

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 μ L of a solution of Fenchlorphos (5 ppm in hexane) as volumetric standard has been added before injection (1 μ L).

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 μ m (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 μ A
Ionisation Mode:	El, 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

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

Precursor	Product	CE	Retention Time	Pesticide	Precursor	Product	CE	Retention Time	Pesticide
212.02	182.02	10	8.09	Aclonifen	246.98	226.98	20	7.80	Chlorfenapyr
264.03	194.02	15	8.09	Aclonifen	248.98	228.98	20	7.80	Chlorfenapyr
181.02	152.04	25	8.85	Acrinathrin	174.98	110.98	10	7.62	Chlorfenson
208.05	181.04	8	8.85	Acrinathrin	301.96	174.98	10	7.62	Chlorfenson
161.07	146.06	12	6.54	Alachlor	266.98	158.99	15	7.09	Chlorfenvinphos-E+Z
188.08	160.07	10	6.54	Alachlor	322.97	266.98	15	7.09	Chlorfenvinphos-E+Z
292.91	222.92	20	6.94	Aldrin	220.04	166.03	23	8.38	Chloridazon
292.91	257.91	20	6.94	Aldrin	220.04	158.03	25	8.38	Chloridazon
293.19	147.10	15	9.24	Amitraz	153.98	120.98	5	4.72	Chlormephos
293.19	162.10	10	9.24	Amitraz	233.97	120.98	14	4.72	Chlormephos
215.09	200.09	10	5.95	Atrazine	263.88	167.92	25	6.18	Chlorothalonil
215.09	173.08	10	5.95	Atrazine	265.88	169.92	25	6.18	Chlorothalonil
132.01	77.01	20	9.43	Azinphos-ethyl	213.06	127.03	15	5.61	Chlorpropham
160.02	104.01	10	9.43	Azinphos-ethyl	213.06	171.04	10	5.61	Chlorpropham
132.02	77.02	20	9.15	Azinphos-Methyl	313.93	257.95	15	6.85	Chlorpyrifos-ethyl
160.03	104.02	10	9.15	Azinphos-Methyl	315.93	259.95	12	6.85	Chlorpyrifos-ethyl
344.10	329.10	20	10.96	Azoxystrobin	285.91	92.97	20	6.49	Chlorpyrifos-methyl
388.11	345.10	15	10.96	Azoxystrobin	285.91	270.91	25	6.49	Chlorpyrifos-methyl
234.12	174.09	10	8.24	Benalaxyl	300.91	222.93	25	6.90	Chlorthal-dimethyl
266.14	148.08	10	8.24	Benalaxyl	331.90	300.91	15	6.90	Chlorthal-dimethyl
166.06	151.06	15	3.94	Bendiocarb	259.01	188.01	15	7.15	Chlozolinate
223.08	166.06	15	3.94	Bendiocarb	188.01	147.01	20	7.15	Chlozolinate
292.10	160.05	21	5.63	Benfluralin	349.05	266.04	15	8.33	Clodinafop-propargyl
292.10	264.09	10	5.63	Benfluralin	349.05	238.04	15	8.33	Clodinafop-propargyl
164.08	149.07	10	9.35	Benfuracarb	304.01	138.01	10	9.54	Clofentezine
190.09	144.07	10	9.35	Benfuracarb	304.01	132.01	10	9.54	Clofentezine
180.91	144.93	15	5.82	BHC, A+B+C+D	321.00	304.00	22	7.51	Clorfluzuron
218.89	182.91	15	5.82	BHC, A+B+C+D	323.00	306.00	20	7.51	Clorfluzuron
154.08	152.08	15	4.51	Bifenil	251.02	139.02	22	7.97	Clorpropilato
154.08	153.08	15	4.51	Bifenil	253.01	139.00	15	7.97	Clorpropilato
181.05	141.04	22	8.77	Bifenthrin	226.01	198.00	12	9.72	Coumaphos
181.05	153.05	6	8.77	Bifenthrin	226.01	163.01	20	9.72	Coumaphos
170.09	115.06	25	9.62	Bitertanol	225.08	198.07	10	6.86	Cyanazine
170.09	141.07	20	9.62	Bitertanol	225.08	189.07	10	6.86	Cyanazine
342.01	140.01	20	10.12	Boscalid (Nicobifen)	206.03	151.02	20	9.90	Cyfluthrin
344.01	140.01	20	10.12	Boscalid (Nicobifen)	226.03	206.03	17	9.90	Cyfluthrin
328.86	313.87	20	7.04	Bromophos-methyl	181.04	152.03	23	9.22	Cyhalothrin, lambda
330.86	315.87	20	7.04	Bromophos-methyl	197.04	141.03	15	9.22	Cyhalothrin, lambda
358.89	302.91	20	7.38	Bromophos-ethyl	163.03	127.02	12	10.07	Cypermethrin+alfametrina
358.89	330.90	10	7.38	Bromophos-ethyl	181.03	152.03	17	10.07	Cypermethrin+alfametrina
340.96	184.98	15	8.81	Bromopropylate	222.09	125.05	20	7.89	Cyproconazole
342.96	184.98	20	8.81	Bromopropylate	224.09	127.05	20	7.89	Cyproconazole
273.14	193.10	10	7.73	Bupirimate	224.13	208.12	20	7.14	Cyprodinil
316.16	208.10	10	7.73	Bupirimate	225.13	210.12	18	7.14	Cyprodinil
104.94	104.00	9	7.75	Buprofezin	234.98	164.98	20	7.75	DDD, o,p
249.13	193.10	10	7.75	Buprofezin	236.98	164.98	20	8.05	DDD, o,p
174.12	146.10	10	4.67	Butylate (Sutan)	234.97	198.97	18	8.05	DDD, p,p
217.15	156.11	5	4.67	Butylate (Sutan)	234.97	164.98	20	7.75	DDD, p,p
149.96	78.98	15	8.58	Captafol	245.96	175.97	25	7.42	DDE o,p
310.92	78.98	10	8.58	Captafol	317.94	245.95	20	7.42	DDE o,p
123.05	79.03	15	4.95	Captafol-captan Met. (THPI)	245.95	175.97	25	7.68	DDE p,p
151.06	122.05	10	4.95	Captafol-captan Met. (THPI)	247.95	175.97	20	7.68	DDE p,p
148.97	69.98	8	7.30	Captan	234.95	164.96	15	7.74	DDT o,p
148.97	104.98	8	7.30	Captan	236.94	164.96	20	7.74	DDT o,p
164.01	149.00	10	5.91	Carbofuran	234.94	198.95	15	8.04	DDT p,p
221.01	164.00	5	5.91	Carbofuran	234.94	164.96	20	8.04	DDT p,p
341.97	156.99	10	8.27	Carbophenothion	252.93	171.95	10	10.89	Deltamethrin+Tralometrina
341.97	295.98	5	8.27	Carbophenothion	252.93	173.95	10	10.89	Deltamethrin+Tralometrina
330.03	310.03	20	8.20	Carfentrazone-ethyl	199.06	93.03	15	6.09	Diazinon
340.03	312.03	20	8.20	Carfentrazone-ethyl	304.10	179.06	15	6.09	Diazinon
372.81	265.87	15	7.47	Chlordane	222.98	204.98	10	6.43	Dichlofenthion
374.81	267.87	15	7.47	Chlordane	278.97	222.98	15	6.43	Dichlofenthion

Precursor	Product	CE	Retention 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	Retention 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	Haloxifop-methyl
375.05	288.04	20	7.33	Haloxifop-methyl

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

Precursor	Product	CE	Retention Time	Pesticide	Precursor	Product	CE	Retention Time	Pesticide
273.87	238.88	15	6.63	Heptachlor	127.03	95.03	20	7.72	Monocrotophos
271.87	236.89	15	6.63	Heptachlor	192.05	127.03	10	7.72	Monocrotophos
182.91	154.93	15	7.26	Heptachlor epoxide B	179.07	125.05	15	3.82	Myclobutanil
134.93	98.95	15	7.26	Heptachlor epoxide B	179.07	90.00	30	7.58	Myclobutanil
352.83	262.87	15	7.23	Heptachlor epoxide A	109.00	79.00	12	7.58	Naled
352.83	281.86	16	7.23	Heptachlor epoxide A	128.07	72.04	10	7.91	Napropamide
124.01	89.01	10	5.26	Heptenophos	271.16	128.07	5	7.91	Napropamide
250.02	89.01	25	7.62	Heptenophos	201.99	138.99	21	8.48	Nitrofen
283.81	213.86	20	7.62	Hexachlorobenzene (HCB)	282.98	252.98	15	8.48	Nitrofen
283.81	248.84	20	7.47	Hexachlorobenzene (HCB)	235.05	139.03	15	5.09	Nuarimol
214.05	172.04	20	7.47	Hexaconazole	314.06	139.03	15	5.09	Nuarimol
214.05	187.04	15	5.26	Hexaconazole	170.07	115.05	20	7.68	Ortho-phenylphenol
184.05	149.04	10	7.62	Hexythiazox	170.07	141.06	20	7.68	Ortho-phenylphenol
227.07	149.04	10	7.62	Hexythiazox	258.05	175.04	10	8.02	Oxadiazon
173.00	145.00	20	10.79	Imazalil	304.06	260.05	10	8.02	Oxadiazon
175.00	147.00	16	10.79	Imazalil	163.07	117.05	40	7.71	Oxadixyl
203.03	106.01	20	8.72	Indoxacarb	163.07	132.06	10	7.71	Oxadixyl
203.03	134.02	20	8.72	Indoxacarb	300.03	223.02	10	7.46	Oxyfluorfen
314.03	245.03	15	8.00	Iprodione	361.03	300.03	12	7.46	Oxyfluorfen
316.03	247.03	15	8.00	Iprodione	236.10	125.06	15	7.01	Paclobutrazol
243.88	187.00	16	6.08	Iprodione degr.	236.10	167.07	15	7.01	Paclobutrazol
243.88	188.00	16	6.08	Iprodione degr.	149.03	119.02	10	6.19	Paraoxon-ethyl
213.07	121.04	17	7.05	Isofenphos	220.05	174.04	10	6.19	Paraoxon-ethyl
213.07	185.06	10	7.05	Isofenphos	230.02	136.01	10	6.92	Paraoxon-methyl
280.15	180.10	15	7.72	Isopropalin	230.02	200.02	10	6.92	Paraoxon-methyl
280.15	238.13	10	7.72	Isopropalin	291.03	109.01	15	6.53	Parathion-ethyl
131.06	116.05	20	8.34	Kresoxim-methyl	291.03	137.02	10	6.53	Parathion-ethyl
206.09	131.06	15	8.34	Kresoxim-methyl	262.99	109.00	15	7.18	Parathion-methyl
153.09	82.05	15	5.00	Lenacil	262.99	246.00	15	7.18	Parathion-methyl
153.09	136.08	15	5.00	Lenacil	248.06	157.04	25	5.75	Penconazole
175.99	120.99	20	4.60	Lufenuron 1	248.06	192.04	15	5.75	Penconazole
175.99	147.99	20	4.60	Lufenuron 1	125.05	89.04	12	7.12	Pencycuron
352.99	173.99	25	6.77	Lufenuron 2	180.07	125.05	12	7.12	Pencycuron
352.99	202.99	25	6.77	Lufenuron 2	252.13	162.08	12	9.64	Pendimethalin
173.02	99.01	10	8.60	Malathion	252.13	191.09	12	9.64	Pendimethalin
173.02	127.01	10	8.60	Malathion	183.04	153.03	15	7.24	Permethrin 1+2
253.04	190.03	20	7.49	Mefenpyr-diethyl	183.04	165.03	15	7.24	Permethrin 1+2
253.04	189.03	20	7.49	Mefenpyr-diethyl	274.03	246.02	10	5.75	Phenthoate
222.11	207.10	15	6.58	Mepanipyrim	274.03	121.01	7	5.75	Phenthoate
223.11	208.10	15	6.58	Mepanipyrim	231.01	203.01	10	9.11	Phorate
234.11	174.11	10	7.81	Metalaxyl	260.01	75.01	5	9.11	Phorate
249.13	190.10	10	7.81	Metalaxyl	181.99	111.00	15	8.79	Phosalone
202.09	174.07	5	7.11	Metamitron	366.99	181.99	10	8.79	Phosalone
202.09	186.08	10	7.11	Metamitron	160.01	77.01	20	6.40	Phosmet
133.05	117.04	20	5.71	Metazachlor	160.01	133.01	15	6.40	Phosmet
209.07	132.05	12	5.71	Metazachlor	227.05	127.03	15	6.29	Phosphamidon I+II
164.05	136.04	20	7.38	Methabenzthiazuron	264.06	127.03	15	6.29	Phosphamidon I+II
164.05	135.04	20	7.38	Methabenzthiazuron	166.10	137.08	10	7.00	Pirimicarb
144.98	57.99	15	8.48	Methidathion	238.14	166.10	15	7.00	Pirimicarb
144.98	84.99	10	8.48	Methidathion	304.12	168.06	15	6.68	Pirimiphos-ethyl
227.01	169.01	20	6.85	Methoxychlor I	333.13	318.12	15	6.68	Pirimiphos-ethyl
227.01	212.01	15	6.85	Methoxychlor I	290.09	233.07	10	9.76	Pirimiphos-methyl
162.08	133.06	15	6.48	Metolachlor	305.10	290.09	15	9.76	Pirimiphos-methyl
238.11	162.08	15	6.48	Metolachlor	180.01	138.01	15	7.29	Prochloraz
198.08	82.03	20	4.64	Metribuzin	308.03	70.01	10	7.29	Prochloraz
198.08	110.05	20	4.64	Metribuzin	283.02	255.02	10	7.66	Procymidone
127.04	109.02	10	9.37	Mevinphos	285.02	257.02	10	7.66	Procymidone
192.04	127.03	12	9.37	Mevinphos	336.94	266.95	20	6.01	Profenofos
269.81	234.84	15	5.18	Mirex	338.94	268.95	20	6.01	Profenofos
271.81	236.84	15	5.18	Mirex	318.10	198.05	15	5.91	Profluralin
126.07	55.03	10	5.67	Molinate (Ordram)	330.10	302.10	5	5.91	Profluralin
187.10	126.07	10	5.67	Molinate (Ordram)	225.16	183.13	10	6.60	Prometon

Precursor	Product	CE	Retention 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	Quinoxifen
272.01	237.00	20	6.03	Quinoxifen
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

Precursor	Product	CE	Retention Time	Pesticide
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	Tolyfluanid
240.09	137.05	15	6.93	Tolyfluanid
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.

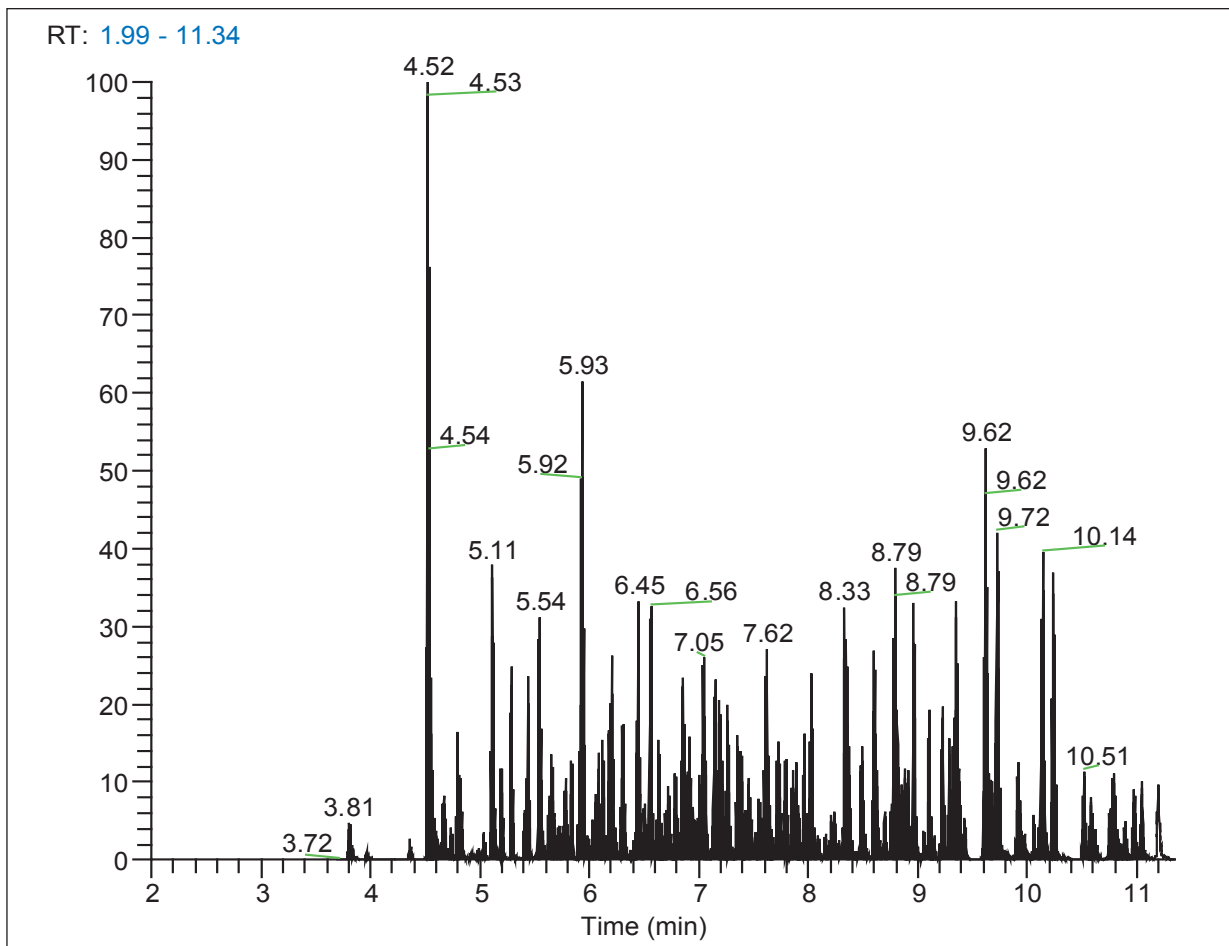


Figure 1: Highly overlapped elution of the compounds in a single run

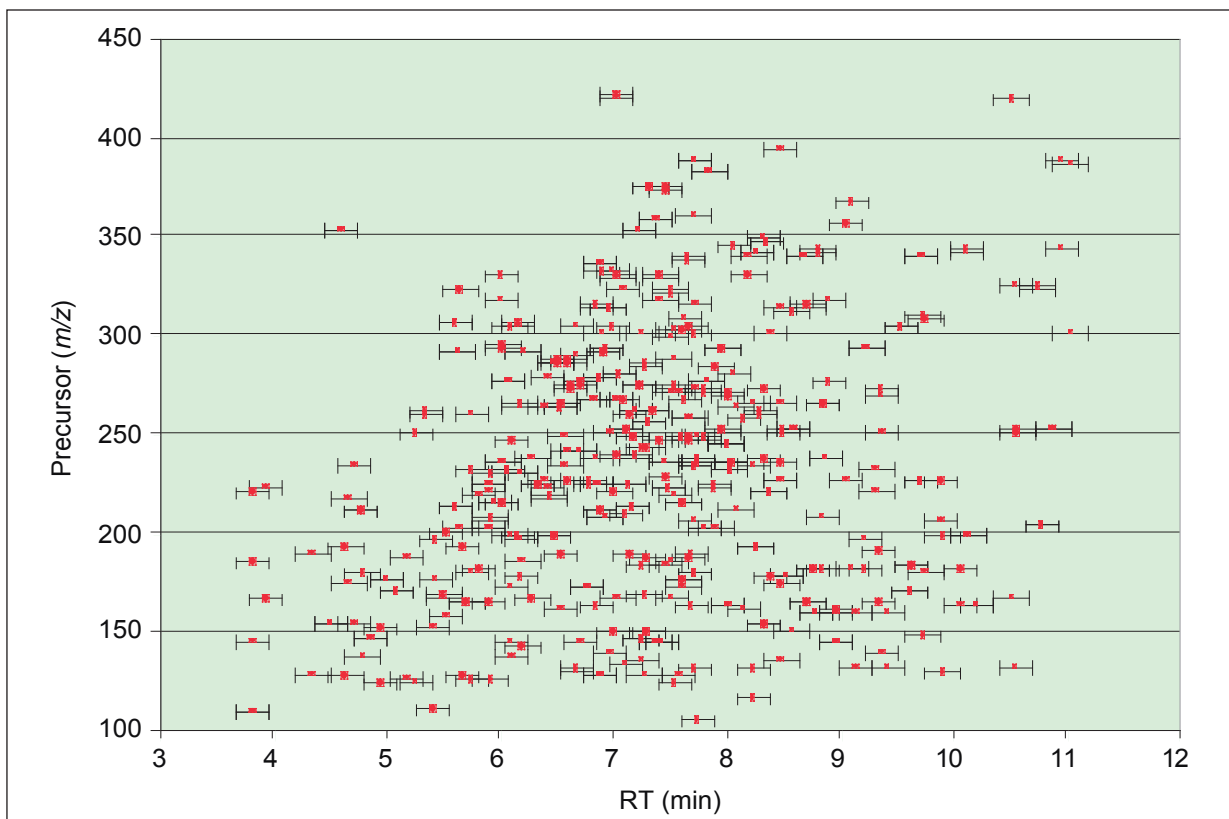


Figure 2: Timed-SRM distribution during the Fast GC chromatography

Figure 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.

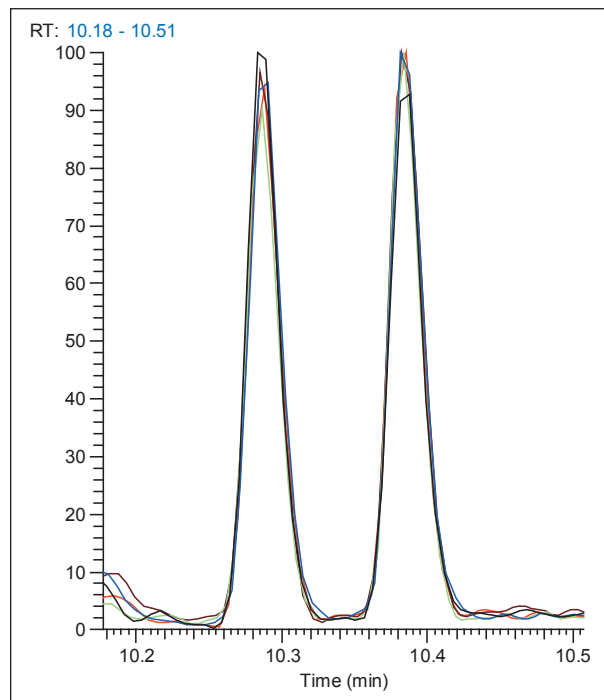


Figure 5: 5 injections of Flucythrinate at 5 ppb in apricot matrix

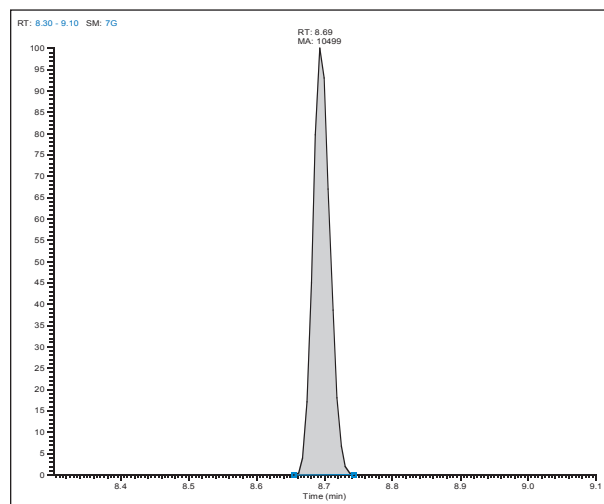


Figure 6: Iprodione at 15 ppb in onion sample

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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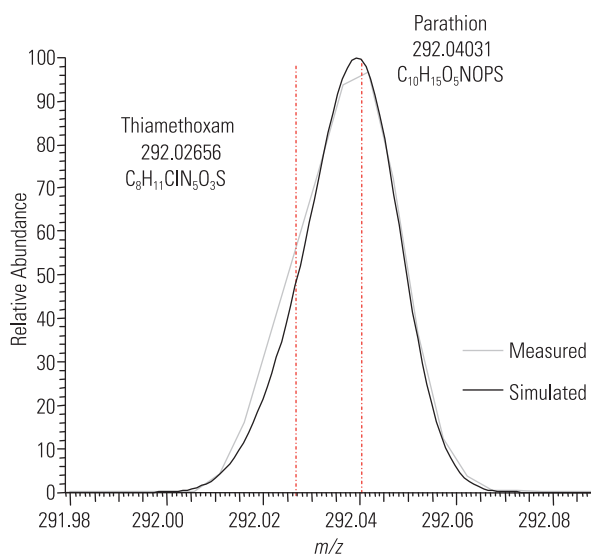
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Results

Resolution of Isobaric Pesticides

In cases where isobaric compounds co-elute, erroneous mass accuracy and elemental composition assignment will occur if the resolving power of the mass spectrometer is insufficient to separate these compounds. Figure 2 shows two pesticides Thiamethoxam ($C_8H_{10}ClN_5O_3S$) and Parathion ($C_{10}H_{14}NO_5PS$), which have protonated molecular ions (MH^+) at 292.02656 and 292.04031, respectively. A resolution higher than 40,000 is needed to resolve the protonated molecular ion of these two compounds completely. This is a pre-requisite for analysis of low concentration compounds in the presence of higher abundant ones. The example in Figure 2 shows an approximate 1:3 mixture of both pesticides measured and simulated.



Influence on Elemental Composition Determination

A limited resolution of 15,000 results in two major limitations. First, the detection of unresolved doublets may result in significant mass errors, which are outside the characteristic accuracy specification of the Exactive instrument. As a consequence, at lower resolution settings, the mass windows for elemental composition determination have to be increased, resulting in much larger number of elemental composition proposals for the unknown or targeted compounds. This can be seen for the example (Figure 3) of Pirimicarb at m/z 239.1503. Due to the presence of an isobaric interference, the peak at 239 shows a mass error of 6.5 ppm. At a resolution of 15,000, the underlying interference causes an apparent shift to higher mass, whereas at higher resolution (here 80,000), the doublet is clearly resolved, and the mass accuracy is well within instrument specifications.

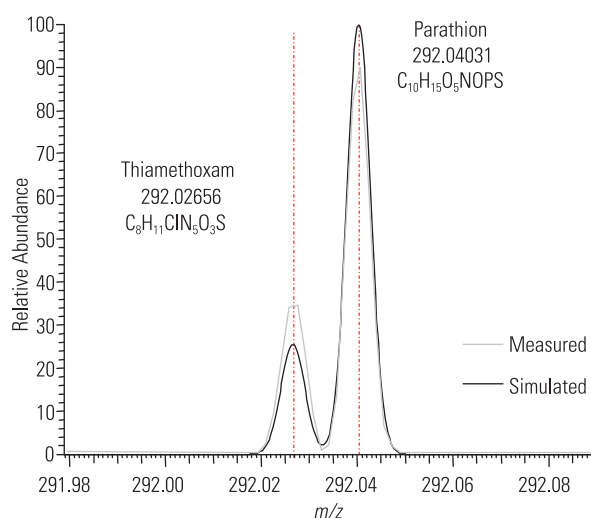


Figure 2: Mass chromatogram of two isobaric pesticides measured at a resolution of 15,000 (left) and 50,000 (right). Superimposed is the simulated mass trace at each resolution setting.

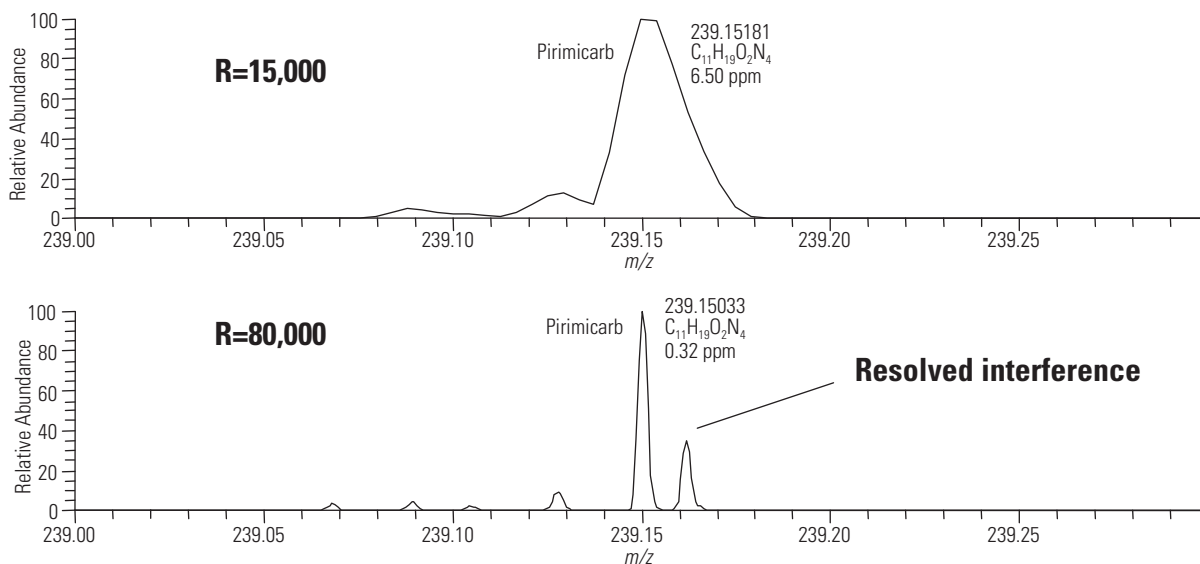


Figure 3: Improved mass accuracy simply by increasing the resolution in order to resolve the doublet. The peak at 15,000 resolution splits up into 2 by increasing the resolution to 80,000.