	–	<LOQ	<LOQ	–	–	<LOQ	0.2225	<LOQ	0.0604	–	<LOQ
27	Azoxystrobin	–	–	<LOQ	<LOQ	<LOQ	–	–	–	–	–	–	–	–	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	–	<LOQ
28	Famoxadone	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Note: <LOQ = when peak was detected but the value was below LOQ, and above LOD. Values highlighted in red were above MRL.

Real world sample analysis, qualitative screening

The samples were also analyzed by the qualitative method, with even more pesticides detected (Table 3).

The concentrations were calculated by injecting specific standards after detection.

Table 3. Pesticides found in mango by the qualitative method.

		Sample no.																			
	Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	Cyfluthrin					<0.03	<0.03	0.05	0.08	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03						
2	Dimethoate								0.6												
3	Epoxiconazole					<0.05						<0.05									<0.05
4	Fenoxaprop-ethyl							<0.01													
5	Mirex											<0.01	<0.01	<0.01	<0.01		<0.01				
6	Omethoate								0.5												
7	Permethrin									<0.03	<0.03	<0.03	<0.03	<0.03	<0.03						
8	Propoxur								0.01												
9	Trichlorophenol 2,4,6							<0.05	<0.05									<0.05	<0.05	<0.05	

The comprehensive method allowed the detection of more than 250 pesticides at one run for screening purposes (Table 4). This method was easily created using the G9250AA Pesticide and Environmental Pollutants MRM Database, since the retention times of the compounds are already listed for the Pesticide Analyzer 411 configuration. In the past, the preparation of the calibration curve for this number of compounds is very troublesome, and the daily checking of method integrity becomes much more involved. Screening first, and preparing calibration curves of identified compounds afterwards, makes the process faster, easier to perform, and far more cost-effective.

Table 4. Pesticides included in the MRM qualitative screening method.

1	3 OH Carbofuran
2	Acephate
3	Acetamiprid
4	Acrinathrin
5	Alachlor
6	Aldrin
7	Ametryn
8	Amitraz
9	Anilazine
10	Atrazine
11	Atrazine-desethyl
12	Azinphos-ethyl
13	Azinphos-methyl
14	Azoxystrobin
15	Benalaxyl
16	Benfluralin
17	Benfuracarb
18	BHC-*alpha* (benzene hexachloride)
19	BHC-*beta*
20	BHC-*delta*
21	BHC-*epsilon*
22	BHC-*gamma* (lindane, *gamma* HCH)
23	Bifenthrin
24	Bromopropylate
25	Butylate
26	Captafol
27	Captan
28	Carbaryl
29	Carbofuran
30	Carbofuran, 3-keto-
31	Carbofuran, 7-phenol-
32	Carbophenothion
33	Carbophenothion-methyl (methyl trithionate)
34	Carbosulfan
35	Chlordane-*cis* (*alpha*)
36	Chlordane-oxy
37	Chlordane-*trans* (*gamma*)
38	Chlorfenson
39	Chlorfenvinphos
40	Chlorobenzilate
41	Chlorothalonil
42	Chlorpropham
43	Chlorpyrifos
44	Chlorpyrifos-methyl
45	Cinerina I
46	Cinerina II
47	Clomazone
48	Cyanazine
49	Cycloate
50	Cyfluthrin I
51	Cyfluthrin II (CAS no. 68359-37-5)
52	Cyfluthrin III (CAS no. 68359-37-5)
53	Cyfluthrin IV (CAS no. 68359-37-5)
54	Cyhalothrin (*gamma*)
55	Cyhalothrin (*lambda*)
56	Cypermethrin I
57	Cypermethrin II
58	Cypermethrin III
59	Cypermethrin IV
60	Cyproconazole
61	Cyromazine
62	DDD-*o,p'*
63	DDD-*p,p'*
64	DDE-*o,p'*
65	DDE-*p,p'*
66	DDT-*o,p'*
67	DDT-*p,p'*
68	Deltamethrin
69	Demeton-S
70	Demeton-S-methyl
71	Demeton-S-methyl sulfone
72	Diazinon
73	Diazinon-oxon (diazoxon)
74	Dichlofluanid
75	Dichlorvos
76	Dicloran (dichloran)
77	Dicofol, *o,p'*-
78	Dicofol, *p,p'*-
79	Dicrotofos (dicrotophos)
80	Dieldrin
81	Difenoconazole I
82	Difenoconazole II (CAS no. 119446-68-3)
83	Dimethenamid
84	Dimethenamid-P
85	Dimethoate
86	Dinocap I
87	Dinocap II
88	Dinocap III
89	Dinocap IV
90	Disulfoton
91	Disulfoton sulfone
92	Diuron
93	Diuron metabolite (3,4-dichlorophenyl isocyanate)
94	DMSA (dichlofluanid metabolite)
95	DMST (tolylfluanid metabolite)
96	Endosulfan I (*alpha* isomer)
97	Endosulfan II (*beta* isomer)
98	Endosulfan sulfate
99	Endrin
100	Endrin aldehyde
101	Endrin ketone
102	Epoxiconazole
103	EPTC
104	Ethion
105	Ethylan (ethyl-DDD, Perthane)
106	Etofenprox (ethofenprox)
107	Famoxadone
108	Fenamidone
109	Fenamiphos (phenamiphos)
110	Fenamiphos sulfone
111	Fenarimol
112	Fenchlorphos oxon
113	Fenitrothion
114	Fenoprop-methyl
115	Fenoxaprop-ethyl
116	Fenoxaprop-*p*-ethyl
117	Fenpropathrin
118	Fenson
119	Fensulfothion
120	Fensulfothion sulfon
121	Fenthion
122	Fenthion oxon sulfone
123	Fenthion sulfone
124	Fenthion sulfoxide
125	Fenvalerate I
126	Fenvalerate II (CAS no. 51630-58-1)
127	Fipronil
128	Fipronil sulfide
129	Fipronil sulfone
130	Fluazinam
131	Flufenoxuron
132	Flumetralin
133	Fluquinconazole

134 Fluthiacet-methyl
135 Flutriafol
136 Folpet
137 Fonofos
138 Formothion
139 Heptachlor
140 Heptachlor endo-epoxide (isomer A)
141 Heptachlor exo-epoxide (isomer B)
142 Hexachlorobenzene
143 Hexazinone
144 Imazalil
145 Iprodione
146 Iprovalicarb I
147 Iprovalicarb II (CAS no. 140923-17-7)
148 Jasmolina I
149 Jasmolina II
150 Kresoxim-methyl
151 Lactofen
152 Malaoxon (metabolite of malathion)
153 Malathion
154 MCPA-butoxyethyl
155 MCPA-methyl
156 MCPB-methyl
157 Metalaxyl
158 Methamidophos
159 Methidathion
160 Methiocarb
161 Methiocarb sulfone
162 Methiocarb sulfoxide
163 Methoxychlor olefin
164 Methoxychlor, *o,p'*-
165 Methoxychlor, *p,p'*-
166 Mevinphos
167 Mirex
168 Molinate
169 Monocrotophos
170 Naled
171 Nitrofen
172 Omethoate
173 Oxadiazon
174 Oxamyl
175 Paraoxon
176 Paraoxon-methyl
177 Parathion
178 Parathion-methyl
179 Pebulate
180 Pendimethalin (penoxaline)
181 Pentachloroaniline
182 Pentachlorobenzene
183 Pentachlorophenol
184 Permethrin I
185 Permethrin II (*trans*)
186 Pethoxamid
187 Petoxamida
188 Phenthoate
189 Phorate
190 Phorate oxon sulfone
191 Phorate sulfone
192 Phorate sulfoxide
193 Phoratoxon
194 Phosalone
195 Phosmet
196 Phosmet oxon
197 Piperonyl butoxide
198 Pirimicarb
199 Pirimiphos-ethyl
200 Pirimiphos-methyl
201 Prochloraz
202 Procymidone
203 Profenofos
204 Profluralin
205 Prometon
206 Prometryn
207 Pronamide (propyzamide)
208 Propaquizafop
209 Propargite
210 Propazine
211 Propham
212 Propiconazole I
213 Propiconazole II (CAS no. 60207-90-1)
214 Propoxur
215 Prothioconazole-desthio
216 Pyraclostrobin
217 Pyrethrin I
218 Pyrethrin II
219 Pyridaphenthion
220 Pyriproxyfen
221 Quintozene
222 Quintozene metabolite (pentachlorophenyl)
223 Ronnel (fenchlorphos)
224 Simazine
225 Spirodiclofen
226 Spiromesifen
227 Tebuconazole
228 Tecnazene (TCNB)
229 Tefluthrin, *cis*-
230 Terbufos
231 Terbufos sulfone
232 Terbuthylazine
233 Terbuthylazine-desethyl
234 Terbutryn
235 Tetrachlorvinphos, E-isomer
236 Tetraconazole
237 Tetradifon
238 Tetrasul
239 Thiabendazole
240 Thiametoxan
241 Thiazopyr
242 Thiobencarb (benthiocarb)
243 Thiometon
251 Trichlorophenol, 2,4,6-
252 Trifloxystrobin
253 Trifluralin
254 Trinexapaque
255 Triphenyl phosphate
256 Vamidothion
257 Vernolate
258 Vinclozolin

Conclusions

This study developed two methods for pesticide residue analysis. The first was used to quantify pesticides that have MRLs determined by Brazilian legislation, with good recovery and detection limits. The second method was used to verify the presence of 258 pesticides and metabolites simultaneously. By having two methods, it is possible to simplify the preparation of daily calibration curves for accurate quantification of listed pesticides, and also check if any pesticide not allowed for use with a particular crop or commodity has been used. For routine pesticide analysis, it is important to check as many compounds as possible. Our study showed that several banned pesticides were still being used, as well as pesticides that should not be used on mango.

References

1. Anon. *Guidance Document on Analytical Quality Control and Validation Procedures for Pesticide Residues Analysis in Food and Feed, SANCO/12571/2013, 19 Nov 2014*. European Commission, Health and Consumer Protection Directorate-General, Brussels, Belgium.
2. Nanakaan Saave. *Export Factsheet – Mangoes*. International Trade Centre, Geneva, Switzerland, **2011**.
3. Araújo, José. *Mercado e Comercialização da Manga*. Embrapa, Brasília - DF, Brazil, **2004**. http://sistemasdeproducao.cnptia.embrapa.br/FontesHTML/Manga/CultivodaMangueira/mercado.htm
4. ANVISA. Brazilian Health Surveillance Agency, Brasília - DF, Brazil. http://portal.ANVISA.gov.br/wps/content/ANVISA+Portal/ANVISA/Inicio/Agrotoxicos+e+Toxicologia
5. Anon. *GC/MS/MS Pesticide Residue Analysis*; Pesticide Analysis Reference Guide, Agilent Technologies, Inc. Publication number 5991-2389EN, **2013**.
6. Anon. *Foods of Plant Origin—Determination of Pesticide Residues Using GC-MS and/or LC-MS/MS Following Acetonitrile Extraction/Partitioning and Clean-up by Dispersive SPE (QuEChERS-method)*. EN 15662 Version 2008. European Standards, Pilsen, Czech Republic.
7. Anon. *Specification for Agricultural Pesticides in Agriculture*. Food and Agriculture Organization of the United Nations, Rome, Italy. http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmps/ps-new/en/
8. Anastassiades, M.; Lehotay, S. J. Fast and Easy multiresidue method employing acetonitrile extraction/partitioning and "Dispersive solid-phase extraction" for the determination of pesticide residues in produce. *J. AOAC Int*. **2003**, *86*, 412-431.
9. Ciscato, C. H. P.; Gebara, A. B.; Monteiro, S. H. Pesticide residue monitoring of Brazilian fruit for export 2006-2007. *Food Additives and Contaminants: Part B* **2009**, *2*, 140-145.
10. Ciscato, C. H. P.; Gebara, A. B.; Barbosa, C. M.; Souza, G. S.; Hamada, N.; Silva, D. L. Pesticide Residues Evaluation in Pulp, Juice and Nectar of Fruits. *Environment and Pollution* **2012**, *1*, 39-43.
11. Anon. *Plano Nacional de Controle de Resíduos e Contaminantes em Produtos de Origem Vegetal*. Ministério da Agricultura Pecuária e Abastecimento (MAPA), Brasília - DF, Brazil. http://www.agricultura.gov.br/vegetal/qualidade-seguranca-alimentos-bebidas/alimentos/residuos-e-contaminantes.

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