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Fast GC-MS/MS for High Throughput Pesticides Analysis

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Key Words

- Fast GC
- GC-MS/MS
- Matrix Selectivity
- Multi-component analysis
- Pesticides
- Productivity
- Quantitation
- Timed-SRM

Introduction

A wide variety of phytosanitary products are commonly applied in agricultural crops in order to increase production yield and obtain high quality products. Consequently, the control of pesticide residue levels by the performance of monitoring programs is currently an increasing concern for producers, traders, and consumers.

The QuEChERS method is the most diffused analytical procedure for preparing samples of fruits and vegetables while performing a multi-residues pesticides analysis in combination with GC-MS and LC-MS systems.[1-3] The analytical benefit of the QuEChERS method is the quick procedure with only a short clean-up step to cover a wide variety of polar and less polar pesticide compounds in a multi-component approach. Due to the reduced clean-up however, the produced sample extracts carry a high concentration of vegetal matrix, that raise a particular challenge to the GC and MS systems.

The application of structure selective MS/MS detection for the quantitation of pesticides residues using multiple reaction monitoring methods (MRM) in fruits and vegetables has been proven to overcome matrix effects.[4-5] The next challenge for commercial routine laboratories is to increase sample throughput to keep pace with the steady increase of the demand for food safety analysis.

In this work the Fast GC and tandem mass spectrometry combination is presented as the analytical system to solve the requirement for matrix robustness with high sample throughput. The Fast GC-MS/MS analytical approach requires a robust, selective and sensitive instrumental system in order to quantify thousands samples/year with short run times. The goal is to obtain a reliable pesticide compound detection and quantification at ppb levels while avoiding breakdown phenomena for the more reactive compounds. The analytical setup and results for the screening and quantitation of 233 pesticides in one Fast GC run is described. For each pesticides compound 2 SRM transitions have been used to comply with EU regulations for compound confirmation gaining 5 EU identification points.[6]

Experimental Conditions

Sample Preparation

10 g of sample was processed in according with the QuEChERS procedures.[1-3] In the clean-up step the graphitized carbon black treatment was not utilized in order to avoid the loss of planar compounds as there are the coplanar PCBs and pyrethroids. 1 mL of final volume of the extracts was reconstituted using acetone/hexane 1:1

after evaporation of the acetonitrile extraction solvent. 10 µL of a solution of Fenchlorphos (5 ppm in hexane) as volumetric standard has been added before injection (1 µL).

A Thermo Scientific TSQ Quantum GC GC-MS/MS system with a Thermo Scientific TRACE GC Ultra gas chromatograph and TriPlus AS liquid autosampler was used for analysis of the samples extracts, equipped and programmed for a Fast GC analysis method, using the following analytical parameters.

TRACE GC Ultra™ Conditions

Carrier Gas:	He, constant flow 1 mL/min
Injector:	PTV splitless mode with Siltek baffled liner 2 mm ID (p/n 453T2120)
PTV Temp. Program:	70 °C, 0.02 min, 12 °C/s to 280 °C, 1.2 min, 14.5 °C/s to 320 °C, 6 min, clean flow 80 mL/min.
Split:	splitless injection, splitflow 50 mL/min at 1.3 min
Column Type:	Restek Rxi-5Sil MS, 20 m, 0.18 mm, 0.18 µm (Restek p/n 43602)
Transfer Line Temp.:	280 °C
GC Oven Program:	80 °C, 1.5 min 30 °C/min to 210 °C 20 °C/min to 320 °C, 2 min

TSQ Quantum GC™ Acquisition Parameter Setting

Source Temperature:	260 °C
Emission Current:	25 µA
Ionisation Mode:	EI, 70 eV
Mass Resolution:	Q1, Q3 at 0.7 Da (FWHM)
Collision Gas:	Ar, 1.5 mTorr
Cycle Time:	0.30 s
Acquisition Mode:	Timed-SRM

Mass Table

467 Timed-SRM transition/Fast GC run, see Table 1

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Fast GC-MS/MS Data for Pesticide Standards *(Table 1)*

Precursor	Product	CE	Rention Time	Pesticide
212.02	182.02	10	8.09	Aclonifen
264.03	194.02	15	8.09	Aclonifen
181.02	152.04	25	8.85	Acrinathrin
208.05	181.04	8	8.85	Acrinathrin
161.07	146.06	12	6.54	Alachlor
188.08	160.07	10	6.54	Alachlor
292.91	222.92	20	6.94	Aldrin
292.91	257.91	20	6.94	Aldrin
293.19	147.10	15	9.24	Amitraz
293.19	162.10	10	9.24	Amitraz
215.09	200.09	10	5.95	Atrazine
215.09	173.08	10	5.95	Atrazine
132.01	77.01	20	9.43	Azinphos-ethyl
160.02	104.01	10	9.43	Azinphos-ethyl
132.02	77.02	20	9.15	Azinphos-Methyl
160.03	104.02	10	9.15	Azinphos-Methyl
344.10	329.10	20	10.96	Azoxystrobin
388.11	345.10	15	10.96	Azoxystrobin
234.12	174.09	10	8.24	Benalaxyl
266.14	148.08	10	8.24	Benalaxyl
166.06	151.06	15	3.94	Bendiocarb
223.08	166.06	15	3.94	Bendiocarb
292.10	160.05	21	5.63	Benfluralin
292.10	264.09	10	5.63	Benfluralin
164.08	149.07	10	9.35	Benfuracarb
190.09	144.07	10	9.35	Benfuracarb
180.91	144.93	15	5.82	BHC, A+B+C+D
218.89	182.91	15	5.82	BHC, A+B+C+D
154.08	152.08	15	4.51	Bifenil
154.08	153.08	15	4.51	Bifenil
181.05	141.04	22	8.77	Bifenthrin
181.05	153.05	6	8.77	Bifenthrin
170.09	115.06	25	9.62	Bitertanol
170.09	141.07	20	9.62	Bitertanol
342.01	140.01	20	10.12	Boscalid (Nicobifen)
344.01	140.01	20	10.12	Boscalid (Nicobifen)
328.86	313.87	20	7.04	Bromophos-methyl
330.86	315.87	20	7.04	Bromophos-methyl
358.89	302.91	20	7.38	Bromophos-ethyl
358.89	330.90	10	7.38	Bromophos-ethyl
340.96	184.98	15	8.81	Bromopropylate
342.96	184.98	20	8.81	Bromopropylate
273.14	193.10	10	7.73	Bupirimate
316.16	208.10	10	7.73	Bupirimate
104.94	104.00	9	7.75	Buprofezin
249.13	193.10	10	7.75	Buprofezin
174.12	146.10	10	4.67	Butylate (Sutan)
217.15	156.11	5	4.67	Butylate (Sutan)
149.96	78.98	15	8.58	Captafol
310.92	78.98	10	8.58	Captafol
123.05	79.03	15	4.95	Captafol-captan Met. (THPI)
151.06	122.05	10	4.95	Captafol-captan Met. (THPI)
148.97	69.98	8	7.30	Captan
148.97	104.98	8	7.30	Captan
164.01	149.00	10	5.91	Carbofuran
221.01	164.00	5	5.91	Carbofuran
341.97	156.99	10	8.27	Carbophenothion
341.97	295.98	5	8.27	Carbophenothion
330.03	310.03	20	8.20	Carfentrazone-ethyl
340.03	312.03	20	8.20	Carfentrazone-ethyl
372.81	265.87	15	7.47	Chlordane
374.81	267.87	15	7.47	Chlordane

Precursor	Product	CE	Rention Time	Pesticide
246.98	226.98	20	7.80	Chlorfenapyr
248.98	228.98	20	7.80	Chlorfenapyr
174.98	110.98	10	7.62	Chlorfenson
301.96	174.98	10	7.62	Chlorfenson
266.98	158.99	15	7.09	Chlorfenvinphos-E+Z
322.97	266.98	15	7.09	Chlorfenvinphos-E+Z
220.04	166.03	23	8.38	Chloridazon
220.04	158.03	25	8.38	Chloridazon
153.98	120.98	5	4.72	Chlormephos
233.97	120.98	14	4.72	Chlormephos
263.88	167.92	25	6.18	Chlorothalonil
265.88	169.92	25	6.18	Chlorothalonil
213.06	127.03	15	5.61	Chlorpropham
213.06	171.04	10	5.61	Chlorpropham
313.93	257.95	15	6.85	Chlorpyrifos-ethyl
315.93	259.95	12	6.85	Chlorpyrifos-ethyl
285.91	92.97	20	6.49	Chlorpyrifos-methyl
285.91	270.91	25	6.49	Chlorpyrifos-methyl
300.91	222.93	25	6.90	Chlorthal-dimethyl
331.90	300.91	15	6.90	Chlorthal-dimethyl
259.01	188.01	15	7.15	Chlozolinate
188.01	147.01	20	7.15	Chlozolinate
349.05	266.04	15	8.33	Clodinafop-propargyl
349.05	238.04	15	8.33	Clodinafop-propargyl
304.01	138.01	10	9.54	Clofentezine
304.01	132.01	10	9.54	Clofentezine
321.00	304.00	22	7.51	Clorfluazuron
323.00	306.00	20	7.51	Clorfluazuron
251.02	139.02	22	7.97	Clorpropilato
253.01	139.00	15	7.97	Clorpropilato
226.01	198.00	12	9.72	Coumaphos
226.01	163.01	20	9.72	Coumaphos
225.08	198.07	10	6.86	Cyanazine
225.08	189.07	10	6.86	Cyanazine
206.03	151.02	20	9.90	Cyfluthrin
226.03	206.03	17	9.90	Cyfluthrin
181.04	152.03	23	9.22	Cyhalothrin, lambda
197.04	141.03	15	9.22	Cyhalothrin, lambda
163.03	127.02	12	10.07	Cypermethrin+alfametrina
181.03	152.03	17	10.07	Cypermethrin+alfametrina
222.09	125.05	20	7.89	Cyproconazole
224.09	127.05	20	7.89	Cyproconazole
224.13	208.12	20	7.14	Cyprodinil
225.13	210.12	18	7.14	Cyprodinil
234.98	164.98	20	7.75	DDD, o,p
236.98	164.98	20	8.05	DDD, o,p
234.97	198.97	18	8.05	DDD, p,p
234.97	164.98	20	7.75	DDD, p,p
245.96	175.97	25	7.42	DDE o,p
317.94	245.95	20	7.42	DDE o,p
245.95	175.97	25	7.68	DDE p,p
247.95	175.97	20	7.68	DDE p,p
234.95	164.96	15	7.74	DDT o,p
236.94	164.96	20	7.74	DDT o,p
234.94	198.95	15	8.04	DDT p,p
234.94	164.96	20	8.04	DDT p,p
252.93	171.95	10	10.89	Deltamethrin+Tralometrina
252.93	173.95	10	10.89	Deltamethrin+Tralometrina
199.06	93.03	15	6.09	Diazinon
304.10	179.06	15	6.09	Diazinon
222.98	204.98	10	6.43	Dichlofenthion
278.97	222.98	15	6.43	Dichlofenthion

Precursor	Product	CE	Rention Time	Pesticide
223.97	122.99	15	6.79	Dichlofluanid
225.97	122.99	15	6.79	Dichlofluanid
205.97	175.97	10	5.92	Dichloran
207.96	177.97	10	5.92	Dichloran
184.95	92.98	17	3.82	Dichlorphos
219.95	184.95	10	3.82	Dichlorphos
270.07	159.04	15	7.80	Diclobutrazol
272.08	161.04	15	7.80	Diclobutrazol
138.97	110.97	20	6.98	Dicofol (1st, 2nd degr.)
250.94	138.97	15	6.98	Dicofol (1st, 2nd degr.)
276.92	206.93	20	7.83	Dieldrin
276.92	240.92	10	7.83	Dieldrin
267.15	225.12	8	6.83	Diethofencarb
267.15	168.09	10	6.83	Diethofencarb
323.05	265.04	15	10.75	Difenoconazole 1+2
325.05	267.04	20	10.75	Difenoconazole 1+2
266.05	246.05	10	8.48	Diflufenican
394.07	266.05	10	8.48	Diflufenican
125.00	79.00	15	5.92	Dimethoate
229.01	87.01	5	5.92	Dimethoate
301.10	165.05	10	11.04	Dimethomorph 1+2
387.12	301.10	12	11.04	Dimethomorph 1+2
268.06	232.05	15	8.02	Diniconazole
270.06	234.05	15	8.02	Diniconazole
305.08	244.07	15	6.17	Dinitramine
307.08	216.06	15	6.17	Dinitramine
167.09	165.09	20	7.04	Diphenamid
239.13	167.09	10	7.04	Diphenamid
167.10	166.09	25	5.51	Diphenylamine
169.10	168.09	20	5.51	Diphenylamine
142.01	109.01	10	6.20	Disulfoton
186.02	153.02	5	6.20	Disulfoton
271.03	243.03	5	7.51	Ditalimfos
299.04	243.03	10	7.51	Ditalimfos
273.88	238.89	15	7.54	Endosulfan A+B
271.88	236.89	15	7.54	Endosulfan A+B
280.91	244.92	5	8.07	Endrin
344.88	280.90	8	8.07	Endrin
192.04	138.03	10	8.26	Epoxiconazole
192.04	111.02	10	8.26	Epoxiconazole
128.08	86.05	5	4.35	EPTC
189.12	128.08	5	4.35	EPTC
245.04	173.03	15	8.00	Etaconazole 1+2
245.04	191.03	10	8.00	Etaconazole 1+2
230.99	129.01	20	8.03	Ethion
230.99	174.99	15	8.03	Ethion
202.14	145.10	20	5.91	Ethoxyquin
202.14	174.12	15	5.91	Ethoxyquin
163.09	135.07	10	10.21	Etofenprox
163.09	107.06	16	10.21	Etofenprox
158.04	130.03	10	5.53	Etoprofos
200.05	158.04	10	5.53	Etoprofos
210.93	182.94	15	4.78	Etridiazole (Terrazole)
210.93	139.95	15	4.78	Etridiazole (Terrazole)
292.06	153.03	10	6.21	Etrimfos
292.09	181.04	10	6.21	Etrimfos
238.08	209.07	20	8.88	Fenamidone
238.08	237.08	20	8.88	Fenamidone
288.10	260.09	10	7.54	Fenamiphos
303.11	260.09	15	7.54	Fenamiphos
139.01	111.01	15	9.38	Fenarimol
251.03	139.01	15	9.38	Fenarimol

Precursor	Product	CE	Rention Time	Pesticide
145.08	117.07	15	8.97	Fenazaquin
160.09	117.07	20	8.97	Fenazaquin
129.04	102.03	15	9.91	Fenbuconazole
198.07	129.04	10	9.91	Fenbuconazole
284.82	269.97	12	6.61	Fenchlorphos (VS)
286.72	272.08	12	6.61	Fenchlorphos (VS)
177.04	113.02	15	8.39	Fenhexamid
301.06	97.02	15	8.39	Fenhexamid
277.02	109.01	8	6.72	Fenitrothion
277.02	260.02	10	6.72	Fenitrothion
265.13	89.04	10	8.86	Fenpropathrin
265.13	210.10	15	8.86	Fenpropathrin
145.13	117.11	10	6.72	Fenpropidin
274.25	98.09	10	6.72	Fenpropidin
128.11	70.06	15	6.89	Fenpropimorph
128.11	110.09	15	6.89	Fenpropimorph
267.98	77.00	20	7.03	Fenson
267.98	141.00	10	7.03	Fenson
293.03	125.01	10	7.97	Fensulfothion
293.03	97.01	16	7.97	Fensulfothion
278.02	109.01	18	6.88	Fenthion
278.02	169.01	20	6.88	Fenthion
167.05	125.04	10	10.52	Fenvalerate 1+2
419.13	225.07	10	10.52	Fenvalerate 1+2
419.94	350.95	15	7.03	Fipronil
421.94	352.95	15	7.03	Fipronil
383.13	254.09	20	7.85	Fluazifop-P-butyl
383.13	282.10	15	7.85	Fluazifop-P-butyl
388.90	352.20	12	7.72	Fluazinam
388.90	354.20	12	7.72	Fluazinam
167.00	77.00	15	7.52	Flubenzimine
186.00	77.00	25	7.52	Flubenzimine
199.07	107.04	22	10.14	Flucitrinate 1+2
199.07	157.06	10	10.14	Flucitrinate 1+2
248.04	154.02	20	7.60	Fludioxonil
248.04	182.03	15	7.60	Fludioxonil
211.04	183.03	10	6.89	Flufenacet
211.04	123.02	10	6.89	Flufenacet
346.95	171.93	26	8.36	Fluopicolide
346.95	176.02	26	8.36	Fluopicolide
313.01	174.01	15	6.96	Fluorocloridone I+II
313.01	187.01	15	6.96	Fluorocloridone I+II
340.01	286.01	25	9.73	Fluquinconazole
340.01	298.01	22	9.73	Fluquinconazole
233.07	152.05	20	7.72	Flusilazole
233.07	165.05	20	7.72	Flusilazole
123.04	75.03	15	7.55	Flutriafol
219.07	123.04	15	7.55	Flutriafol
250.06	200.05	20	10.57	Fluvalinate tau
252.06	200.05	20	10.57	Fluvalinate tau
261.60	129.80	15	7.35	Folpet
261.60	234.40	5	7.35	Folpet
146.98	103.24	15	4.86	Folpet met.
146.98	104.39	15	4.86	Folpet met.
137.02	109.01	10	6.11	Fonofos
246.03	137.02	10	6.11	Fonofos
224.01	125.01	15	6.34	Formothion
224.01	196.01	10	6.34	Formothion
242.11	95.04	15	7.26	Furalaxyl
301.13	225.10	10	7.26	Furalaxyl
375.05	316.04	10	7.33	Haloxyfop-methyl
375.05	288.04	20	7.33	Haloxyfop-methyl

Fast GC-MS/MS Data for Pesticide Standards *(Table 1 continued)*

Precursor	Product	CE	Rention Time	Pesticide
273.87	238.88	15	6.63	Heptachlor
271.87	236.89	15	6.63	Heptachlor
182.91	154.93	15	7.26	Heptachlor epoxide B
134.93	98.95	15	7.26	Heptachlor epoxide B
352.83	262.87	15	7.23	Heptachlor epoxide A
352.83	281.86	16	7.23	Heptachlor epoxide A
124.01	89.01	10	5.26	Heptenophos
250.02	89.01	25	7.62	Heptenophos
283.81	213.86	20	7.62	Hexachlorobenzene (HCB)
283.81	248.84	20	7.47	Hexachlorobenzene (HCB)
214.05	172.04	20	7.47	Hexaconazole
214.05	187.04	15	5.26	Hexaconazole
184.05	149.04	10	7.62	Hexythiazox
227.07	149.04	10	7.62	Hexythiazox
173.00	145.00	20	10.79	Imazalil
175.00	147.00	16	10.79	Imazalil
203.03	106.01	20	8.72	Indoxacarb
203.03	134.02	20	8.72	Indoxacarb
314.03	245.03	15	8.00	Iprodione
316.03	247.03	15	8.00	Iprodione
243.88	187.00	16	6.08	Iprodione degr.
243.88	188.00	16	6.08	Iprodione degr.
213.07	121.04	17	7.05	Isofenphos
213.07	185.06	10	7.05	Isofenphos
280.15	180.10	15	7.72	Isopropalin
280.15	238.13	10	7.72	Isopropalin
131.06	116.05	20	8.34	Kresoxim-methyl
206.09	131.06	15	8.34	Kresoxim-methyl
153.09	82.05	15	5.00	Lenacil
153.09	136.08	15	5.00	Lenacil
175.99	120.99	20	4.60	Lufenuron 1
175.99	147.99	20	4.60	Lufenuron 1
352.99	173.99	25	6.77	Lufenuron 2
352.99	202.99	25	6.77	Lufenuron 2
173.02	99.01	10	8.60	Malathion
173.02	127.01	10	8.60	Malathion
253.04	190.03	20	7.49	Mefenpyr-diethyl
253.04	189.03	20	7.49	Mefenpyr-diethyl
222.11	207.10	15	6.58	Mepanipyrim
223.11	208.10	15	6.58	Mepanipyrim
234.11	174.11	10	7.81	Metalaxyl
249.13	190.10	10	7.81	Metalaxyl
202.09	174.07	5	7.11	Metamitron
202.09	186.08	10	7.11	Metamitron
133.05	117.04	20	5.71	Metazachlor
209.07	132.05	12	5.71	Metazachlor
164.05	136.04	20	7.38	Methabenzthiazuron
164.05	135.04	20	7.38	Methabenzthiazuron
144.98	57.99	15	8.48	Methidathion
144.98	84.99	10	8.48	Methidathion
227.01	169.01	20	6.85	Methoxychlor I
227.01	212.01	15	6.85	Methoxychlor I
162.08	133.06	15	6.48	Metolachlor
238.11	162.08	15	6.48	Metolachlor
198.08	82.03	20	4.64	Metribuzin
198.08	110.05	20	4.64	Metribuzin
127.04	109.02	10	9.37	Mevinphos
192.04	127.03	12	9.37	Mevinphos
269.81	234.84	15	5.18	Mirex
271.81	236.84	15	5.18	Mirex
126.07	55.03	10	5.67	Molinate (Ordram)
187.10	126.07	10	5.67	Molinate (Ordram)

Precursor	Product	CE	Rention Time	Pesticide
127.03	95.03	20	7.72	Monocrotophos
192.05	127.03	10	7.72	Monocrotophos
179.07	125.05	15	3.82	Myclobutanil
179.07	90.00	30	7.58	Myclobutanil
109.00	79.00	12	7.58	Naled
128.07	72.04	10	7.91	Napropamide
271.16	128.07	5	7.91	Napropamide
201.99	138.99	21	8.48	Nitrofen
282.98	252.98	15	8.48	Nitrofen
235.05	139.03	15	5.09	Nuarimol
314.06	139.03	15	5.09	Nuarimol
170.07	115.05	20	7.68	Ortho-phenylphenol
170.07	141.06	20	7.68	Ortho-phenylphenol
258.05	175.04	10	8.02	Oxadiazon
304.06	260.05	10	8.02	Oxadiazon
163.07	117.05	40	7.71	Oxadixyl
163.07	132.06	10	7.71	Oxadixyl
300.03	223.02	10	7.46	Oxyfluorfen
361.03	300.03	12	7.46	Oxyfluorfen
236.10	125.06	15	7.01	Paclobutrazol
236.10	167.07	15	7.01	Paclobutrazol
149.03	119.02	10	6.19	Paraoxon-ethyl
220.05	174.04	10	6.19	Paraoxon-ethyl
230.02	136.01	10	6.92	Paraoxon-methyl
230.02	200.02	10	6.92	Paraoxon-methyl
291.03	109.01	15	6.53	Parathion-ethyl
291.03	137.02	10	6.53	Parathion-ethyl
262.99	109.00	15	7.18	Parathion-methyl
262.99	246.00	15	7.18	Parathion-methyl
248.06	157.04	25	5.75	Penconazole
248.06	192.04	15	5.75	Penconazole
125.05	89.04	12	7.12	Pencycuron
180.07	125.05	12	7.12	Pencycuron
252.13	162.08	12	9.64	Pendimethalin
252.13	191.09	12	9.64	Pendimethalin
183.04	153.03	15	7.24	Permethrin 1+2
183.04	165.03	15	7.24	Permethrin 1+2
274.03	246.02	10	5.75	Phenthoate
274.03	121.01	7	5.75	Phenthoate
231.01	203.01	10	9.11	Phorate
260.01	75.01	5	9.11	Phorate
181.99	111.00	15	8.79	Phosalone
366.99	181.99	10	8.79	Phosalone
160.01	77.01	20	6.40	Phosmet
160.01	133.01	15	6.40	Phosmet
227.05	127.03	15	6.29	Phosphamidon I+II
264.06	127.03	15	6.29	Phosphamidon I+II
166.10	137.08	10	7.00	Pirimicarb
238.14	166.10	15	7.00	Pirimicarb
304.12	168.06	15	6.68	Pirimiphos-ethyl
333.13	318.12	15	6.68	Pirimiphos-ethyl
290.09	233.07	10	9.76	Pirimiphos-methyl
305.10	290.09	15	9.76	Pirimiphos-methyl
180.01	138.01	15	7.29	Prochloraz
308.03	70.01	10	7.29	Prochloraz
283.02	255.02	10	7.66	Procymidone
285.02	257.02	10	7.66	Procymidone
336.94	266.95	20	6.01	Profenofos
338.94	268.95	20	6.01	Profenofos
318.10	198.05	15	5.91	Profluralin
330.10	302.10	5	5.91	Profluralin
225.16	183.13	10	6.60	Prometon

Precursor	Product	CE	Rention Time	Pesticide
225.16	210.15	10	6.60	Prometon
226.13	184.10	12	5.43	Prometryn
241.15	184.10	15	5.43	Prometryn
176.06	120.04	10	6.44	Propachlor
196.07	120.04	10	6.44	Propachlor
217.01	161.00	10	8.49	Propanil
219.01	163.00	10	8.49	Propanil
135.06	107.05	15	6.03	Propargite
173.08	105.05	12	6.03	Propargite
236.07	166.05	15	4.79	Propetamphos
236.07	194.06	5	4.79	Propetamphos
137.07	93.05	8	8.30	Propham
179.09	93.05	15	8.30	Propham
259.02	173.02	20	5.41	Propiconazole 1+2
261.02	175.02	20	5.41	Propiconazole 1+2
110.00	64.00	10	6.10	Propoxur
152.00	110.00	10	6.10	Propoxur
145.01	109.01	15	7.63	Propyzamide
173.01	109.01	18	7.63	Propyzamide
266.97	238.97	10	10.56	Prothiofos
308.97	238.97	5	10.56	Prothiofos
132.03	77.02	15	9.33	Pyraclostrobin
325.08	132.03	20	9.33	Pyraclostrobin
221.05	193.04	10	9.74	Pyrazophos
232.05	204.05	10	9.74	Pyrazophos
147.06	117.04	20	8.69	Pyridaben
309.12	147.06	15	8.69	Pyridaben
340.06	109.02	10	7.20	Pyridaphenthion
340.06	199.04	10	7.20	Pyridaphenthion
262.03	192.02	20	6.16	Pyrifenox 1+2
262.03	200.02	20	6.16	Pyrifenox 1+2
198.11	118.07	35	7.25	Pyrimethanil
198.11	183.10	15	7.25	Pyrimethanil
146.03	91.02	15	8.34	Quinalphos
146.03	118.02	15	8.34	Quinalphos
237.05	208.00	20	6.03	Quinoxyfen
272.01	237.00	20	6.03	Quinoxyfen
292.84	234.87	15	6.68	Quintozene (PCNB)
294.84	236.87	20	6.68	Quintozene (PCNB)
129.93	94.95	22	8.53	S421
131.93	96.95	22	8.53	S421
178.01	81.00	24	5.65	Sethoxydim
178.01	107.95	21	5.65	Sethoxydim
202.01	146.01	15	7.31	Sulfotep
322.02	202.01	15	7.31	Sulfotep
255.78	159.87	12	8.50	Sulphur
255.78	95.83	24	8.50	Sulphur
250.12	125.06	20	8.97	Tebuconazole
252.12	127.06	20	8.97	Tebuconazole
145.00	117.00	10	8.91	tebufenozide
160.00	145.00	15	8.91	tebufenozide
276.13	171.08	15	5.35	Tebufenpyrad
318.15	145.07	15	5.35	Tebufenpyrad
260.88	202.90	15	6.19	Tecnazene
258.88	200.90	15	6.19	Tecnazene
177.02	127.02	20	6.07	Tefluthrin
197.03	141.02	15	6.07	Tefluthrin
231.04	175.03	15	6.02	Terbufos
231.04	203.03	10	6.02	Terbufos
214.10	104.05	10	6.70	Terbuthylazine
214.10	132.06	10	6.70	Terbuthylazine
241.14	185.10	10	7.42	Terbutryn
241.14	170.10	15	7.42	Terbutryn
328.91	108.97	22	6.89	Tetrachlorvinphos
330.91	108.97	22	6.89	Tetrachlorvinphos
336.02	218.01	20	9.06	Tetraconazole
336.02	204.01	20	9.06	Tetraconazole
226.93	198.94	18	8.72	Tetradifon
355.88	228.93	10	8.72	Tetradifon
164.09	107.06	17	6.55	Tetramethrin
164.09	135.07	10	6.55	Tetramethrin
264.96	92.99	20	7.20	Tolclofos-methyl
264.96	249.96	15	7.20	Tolclofos-methyl
238.09	137.05	15	6.93	Tolylfluanid
240.09	137.05	15	6.93	Tolylfluanid
208.07	111.04	25	7.28	Triadimefon
208.07	181.06	10	7.28	Triadimefon
128.05	100.04	10	8.15	Triadimenol
168.06	70.03	10	8.15	Triadimenol
161.03	105.02	13	3.82	Triazophos
257.05	162.03	10	3.82	Triazophos
161.94	160.93	8	7.69	Triciclazole
188.98	160.93	20	7.69	Triciclazole
116.04	89.03	15	8.24	Trifloxystrobin
131.04	130.04	10	8.24	Trifloxystrobin
306.10	160.05	15	5.61	Trifluralin
306.10	264.09	15	5.61	Trifluralin
145.02	87.01	10	7.43	Vamidothion
145.02	112.02	10	7.43	Vamidothion
284.97	212.00	15	6.51	Vinclozolin
286.97	214.00	15	6.51	Vinclozolin
187.01	159.01	15	7.67	Zoxamide
258.02	187.01	15	7.67	Zoxamide
187.02	159.01	15	7.30	Zoxamide-metab.
242.01	214.01	15	7.30	Zoxamide-metab.

Table 1: 467 Timed-SRM transitions used in one run for pesticide compound detection and quantitation

Sample Measurements

More than 3,500 samples were analysed in 6 months. A weekly calibration curve for each of the pesticide components in the assay and volumetric standard quantification has been performed.

Figure 1 shows the highly overlapped elution of the compounds in a single run. The SRM distribution in Figure 2 shows the typical low homogeneity of the retention time distribution of a Fast GC run. The unique acquisition mode “Timed-SRM” of the TSQ Quantum series instruments meets the optimum acquisition conditions for each compound by only monitoring the pesticides compound in a small window around the compound retention time. With a short retention time window of 18 seconds for every compound, even in the highest density elution zone, there are up to 80 SRM scans with a scan time lower than 4 ms. For the other areas of the chromatogram, scan times of up to 30 ms are resulting.

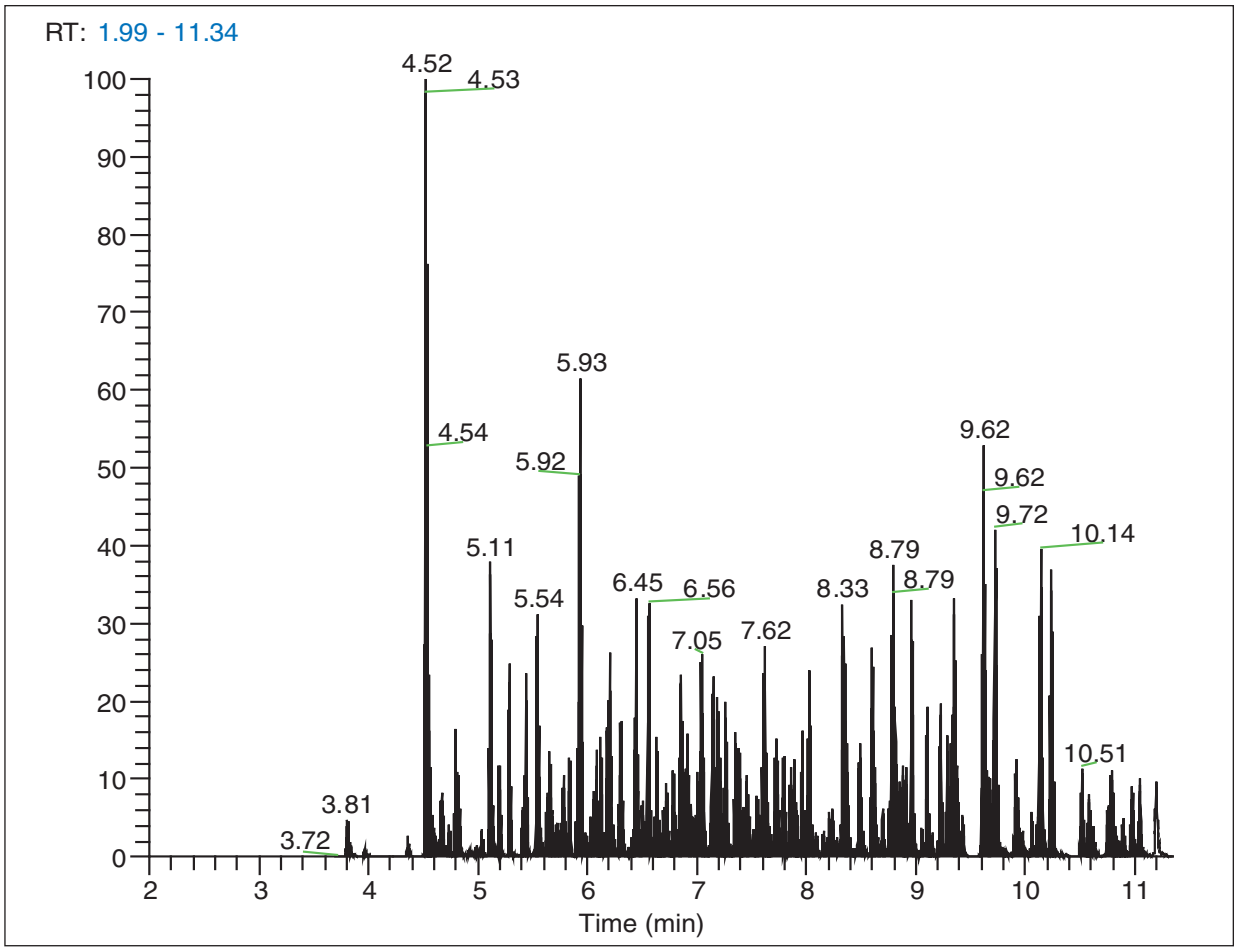

Figure 1: Highly overlapped elution of the compounds in a single run

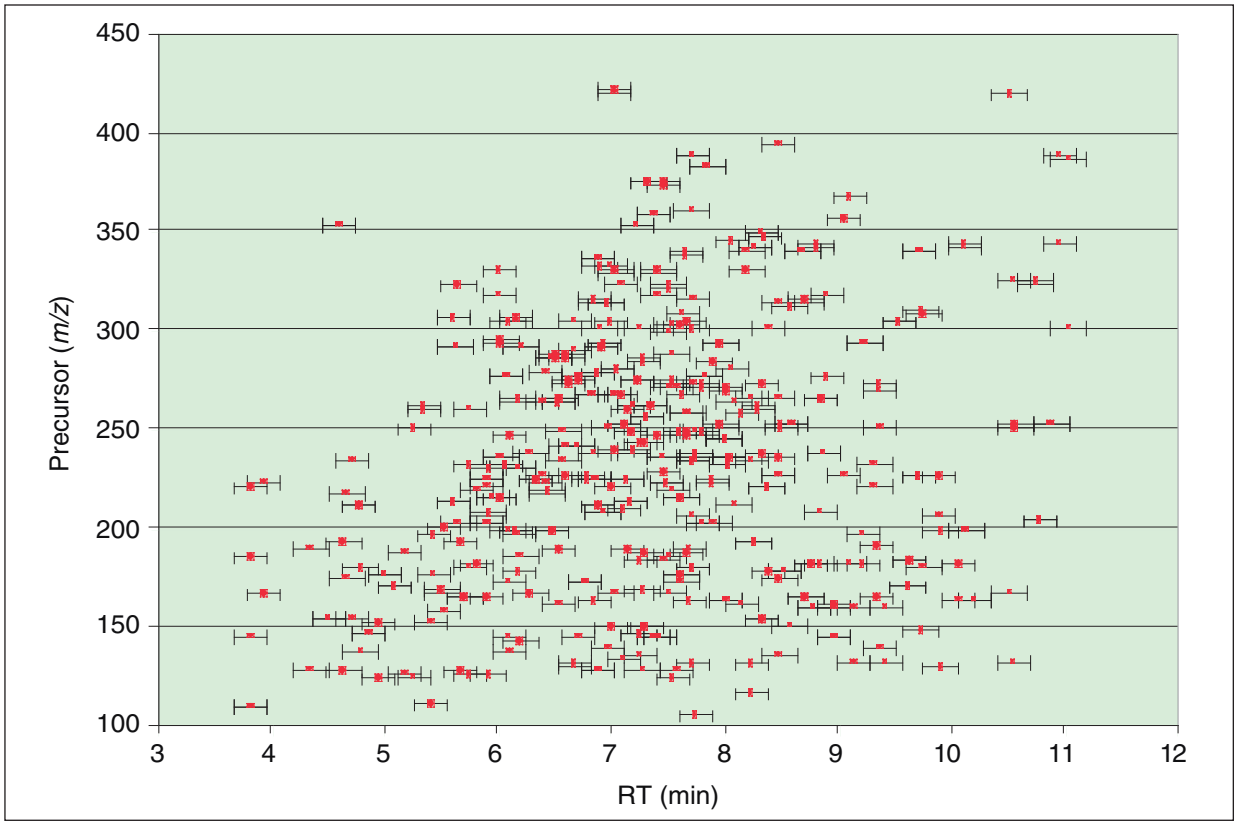

Figure 2: Timed-SRM distribution during the Fast GC chromatography

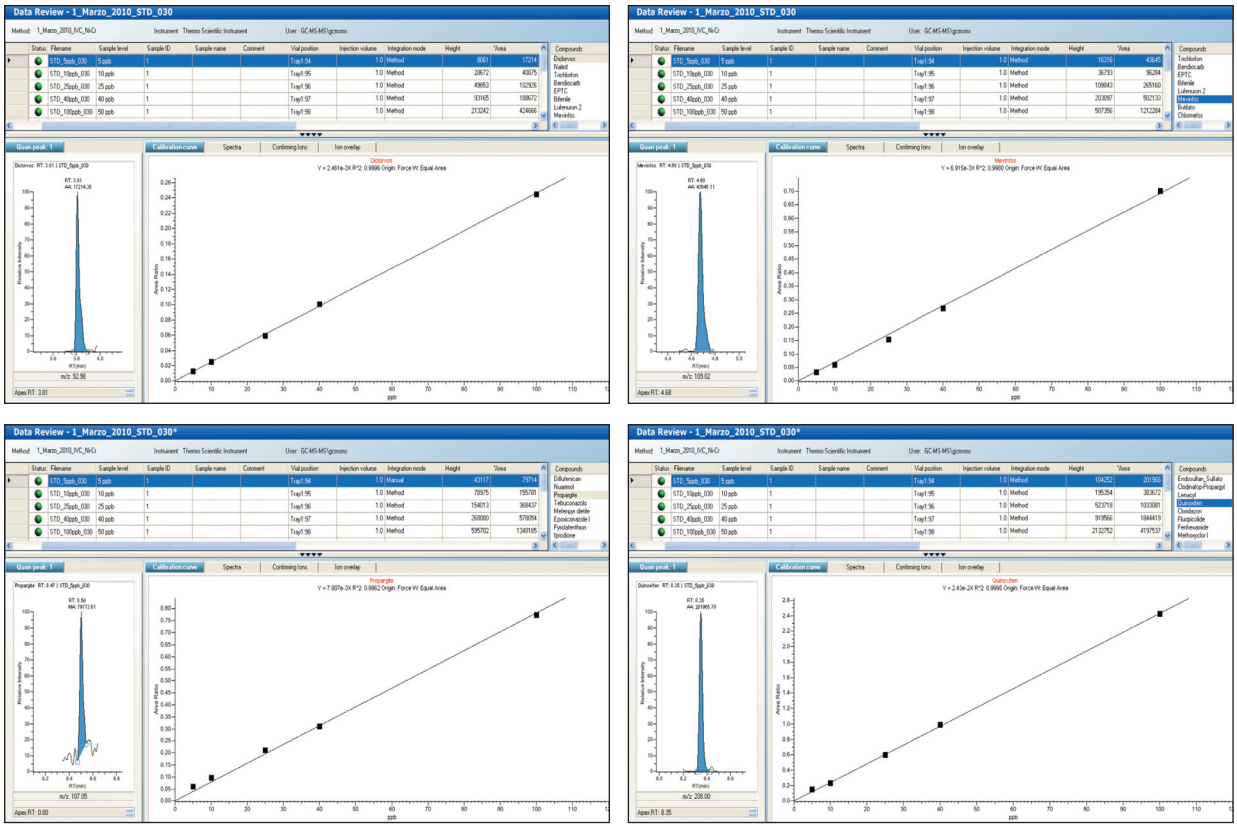

Figure 3: Calibration curve and integrated peak area of the lowest level (5 ppb) in apple matrix (Dichlorvos, Mevinphos, Propargite, Quinoxifen)

Results

Figure 3 shows the operative calibration curves and integrated peak area of the lowest calibration level (5 ppb) in apple matrix. The correlation factor of the linear calibration was always higher than 0.9950. A great sensitivity could be shown at the 5 ppb level with a S/N better than 15 for the compounds investigated.

The analysis was run at the increased mass resolution set to 0.7 Da peak width (FWHM) in Q1 and Q3. The hyperbolic rods of the mass separating quadrupoles produce a high precision quadrupolar electrical field that allow a high ion transmission coupled with increased selectivity against the unspecific matrix of the extracts. The curved square rods of the collision cell provide increased efficiency of the fragmentation especially with high ion transmission for high sensitivity. The often observed high background of neutral compounds is efficiently removed by the 90° bended collision cell and the off axis multiplier for low noise detection with high S/N values at low pesticides concentrations in these matrix samples.

For the large number of pesticide compounds in a Fast GC separation Figure 4 shows the sampling rate with the chromatographic profile of Flusilazole at the lowest calibration point of 5 ppb in apple matrix. The high statistics of sampling is the instrumental characteristics that allow the high repeatability and precision of peak integration.

With the Timed-SRM acquisition setting the two mass separating quadrupoles Q1 and Q3 increase the efficiency of sampling with only short acquisition windows around the expected compound retention time of every eluted compound. This acquisition mode is ideally suited for Fast GC separations.

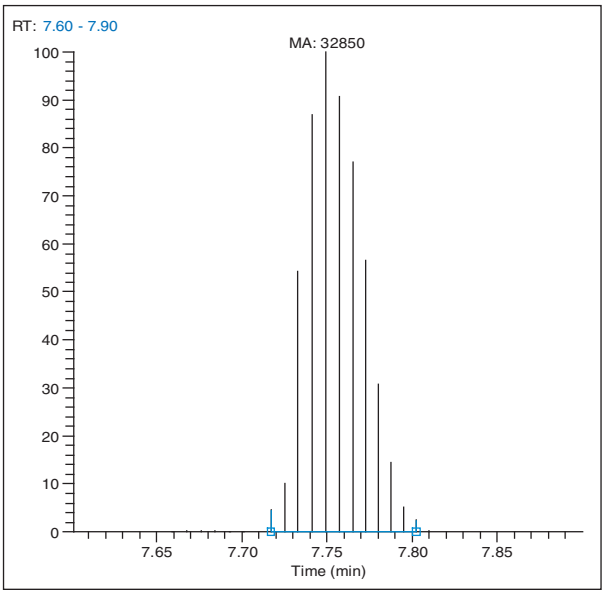

Figure 4: Flusilazole at 5 ppb in apple matrix

Figure 5 shows the superimposed chromatographic profiles of 5 repeated injections of Flucythrinate at 5 ppb in apricot matrix. The coefficients of variation (CV%) of the area integration was in the range and below of 10%. These results demonstrate the compatibility of the Fast GC solution with the TSQ Quantum GC for a true fast and reliable quantification.

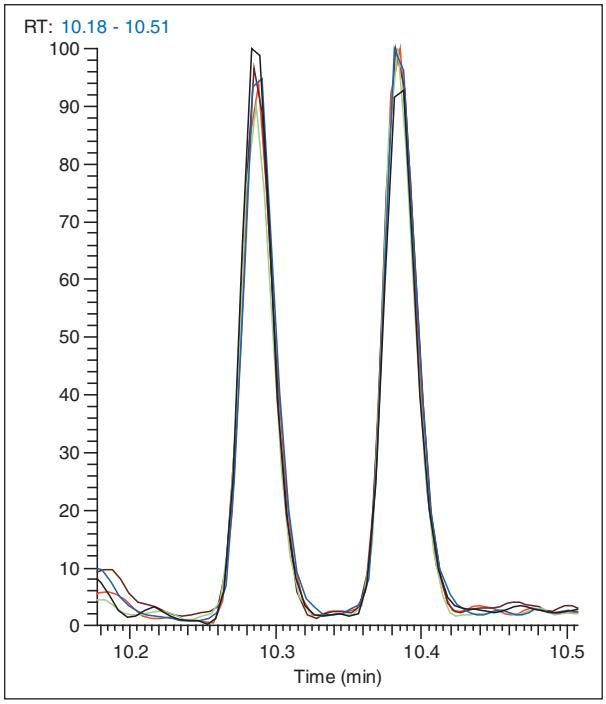

Figure 5: 5 injections of Flucythrinate at 5 ppb in apricot matrix

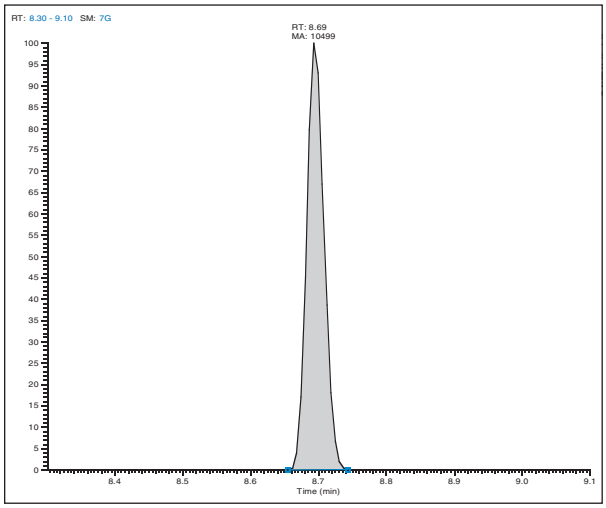

Figure 6: Iprodione at 15 ppb in onion sample

As one of the compounds with most critical chromatographic behavior, Figure 6 shows the elution profile of Iprodione at the 15 ppb level in an onion sample. A very symmetrical peak shape is associated with a very good sensitivity demonstrating the inertness and integrity of the chromatographic system from injector to transfer line and ion source. The high speed of the analysis additionally decreases the residence.

Conclusion

With the described method, a very good linearity, sensitivity and robustness have been obtained at the sensitivity levels required for being fully compatible with the reliable quantification of pesticides in vegetal matrix, with very limited breakdown phenomena and without any tailing chromatographic peaks.

The Fast GC-MS approach using the TSQ Quantum GC-MS/MS system is not only a faster method to obtain high throughput of analysis, but also the productive solution to improve the general quality of the analytical results. The Thermo Fisher TSQ Quantum GC-MS/MS system has proven to provide fast data acquisition for reliable integration of short Fast GC peaks with high selectivity and sensitivity.

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