Evaluation of interferences between matrix-analyte for the correct identification of the pesticides by GC-QqQ-MS/MS and LC-QqQ-MS/MS

CONTENTS

1. Aim and scope

This report study the influence of the interferences coming from the matrices of different commodities by using the most applied multiresidue extraction methods in the EU laboratories by LC and GC-MS/MS.

2. Short description

Twenty five homogenous blank samples (apple, aubergine, avocado, banana, broccoli, carrot, cauliflower, celery, cherry, cucumber, green beans, green tea, leek, lemon, lettuce, melon, onion, orange, parsley, pear, pepper, potato, pumpkin, strawberry and tomato) were extracted with acetone, ethyl acetate and acetonitrile and the obtained extracts were analysed by GC-MS/MS and LC-MS/MS. The interferences taken into account were those whose relative abundance were higher than 50% respect to the standard in tomato at 0.010 mg/kg and their retention time were within ± 0.2 min according to the analyte in the standard mix.

3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes of 10 µL to 5000 µL and 1 mL to 3 mL
- 250 ml PTFE centrifuge tubes
- 50 mL PTFE centrifuge tubes
- 15 mL PTFE centrifuge tubes
- Vortex
- Automatical shaker (Agitax, Cirta Lab)
- Turrax homogeniser
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 3300 rpm
- Injection vials, 2 ml, suitable for LC and GC auto-sampler

4. Chemicals

- Acetone p.a.
- Petroleum ether
- Dichloromethane
- Acetonitrile HPLC grade
- Ethyl acetate HPLC grade
- Anhydrous sodium sulphate
- Anhydrous magnesium sulphate
- Sodium hidrogenocitrate sesquihydrate
- Tri-sodium citrate dihydrate

- Sodium chloride
- Primary Secondary Amine (PSA)
- Formic acid
- Ultra-pure water
- Pesticides standards

5. Procedure

5.1. Sample preparation

Following Document No. SANCO/12571/2013, the sample was perfectly homogenised by grinding finely at its arrival to the laboratory.

5.2. Extraction methods

Twenty five blank samples were extracted with four different methods described below to compare the interferences matrix-analyte found.

5.2.1. NL-method

1. Weigh 15 g ± 0.1 g of sample in 250 mL PTFE centrifuge tube.
2. Add 20 mL of acetone and 15 g Na_2SO_4.
3. Blend the sample using a Turrax homogeniser for 30 s at 1500 rpm (extraction step).
4. Add 20 ml of petroleum ether and 10 ml of dichloromethane.
5. Blend it again by Turrax for 30 s at 1500 rpm (partitioning step).
6. Centrifuge for 5 min at 3700 rpm.
7. Evaporate an aliquot of the extract with a nitrogen stream until dryness.
   a. for LC analysis evaporate 167 µL extract and reconstitute with 250 µL acetonitrile : water (2:8, v/v).
   b. for GC analysis evaporate 167 µL extract and reconstitute with 50 µL of ethyl acetate.

   With this treatment, 1 mL of sample extract represents 0.2 g of sample in LC and in GC the final matrix concentration is 1 g/mL.

5.2.2. *Ethyl acetate method*

1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 10 mL of ethyl acetate, 8 g $MgSO_4$ and 1.5 g NaCl.
3. Shake automatically for 15 min.
4. Centrifuge for 5 min at 3700 rpm.
5. For LC, evaporate 50 µL of the extract with a nitrogen stream and reconstitute with 250 µL of acetonitrile : water (2:8, v/v). For GC analysis, an aliquot of the extract is injected directly.

With this treatment, 1 mL of sample extract represents 0.2 g of sample in LC and in GC the final matrix concentration is 1 g/mL.

5.2.3. *Citrate QuEChERS*

1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetonitrile.
3. Shake automatically for 4 min.
4. Add 4 g of $MgSO_4$, 1 g NaCL, 1 g trisodium citrate dehydrate and 0.5 g sodium hydrogenocitrate sesquihydrate.
5. Shake automatically for 4 min.
6. Centrifuge for 5 min at 3700 rpm.
7. Transfer 5 mL of the supernatant into 15 mL PTFE centrifugue tube containing 750 mg $MgSO_4$ and 125 mg PSA.
8. Vortex for 30 seconds.
9. Centrifuge for 5 min at 3700 rpm.
10. For GC, evaporate 50 µL of the extract and reconstitute with 50 µL of ethyl acetate. For LC analysis, 50 µL of the extract were diluted with 200 µL of water.
    With this treatment, 1 mL of sample extract represents 0.2 g of sample in LC and in GC the final matrix concentration is 1 g/mL.

5.2.4. *Citrate QuEChERS without clean-up*

This procedure was the sample than the previous one excluding the steps number 7 and 8.

5.3. Measurement

Both LC and GC systems were operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments with two SRM transitions were used. The mass transitions used are presented in Appendix I.

5.4. Instrumentation and analytical conditions for the LC- MS/MS system

5.4.1. Liquid chromatograph (1290 UPLC, Agilent Technologies)

- Column: Zorbax Eclipse Plus C8 2.1 mm x 100 mm and 1.8 µm particle size (Agilent)
- Mobile phase A: Water (0.1% formic acid)
- Mobile phase B: Acetonitrile (0.1% formic acid and 5% H_2O)
- Column temperature: 35°C
- Flow rate: 0.3 mL/min
- Injection volume: 5 µL

Mobile phase gradient for pesticides analyse

Time [min]	Mobile phase A	Mobile phase B
0	80%	20%
2	80%	20%
15	0%	100%
17	0%	100%

Re-equilibration with initial mobile phase: 2.5 minutes.

5.4.2. Triple quadrupole mass spectrometer (6490, Agilent Technologies)

- Ionisation mode: Positive and negative mode
- Drying gas temperature: 120 °C
- Drying gas flow: 13L/min
- Nebuliser pressure: 45 psi
- Sheath gas temperature: 375°C
- Sheath gas flow: 10 L/min
- Fragmentor: 380 V
- Capillary voltage: 3000 V (in positive and negative mode)
- Nebuliser and collision gas: nitrogen

5.5. Instrumentation and analytical conditions for the GC- MS/MS system

5.5.1. Gas chromatograph (7890 A GC system, Agilent Technologies)

- Column: HP 5MS UI 15 m × 0.25 mm ID and 0.25 µm
- Injection mode: Splitless
- Ultra-Inert liner with a glass wool frit
- Injection volume: 2 µl
- Injector temperature: held at 80°C (0.1 min) and then ramped up to 300°C at 600°C/min.
- Carrier gas: helium at constant pressure (14.1 psi)
- Carrier gas purity: 99.999%
- Oven temperature: 70°C for 1 min, programmed to 150°C at 50°C/min, then to 200°C at 6°C/min and finally to 280°C at 16°C/min and kept at 280°C for 4.07 min.

5.5.2. Triple quadrupole mass spectrometer (7000, Agilent Technologies)

- Ionisation mode: electron impact ionisation
- Transfer line temperature: 280 °C
- Ion source temperature: 280 °C
- Quadrupoles temperature: 150°C

- Quenching gas: helium
- Quenching gas flow: 2.25 mL/min
- Collision gas: nitrogen
- Collision gas flow: 1.5 mL/min
- Collision gas purity: 99.999%
- Solvent delay: 2 minutes

6. Evaluation of the commodities.
   The 25 different commodities were extracted with the four extraction methods and their extracts were injected both in LC and GC systems. Each of the matrices was evaluated taking into account the presence of a signal in the ± 0.2 min retention time of the compound and with intensity at least 50 % of the standard signal at 0.010 mg/kg.
   To develop this study in LC, 160 pesticides were monitored. In Appendix II, Figure 1 is represented the percentage of compounds with some interference, either in one transition (blue) or in both transitions (green). As can be seen, the highest percentage did not reach 4% in any case. In general, not big differences could be observed.
   The extracts were also injected in GC and their data compiled in Figure 2, taking into account the 220 pesticides. In this case, the presence of interferences that could affect to identification/quantification is significantly bigger than in LC. In general, the highest percentage of interferences was found when NL-method was applied, going up to 14% for the case of avocado matrix.
   In Figure 3 all the results obtained per extraction method, the 380 compounds (LC and GC), two transitions per each and the 25 matrices are plotted considering ± 0.2 min (blue) and ± 0.1 min (red) as retention time window. In the view of the results, the number of interferences was very low (close to 1 % in LC and 2 % in GC as maximum, both for NL-method). Reducing retention time window to ± 0.1 min, the probability to find a peak of the matrix interfering with the pesticide was also decreased, but not drastically.

7. "Potential" false negatives.
   It was considered a "potential" false negative a not resolved interference observed in the blank from the pesticide peak which affected to the ion ratio making the difference higher than 30 % from expected one, as it is established at the AQC procedures. These results have been represented in Figure 4.
   In LC the worst result was obtained for avocado with NL-method, and it was around 4% the number of "potential" false negatives. For the rest, they were below or close to 2%, except for green beans with citrate QuEChERS and leek with citrate QuEChERS without clean-up. The compound showing more "potential" false negatives is fenthion-sulfoxide (interfering in 7 out of 10

matrices), followed by chlorpyrifos methyl, fenhexamid, dichlorvos and phosmet from the list of compounds evaluated.
In GC the worst result was obtained for avocado with NL-method, with around 6 % of compounds evaluated showing "potential" false negatives. In general, NL-method was the extraction method providing higher percentage of compounds with "potential" false negatives. In the case of leek and banana the method with higher number of "potential" false negative was citrate QuEChERS without clean-up and in orange was ethyl acetate. Phenothrin was the compound generating "potential" false negatives in almost all matrices tested, followed by molinate, fenpropidin, tolylfluanid, chlorbromuron and isoprothiolane.

8. References

- Ana Lozano, Barbara Kiedrowska, Jos Scholten, Marijke de Kroon, André de Kok, Amadeo R. Fernández-Alba. "Miniaturisation and optimisation of the Dutch mini-Luke extraction method for implementation in the routine multi-residue analysis of pesticides in fruits and vegetables". Food Chemistry 192 (2016) 668–681
- Samanta Uclés, Noelia Belmonte, Milagros Mezcua, Ana B. Martínez, M. Jesus Martinez-Bueno, Miguel Gamón & Amadeo R. Fernández-Alba. "Validation of a multiclass multiresidue method and monitoring results for 210 pesticides in fruits and vegetables by gas chromatography-triple quadrupole mass spectrometry". Journal of Environmental Science and Health, Part B (2014) 49, 557–568.
- Ana Lozano, Łukasz Rajskia, Noelia Belmonte-Valles, Ana Uclés, Samanta Uclés, Milagros Mezcua, Amadeo R. Fernández-Alba. "Pesticide analysis in teas and chamomile by liquid chromatography and gas chromatography tandem mass spectrometry using a modified QuEChERS method: Validation and pilot survey in real samples". Journal of Chromatography A, 1268 (2012) 109- 122.
- **Analytical quality control and method validation procedures for pesticide residues analysis in food and feed.** Document Nº SANCO/12571/2013.

- **http://www.eurl-pesticides.eu**

APPENDIX I: MASS TRANSITIONS

Table 1. Detection and chromatographic parameters for the selected compounds analysed by LC-MS/MS.

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
1	2,4-D	7.88	219>161	15	221>163	15
2	Acephate	1.15	184>143	5	184>125	15
3	Acetamiprid	4.43	223>126	20	223>56	15
4	Aldicarb	5.73	213>116	10	213>89	15
5	Aldicarb-Sulfone	1.78	223>148	5	223>86	10
6	Aldicarb-Sulfoxide	1.27	207>132	5	207>89	10
7	Azinphos-Methyl	9.15	318>261	0	318>132	8
8	Azoxystrobin	9.63	404>372	10	404>344	20
9	Benfuracarb	12.69	411>252	10	411>195	20
10	Bifenazate	10.18	301>198	10	301>170	20
11	Bitertanol	10.24	338>269	5	338>99	10
12	Boscalid	9.72	343>307	16	343>272	32
13	Bromuconazole	9.5	378>159	20	378>70	20
14	Bupirimate	8.49	317>272	20	317>166	20
15	Buprofezin	10.27	306>201	10	306>116	15
16	Carbaryl	7.49	202>145	10	202>127	20
17	Carbendazim	1.26	192>160	15	192>132	20
18	Chlorantraniliprol	8.63	484>453	16	484>286	8
19	Chlorfenvinphos	10.9	359>155	8	359>99	28
20	Chlorpyrifos-Methyl	11.79	322>290	14	322>125	16
21	Clofentezin	11.44	303>138	12	303>102	40
22	Clomazone	8.59	240>128	10	240>125	20
23	Cyazofamid	11.05	325>261	10	325>108	15
24	Cymoxanil	5.08	199>128	4	199>111	12
25	Cyproconazole	9.15	292>125	32	292>70	16
26	Cyprodinil	7.9	226>93	40	226>77	40
27	Cyromazine	0.88	167>125	15	167>60	20
28	Demeton-S-Methylsulfoxide	1.42	247>169	8	247>109	24
29	Diazinon	11.41	305>169	15	305>153	20
30	Dichlorvos	6.53	221>109	15	221>79	30
31	Dicrotophos	2.06	238>112	8	238>72	28
32	Diethofencarb	9.21	268>226	5	268>180	15
33	Difenoconazole	10.02	406>337	15	406>251	20
34	Diflubenzuron	10.08	311>158	8	311>141	32
35	Dimethoate	4.31	230>199	5	230>171	10
36	Dimethomorph	8.7	388>301	20	388>165	20
37	Diniconazole	10.53	326>159	28	326>70	28
38	Dithianon	13.88	296>264	32	296>164	41
39	Dodine	8.85	228>60	20	228>57	20

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
40	Epoxiconazole	9.63	330>121	16	330>101	52
41	Ethion	13.32	385>199	5	385>171	10
42	Ethirimol	2.53	210>140	20	210>43	52
43	Ethoprophos	9.84	243>131	15	243>97	30
44	Fenamidone	9.75	312>92	28	312>65	56
45	Fenamiphos	9.56	304>234	12	304>217	20
46	Fenamiphos-Sulfone	6.95	336>266	16	336>188	24
47	Fenamiphos-Sulfoxide	5.8	320>292	8	320>108	44
48	Fenarimol	9.3	331>268	20	331>259	20
49	Fenazaquin	12.54	307>161	15	307>147	15
50	Fenbuconazole	10.18	337>125	40	337>70	33
51	Fenhexamid	9.77	302>97	25	302>55	30
52	Fenoxycarb	10.38	302>116	5	302>88	20
53	Fenpropimorph	7.74	304>147	30	304>130	25
54	Fenpyrazamide	9.99	332>272	10	332>230	20
55	Fenpyroximate	13.13	422>366	12	422>107	64
56	Fenthion	11.25	279>247	8	279>169	12
57	Fenthion-Sulfone	14.7	310>125	15	310>109	15
58	Fenthion-Sulfoxide	7.14	295>280	16	295>109	32
59	Fipronil	11.18	435>330	12	435>250	28
60	Flonicamid	4.31	230>199	4	230>125	16
61	Fluazifop	9.27	328>282	15	328>254	20
62	Flubendiamine	11.09	681>274	15	681>254	20
63	Fludioxonil	9.38	247>169	32	247>152	32
64	Flufenacet	10.6	364>194	15	364>152	15
65	Flufenoxuron	12.95	489>158	20	489>141	56
66	Fluopyram	10.18	397>208	20	397>173	20
67	Fluquinconazole	9.74	376>307	24	376>108	56
68	Flusilazol	10.08	316>247	12	316>165	24
69	Flutriafol	7.56	302>95	56	302>70	16
70	Formetanate	1.02	222>165	8	222>65	52
71	Fosthiazate	7.59	284>228	10	284>104	20
72	Haloxyfop	10.32	362>316	12	362>288	24
73	Hexaconazole	10.21	314>159	30	314>70	20
74	Hexythiazox	13.11	353>228	10	353>168	15
75	Imazalil	6.56	297>255	15	297>159	45
76	Imidacloprid	3.86	256>209	15	256>195	15
77	Indoxacarb	12.19	528>218	20	528>203	45
78	Ioxynil	8.41	370>215	30	370>127	30
79	Iprovalicarb	9.58	321>203	0	321>119	16
80	Isofenfos methyl	11.64	231>199	15	231>121	15
81	Isoprocarb	8.19	194>152	5	194>95	15
82	Isoxaflutole	9.73	360>251	15	360>220	50
83	Kresoxim-Methyl	11.06	314>267	0	314>222	10

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
84	Linuron	9.18	249>160	20	249>133	36
85	Lufenuron	12.62	509>339	10	509>326	10
86	Mandipropamid	9.82	412>356	4	412>328	24
87	Mepanypirim	9.69	224>207	10	224>191	10
88	Meptyldinocap	13.93	295>193	42	295>163	10
89	Metalaxyl	7.82	280>220	5	280>192	50
90	Metconazole	10.28	320>125	48	320>70	24
91	Methamidophos	1.12	142>125	10	142>94	10
92	Methidathion	9.14	303>145	0	303>85	15
93	Methiocarb	9.12	226>121	12	226>169	5
94	Methiocarb-Sulfoxide	2.8	242>185	10	242>170	20
95	Methomyl	2.09	163>106	4	163>8	0
96	Methoxyfenozide	10.21	369>149	15	369>133	20
97	Metobromuron	8.11	259>170	15	259>148	10
98	Monocrotophos	1.62	224>193	5	224>127	10
99	Myclobutanil	9.6	289>125	20	289>70	15
100	Nitempyram	1.67	271>225	10	271>99	10
101	Omethoate	1.21	214>183	5	214>125	20
102	Oxadixyl	6.1	279>219	5	279>132	32
103	Oxamyl	1.76	237>90	5	237>90	10
104	Oxyfluorfen	12.82	362>252	25	362>237	30
105	Paclobutrazol	8.9	294>125	36	294>70	16
106	Penconazole	10.2	284>159	20	284>70	15
107	Pencycuron	11.7	329>125	24	329>89	60
108	Pendimethalin	13.07	282>212	4	282>194	16
109	Phenthoate	11.48	321>247	4	321>79	44
110	Phosalone	11.87	368>182	8	368>111	44
111	Phosmet	9.44	318>160	8	318>133	36
112	Phoxim	11.91	299>129	4	299>77	24
113	Pirimicarb	2.47	239>182	15	239>72	20
114	Pirimiphos-Methyl	11.14	306>164	20	306>108	20
115	Prochloraz	8.75	376>308	10	376>266	15
116	Profenofos	12	375>347	5	375>305	15
117	Propamocarb	1.14	189>144	10	189>102	15
118	Propaquizafop	12.17	444>371	15	444>100	20
119	Propargite	13.53	368>231	0	368>57	20
120	Propiconazole	10.52	342>159	32	342>69	16
121	Propoxur	7.02	210>168	5	210>111	10
122	Propyzamide	9.81	256>190	10	256>173	20
123	Proquinazid	13.18	373>331	20	373>289	20
124	Prothioconazole	10.35	342>306	15	342>100	20
125	Prothiofos	14.2	345>241	20	345>161	40
126	Pymetrozine	0.89	218>105	20	218>51	60
127	Pyraclostrobin	11.41	388>194	8	388>163	20

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
128	Pyrethrin	13.71	329>161	5	329>143	20
129	Pyridaben	13.84	365>309	10	365>147	20
130	Pyridate	14.6	379>351	5	379>207	10
131	Pyrimethanil	6.22	200>183	20	200>107	20
132	Pyriproxyfen	12.63	322>185	20	322>96	10
133	Quinoclamine	6.13	208>105	25	208>77	40
134	Quinoxyfen	11.64	308>272	25	308>197	35
135	Quizalofop-ethyl	12.05	373>271	24	373>255	36
136	Rotenone	10.35	395>213	20	395>192	20
137	Spinosyn A	8.8	733>142	20	733>98	20
138	Spinosyn D	9.21	747>142	20	747>98	20
139	Spirodiclofen	14.26	411>313	5	411>71	15
140	Spiromesifen	14.2	371>273	5	371>255	20
141	Spirotetramat	9.32	374>330	15	374>270	20
142	Spiroxamine	7.79	298>144	20	298>100	20
143	Tebuconazole	9.9	308>125	20	308>70	20
144	Tebufenozide	10.92	353>297	5	357>133	15
145	Tebufenpyrad	12.13	334>145	20	334>117	47
146	Teflubenzuron	11.74	379>359	0	379>339	4
147	Terbuthylazine	9.05	230>174	15	230>146	20
148	Tetraconazole	9.99	372>159	36	372>70	20
149	Thiabendazol	1.29	202>175	30	202>131	40
150	Thiacloprid	5.27	253>186	10	253>126	20
151	Thiamethoxam	2.52	292>211	10	292>181	20
152	Thiodicarb	6.87	355>108	8	355>88	8
153	Tolclofos-Methyl	11.71	301>269	10	301>125	15
154	Triadimenol	9	296>227	5	296>70	10
155	Triazophos	10.38	314>286	10	314>162	20
156	Trichlorfon	2.97	257>221	4	257>109	12
157	Trifloxystrobin	12.29	409>206	10	409>186	20
158	Triflumuron	11.12	359>156	8	359>139	32
159	Triticonazole	9.09	318>125	41	318>70	33
160	Zoxamide	11.37	336>187	16	336>159	44

Table 2. Acquisition and chromatographic parameters for the selected compounds analysed by GC-MS/MS.

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
1	2,4'-DDE	11.25	246>176	30	246>211	20
2	2,4'-DDT + 4,4'-DDD	12.91	235>165	20	235>199	15
3	3,5-Dichloroaniline	3.67	161>99	25	161>90	20
4	3-Chloroaniline	2.76	127>92	15	127>100	10
5	4,4'-DDE	12.02	246>176	30	246>211	20
6	4,4'-DDT	13.51	235>165	20	235>199	20
7	Acrinathrin	15.37	208>181	5	209>141	20
8	Alachlor	8.52	188>160	10	188>130	40
9	Aldrin	9.26	293>186	40	293>257	8
10	Ametryn	8.63	227>185	5	227>212	8
11	Anthraquinone	9.41	208>180	10	208>152	20
12	Atrazine	6.59	215>58	10	215>173	5
13	Azoxystrobin	18.34	344>329	10	344>156	40
14	Benalaxyl	13.39	148>105	20	204>176	2
15	Bifenox	14.6	311>279	14	311>216	25
16	Bifenthrin	14.44	181>166	10	181>115	50
17	Biphenyl	3.56	154>102	40	154>126	40
18	Bixafen	16.77	159>139	15	413>159	12
19	Boscalid	16.39	140>112	10	140>76	25
20	Bromopropilate	14.33	341>185	20	341>155	20
21	Bupirimate	12.44	273>193	5	273>108	15
22	Buprofezin	12.29	305>172	5	305>140	10
23	Butralin	10.12	266>174	20	266>190	12
24	Butylate	3.79	156>57	5	174>146	3
25	Cadusafos	5.9	159>97	10	213>73	10
26	Captan	10.64	149>79	15	149>105	5
27	Carbofuran	6.52	164>149	12	164>122	12
28	Carbophenothion	13.33	199>143	10	342>157	10
29	Carbosulfan	14.27	164>149	12	164>122	12
30	Chinomethionat	10.99	234>206	10	206>148	15
31	Chlorbromuron	3.66	233>124	25	233>205	12
32	Chlordane	11.03-11.42	373>266	20	373>301	10
33	Chlorfenapyr	12.65	247>227	15	247>200	25
34	Chlorfenvinphos	10.83	267>159	20	267>81	40
35	Chlorobenzilate	12.71	139>111	15	139>75	30
36	Chlorothalonil	7.39	266>231	20	266>133	40
37	Chlorpropham	5.53	213>171	5	213>127	5
38	Chlorpyrifos	9.63	313>258	15	313>286	5
39	Chlorpyrifos-Methyl	8.3	288>93	26	286>271	16
40	Chlorthal-Dimethyl	9.72	330>299	12	330>221	35

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
41	Chlozolinate	10.71	259>188	10	331>216	5
42	Coumaphos	15.86	210>182	10	362>109	15
43	Cyfluthrin	16.14-16.30	163>127	5	226>206	10
44	Cypermethrin	16.38-16.54	163>127	5	209>141	20
45	Cyproconazole	12.49	139>111	14	222>125	18
46	Cyprodinil	10.36	224>208	20	224>197	21
47	Deltamethrin	17.99	253>93	20	253>172	5
48	Desmethyl-Pirimicarb	8.1	152>96	12	224>152	8
49	Diazinon	7.24	304>179	15	304>137	30
50	Dichlofluanid	9.21	224>123	8	167>124	5
51	Dichlorvos	2.93	185>93	15	185>109	15
52	Diclobutrazole	12.25	270>159	15	270>201	8
53	Dicloran	6.28	206>176	5	206>148	20
54	Dicofol	9.63	139>111	10	250>139	8
55	Dieldrin	11.94	279>243	8	345>263	8
56	Diethofencarb	9.61	207>179	5	207>151	10
57	Dimethenamid	8.11	230>154	10	154>111	10
58	Dimethipin	6.55	118>58	10	118>70	5
59	Diphenylamine	5.25	169>77	35	168>140	40
60	Disulfoton	7.27	142>109	5	142>81	12
61	Disulfoton-Sulfoxide	3.28	125>97	3	212>153	15
62	DMST	6.7	106>79	8	214>106	15
63	Dodemorph	10.01-10.43	154>82	20	154>97	10
64	Endosulphan, alpha-	11.33	239>204	15	241>206	25
65	Endosulphan, beta-	12.58	241>206	14	239>204	15
66	Endosulphansulphate	13.38	387>289	5	387>206	40
67	Endrin	12.39	263>193	35	263>228	25
68	EPN	14.34	157>77	25	157>110	15
69	Epoxiconazole	14.04	192>138	10	192>111	35
70	Ethion	13.02	231>129	25	231>175	5
71	Ethofumesate	9.17	207>161	5	207>137	10
72	Ethoprophos	5.37	158>97	15	158>114	5
73	Ethoxyquin	6.42	202>174	15	202>159	30
74	Etofenprox	16.61	163>107	15	163>135	5
75	Etrimfos	7.58	292>181	5	292>153	20
76	Fenamidone	14.56	268>180	20	238>103	20
77	Fenarimol	15.23	139>111	15	219>107	10
78	Fenazaquin	14.57	160>145	5	160>117	20
79	Fenbuconazole	16.11	198>129	5	129>102	15
80	Fenchlorphos	8.67	285>270	18	285>240	30
81	Fenhexamid	13.46	177>78	20	177>113	10
82	Fenitrothion	9.04	277>260	5	277>109	20

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
83	Fenpropathrin	14.52	181>152	26	265>210	10
84	Fenpropidin	8.93	98>55	12	273>98	3
85	Fenpropimorph	9.67	128>70	12	128>110	10
86	Fenthion	9.58	278>109	20	278>169	20
87	Fenvalerate/Esfenvalerate RR/SS	17.39	167>125	12	125>89	22
88	Fenvalerate/Esfenvalerate RS/SR	17.18	167>125	12	125>89	22
89	Fipronil	10.93	213>178	10	213>143	20
90	Fipronil-Desulfinil	8.71	388>333	20	333>281	15
91	Fipronil-Sulfone	12.43	383>255	20	383>213	25
92	Flamprop-Isopropyl	12.93	276>105	5	304>105	12
93	Flamprop-Methyl	12.29	276>105	8	230>170	15
94	Flonicamid	5.22	174>146	15	174>126	25
95	Fluacrypirim	13.36	145>102	30	145>115	15
96	Fluazifop-p-Butyl	12.68	282>91	15	282>238	20
97	Flucythrinate I	16.55	199>157	5	157>107	15
98	Flucythrinate II	16.73	199>157	5	157>107	15
99	Fludioxonil	12.08	248>127	30	248>154	25
100	Fluopicolide	13.7	209>182	20	173>109	25
101	Fluopyram	10.9	173>145	15	223>196	15
102	Fluquinconazole	15.84	340>298	20	340>286	30
103	Flusilazole	12.34	233>165	20	233>152	20
104	Flutolanil	11.93	323>173	13	323>281	4
105	Flutriafol	11.62	219>123	12	219>95	20
106	Fluvalinate-tau	17.43	250>55	18	250>200	22
107	Folpet	10.82	147>103	5	147>76	25
108	Fonofos	6.94	137>109	5	246>137	5
109	Formothion	7.78	170>93	5	224>125	20
110	Fosthiazate	10.13	195>103	5	195>139	5
111	HCB	6.19	284>249	25	284>214	40
112	HCH, alpha-	6.03	219>183	5	219>145	25
113	HCH, beta-	6.6	219>183	10	219>145	25
114	Heptachlor	8.38	272>237	10	272>143	40
115	Heptachlorepoxid, cis-	10.37	217>182	22	183>119	25
116	Heptachlorepoxid, trans-	10.49	183>155	15	183>119	30
117	Heptenophos	4.89	124>89	15	215>200	10
118	Hexaconazole	11.8	214>159	22	214>172	22
119	Indoxacarb	17.96	203>134	10	264>148	28
120	Iprodione	14.23	314>245	10	314>56	20
121	Iprovalicarb I	12.31	158>116	5	158>98	10
122	Iprovalicarb II	12.51	158>116	5	158>98	10
123	Isazofos	7.53	161>119	5	257>162	5
124	Isocarbophos	7.83	136>108	14	230>212	8

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
125	Isofenphos-Ethyl	10.82	213>121	15	213>185	3
126	Isofenphos-Methyl	10.38	199>121	10	199>167	10
127	Isoprothiolane	11.96	162>85	15	162>134	5
128	Isopyrazam	15.49	159>139	10	359>303	8
129	Kresoxim-Methyl	12.46	206>116	5	206>131	10
130	Lambda-Cyhalotrin	15.22	197>141	10	197>161	5
131	Lindane	6.72	219>183	5	181>145	12
132	Malaoxon	8.46	127>99	5	195>125	16
133	Malathion	9.42	173>99	15	158>125	8
134	Mecarbam	10.87	159>131	5	329>160	3
135	Mepanypirim	11.58	223>207	30	222>179	30
136	Merphos	12.1	169>57	8	169>113	3
137	Metalaxyl	8.67	206>132	20	206>162	8
138	Metazachlor	10.44	209>133	10	133>117	25
139	Metconazole	14.57	125>89	20	125>99	20
140	Methidathion	11.17	145>85	5	145>58	15
141	Methiocarb	9.04	168>153	10	153>109	10
142	Methiocarb-Sulfone	8.75	121>77	12	185>121	5
143	Methoxychlor	14.45	227>169	25	227>115	40
144	Metolachlor	9.48	238>162	8	162>133	12
145	Mevinphos	3.81	127>109	10	127>95	15
146	Molinate	4.54	126>55	12	126>83	3
147	Myclobutanil	12.26	179>125	10	179>152	5
148	Napropamide	11.76	128>72	3	271>128	3
149	Nuarimol	13.74	203>107	10	235>139	12
150	Ofurace	13.29	232>158	20	232>186	5
151	Orthophenylphenol	4.39	170>141	30	170>115	40
152	Oxadixyl	12.97	163>132	15	163>117	25
153	Paclobutrazol	11.32	236>125	10	236>167	20
154	Paraoxon-Methyl	7.31	109>79	5	230>106	20
155	Parathion-Ethyl	9.65	291>109	10	291>81	10
156	Parathion-Methyl	8.3	263>109	10	233>124	10
157	Pebulate	3.99	128>57	5	161>128	3
158	Penconazole	10.56	248>157	25	248>192	15
159	Pendimethalin	10.51	252>162	10	252>191	10
160	Pentachloroaniline	7.77	263>192	25	263>227	15
161	Permethrin I	15.7	163>127	5	183>153	15
162	Permethrin II	15.8	163>127	5	183>153	15
163	Phenothrin I	14.7	123>81	8	183>153	15
164	Phenothrin II	14.8	123>81	8	183>153	15
165	Phenthoate	10.88	274>121	10	274>246	5
166	Phorate	5.98	231>129	20	231>175	20
167	Phorate-Sulfone	9.47	153>97	10	199>143	8
168	Phosmet	14.27	160>77	30	160>133	15

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
169	Phosmet-Oxon	13.52	160>77	30	160>133	15
170	Phthalimide	4.04	147>103	5	147>76	30
171	Picolinafen	14.41	238>145	25	376>238	25
172	Picoxystrobin	11.9	335>173	10	303>157	15
173	Pirimicarb	7.84	238>166	10	166>96	20
174	Pirimiphos-Methyl	9.11	290>151	15	305>180	5
175	Procymidone	11	283>96	8	283>255	8
176	Profenofos	11.99	337>267	16	337>309	6
177	Prometon	6.58	225>183	3	225>168	10
178	Prometryn	8.74	241>184	12	241>226	8
179	Propaphos	11.35	220>140	12	220>125	25
180	Propargite	13.87	135>107	15	135>77	25
181	Propazine	6.7	214>172	8	229>187	3
182	Propiconazole I	13.5	259>173	10	259>191	8
183	Propiconazole II	13.6	259>173	10	259>191	8
184	Propyzamide	6.97	173>145	16	173>109	32
185	Prosulfocarb	8.77	128>86	3	251>128	5
186	Prothiofos	11.89	309>239	15	309>221	25
187	Pyraclostrobin	17.23	132>77	20	132>104	10
188	Pyrazofos	15.36	221>193	10	221>149	15
189	Pyridaben	15.78	147>117	20	147>132	10
190	Pyrifenox	11.35	262>227	10	262>200	20
191	Pyrimethanil	7.09	198>118	25	198>156	25
192	Pyriproxyfen	14.95	136>78	18	136>96	8
193	Quinalphos	10.85	146>91	30	157>129	15
194	Quinoxyfen	13.4	307>272	5	307>237	25
195	Quintozene	6.83	295>237	15	295>265	10
196	Secbumeton	7.52	225>169	5	225>196	5
197	Spirodiclofen	15.69	312>259	10	312>109	20
198	Spiromesifen	14.19	272>254	3	272>209	12
199	Sulfotep	5.905	202>146	10	238>146	10
200	Sulprofos	13.2	156>141	15	322>156	10
201	Tebuconazole	13.75	250>125	20	250>153	12
202	Tebufenpyrad	14.56	333>171	20	333>276	5
203	Tecnazene	5.12	215>179	12	203>143	20
204	Tefluthrin	7.54	177>127	15	177>137	15
205	Terbufos	6.88	231>129	25	231>175	10
206	Terbumeton	6.79	169>154	5	225>169	3
207	Terbutryn	9.06	241>185	3	241>170	10
208	Tetrachlorvinphos	11.51	329>109	25	329>79	35
209	Tetraconazole	9.98	336>204	30	336>218	30
210	Tetradifon	14.71	356>159	10	356>229	10
211	Tetrahydrophthalimide	4.13	151>80	5	151>122	8
212	Tetramethrin I	14.32	164>77	30	164>107	15

#	Name	Rt (min)	SRM1	CE1 (eV)	SRM2	CE2 (eV)
213	Tetramethrin II	14.43	164>77	30	164>107	15
214	Tolclofos-Methyl	8.4	265>250	15	265>220	25
215	Tolylfluanid	10.63	137>91	20	238>137	10
216	Triadimefon	9.74	208>181	5	208>127	15
217	Triazophos	13.26	161>134	5	161>106	10
218	Trifloxystrobin	13.66	222>190	3	222>130	15
219	Trifluralin	5.82	306>264	10	264>160	15
220	Vinclozolin	8.33	212>172	15	212>109	40

APPENDIX II: RESULTS

Figure 1. Percentage of possible interferences analyzed by LC for each of the four methods in the ± 0.2 min retention time range. In blue, percentage of compounds presenting the interference in only one transition, and in green, percentage of compounds with interferences in both transitions.

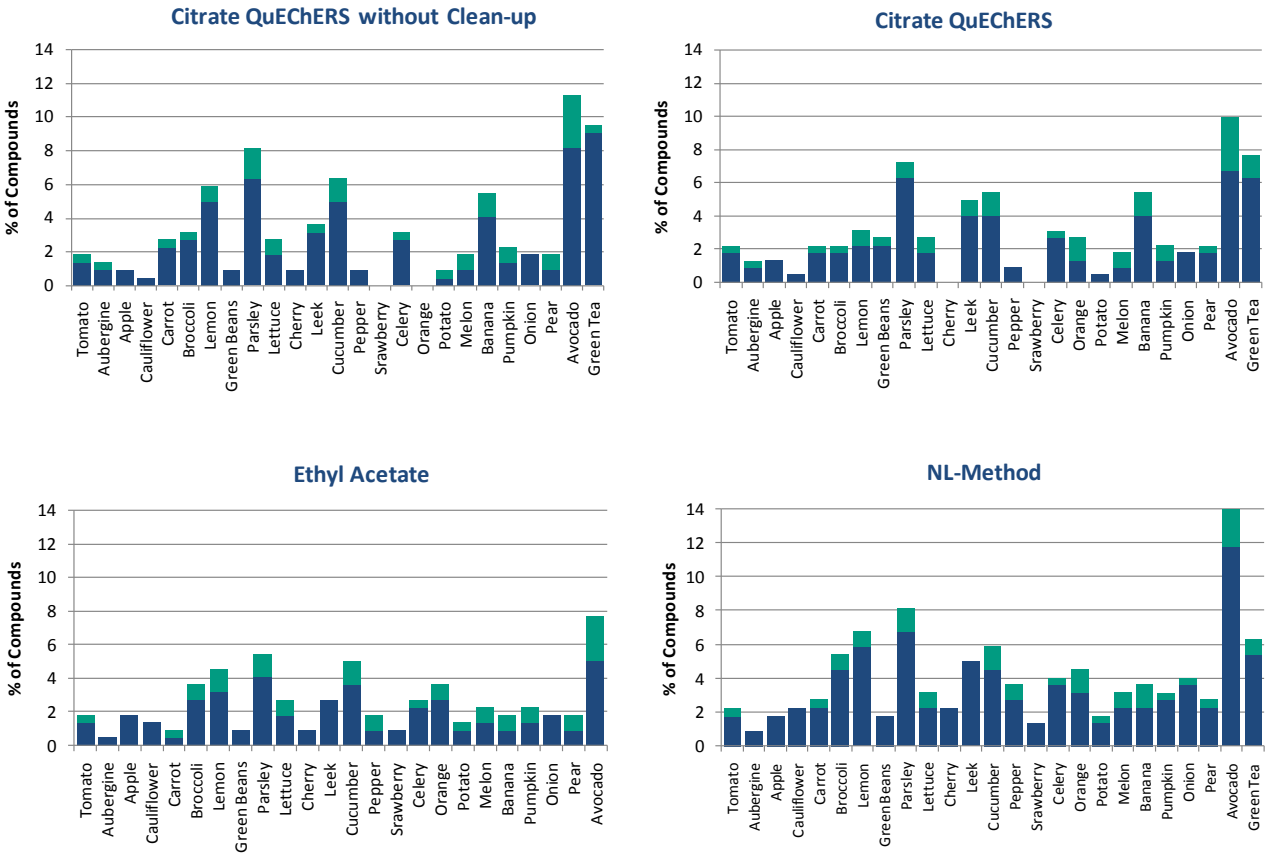

Table 2. Percentage of possible interferences analyzed by GC for each of the four methods in the ± 0.2 min retention time range.

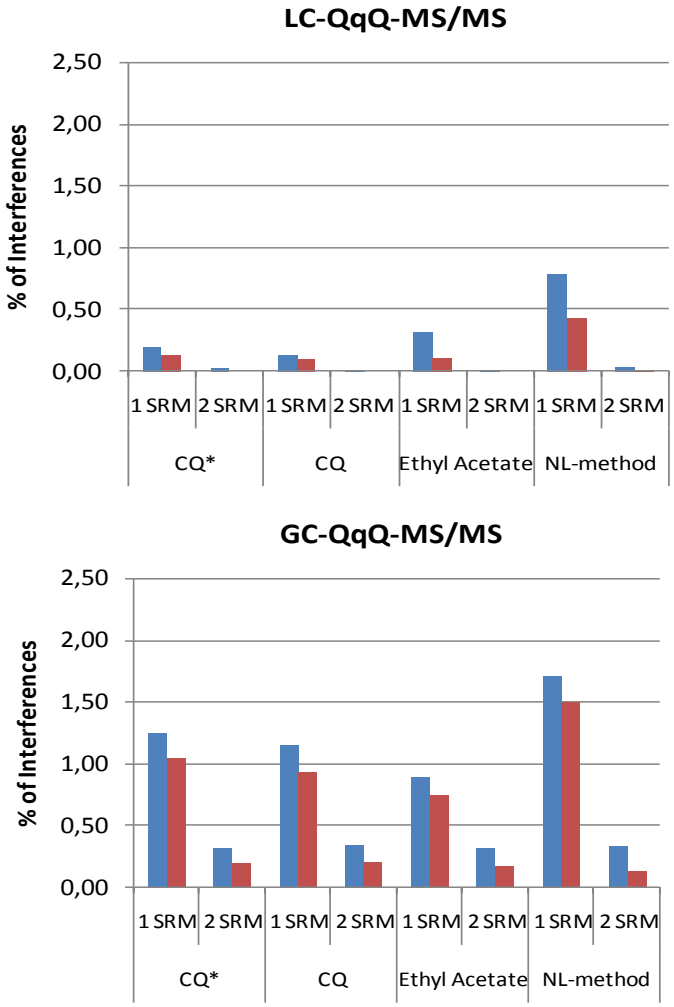

Figure 3. Total percentage of interferences per extraction method (citrate QuEChERS without clean-up, CQ*, citrate QuEChERS, CQ, ethyl acetate and NL-method), considering ± 0.2 min (blue) and ± 0.1 min (red) for retention time, and showing results found for one transition (1 SRM) or both transitions (2 SRM).

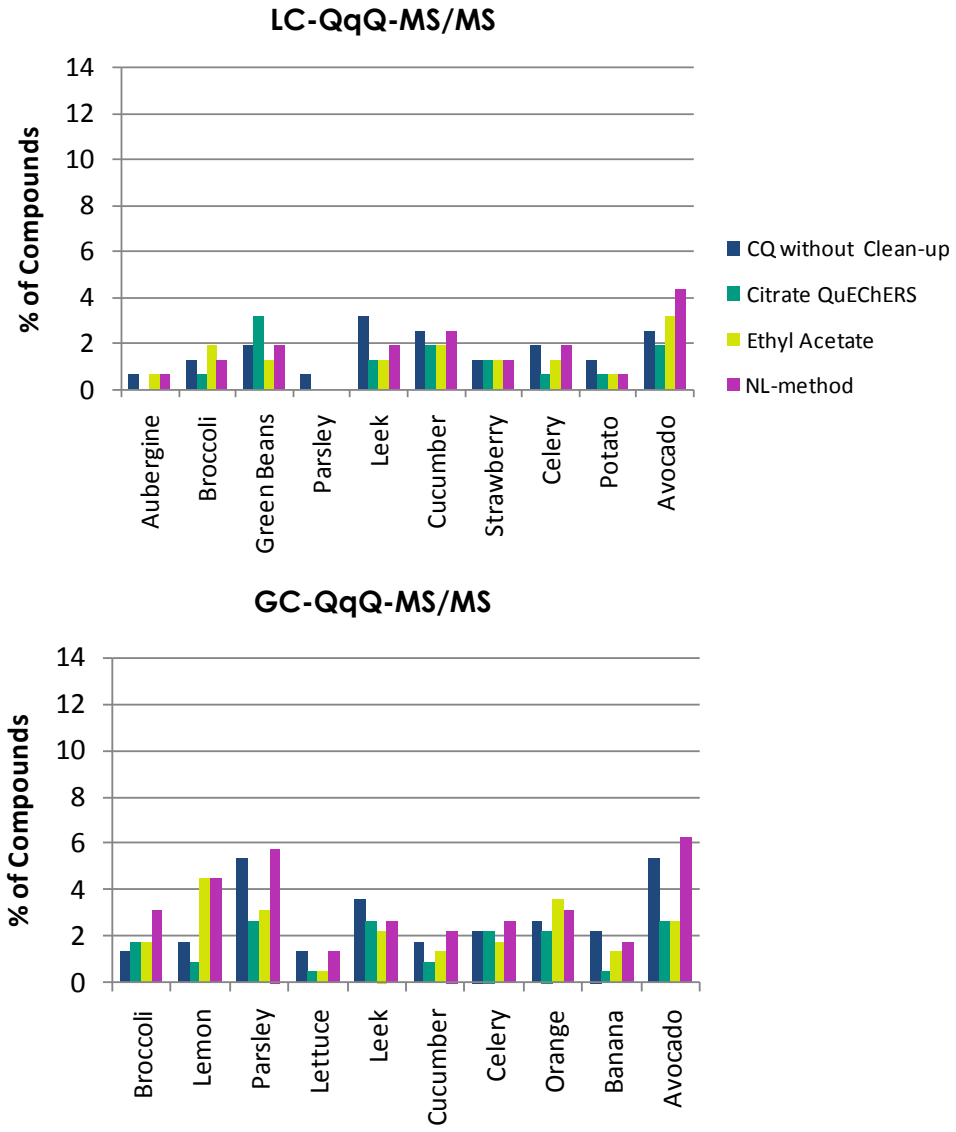

Figure 5. "Potential" false negatives detected in LC and GC for the selected matrices and with the four extraction methods: citrate QuEChERS without clean-up (blue), citrate QuEChERS (green), ethyl acetate (yellow) and NL-method (pink).