Application Note: 52027

Fast GC-MS/MS for High Throughput Pesticides Analysis

Igor Fochi, Elena Ciceri, Hans-Joachim Huebschmann, Thermo Fisher Scientific, Milan, Italy
Ciro D'Aniello, Laboratorio D'Aniello – Via Nazionale, 81 S. Egidio M. Albino, Salerno, Italy

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

A sample size of 10 g was processed according to 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
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:	5 MS, 20 m, 0.18 mm, 0.18 µm
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
Ionization 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

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

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

Pesticide	Retention Time	CE	Precursor	Product
Chlordane	7.47	15	372.81	265.87
Chlordane	7.47	15	374.81	267.87
Chlorfenapyr	7.80	20	246.98	226.98
Chlorfenapyr	7.80	20	248.98	228.98
Chlorfenson	7.62	10	174.98	110.98
Chlorfenson	7.62	10	301.96	174.98
Chlorfenvinphos-E+Z	7.09	15	266.98	158.99
Chlorfenvinphos-E+Z	7.09	15	322.97	266.98
Chloridazon	8.38	23	220.04	166.03
Chloridazon	8.38	25	220.04	158.03
Chlormephos	4.72	5	153.98	120.98
Chlormephos	4.72	14	233.97	120.98
Chlorothalonil	6.18	25	263.88	167.92
Chlorothalonil	6.18	25	265.88	169.92
Chlorpropham	5.61	15	213.06	127.03
Chlorpropham	5.61	10	213.06	171.04
Chlorpyrifos-ethyl	6.85	15	313.93	257.95
Chlorpyrifos-ethyl	6.85	12	315.93	259.95
Chlorpyrifos-methyl	6.49	20	285.91	92.97
Chlorpyrifos-methyl	6.49	25	285.91	270.91
Chlorthal-dimethyl	6.90	25	300.91	222.93
Chlorthal-dimethyl	6.90	15	331.90	300.91
Chlozolinate	7.15	15	259.01	188.01
Chlozolinate	7.15	20	188.01	147.01
Clodinafop-propargyl	8.33	15	349.05	266.04
Clodinafop-propargyl	8.33	15	349.05	238.04
Clofentezine	9.54	10	304.01	138.01
Clofentezine	9.54	10	304.01	132.01
Clorfluazuron	7.51	22	321.00	304.00
Clorfluazuron	7.51	20	323.00	306.00
Clorpropilato	7.97	22	251.02	139.02
Clorpropilato	7.97	15	253.01	139.00
Coumaphos	9.72	12	226.01	198.00
Coumaphos	9.72	20	226.01	163.01
Cyanazine	6.86	10	225.08	198.07
Cyanazine	6.86	10	225.08	189.07
Cyfluthrin	9.90	20	206.03	151.02
Cyfluthrin	9.90	17	226.03	206.03
Cyhalothrin, lambda	9.22	23	181.04	152.03
Cyhalothrin, lambda	9.22	15	197.04	141.03
Cypermethrin+Alfametrin	10.07	12	163.03	127.02
Cypermethrin+Alfametrin	10.07	17	181.03	152.03
Cyproconazole	7.89	20	222.09	125.05
Cyproconazole	7.89	20	224.09	127.05
Cyprodinil	7.14	20	224.13	208.12
Cyprodinil	7.14	18	225.13	210.12
DDD, o,p	7.75	20	234.98	164.98
DDD, o,p	8.05	20	236.98	164.98
DDD, p,p	8.05	18	234.97	198.97
DDD, p,p	7.75	20	234.97	164.98
DDE o,p	7.42	25	245.96	175.97
DDE o,p	7.42	20	317.94	245.95
DDE p,p	7.68	25	245.95	175.97
DDE p,p	7.68	20	247.95	175.97
DDT o,p	7.74	15	234.95	164.96
DDT o,p	7.74	20	236.94	164.96
DDT p,p	8.04	15	234.94	198.95
DDT p,p	8.04	20	234.94	164.96
Deltamethrin+Tralometrin	10.89	10	252.93	171.95
Deltamethrin+Tralometrin	10.89	10	252.93	173.95
Diazinon	6.09	15	199.06	93.03
Diazinon	6.09	15	304.10	179.06

Pesticide	Retention Time	CE	Precursor	Product
Dichlofenthion	6.43	10	222.98	204.98
Dichlofenthion	6.43	15	278.97	222.98
Dichlofluanid	6.79	15	223.97	122.99
Dichlofluanid	6.79	15	225.97	122.99
Dichloran	5.92	10	205.97	175.97
Dichloran	5.92	10	207.96	177.97
Dichlorphos	3.82	17	184.95	92.98
Dichlorphos	3.82	10	219.95	184.95
Diclobutrazol	7.80	15	270.07	159.04
Diclobutrazol	7.80	15	272.08	161.04
Dicofol (1st, 2nd degr.)	6.98	20	138.97	110.97
Dicofol (1st, 2nd degr.)	6.98	15	250.94	138.97
Dieldrin	7.83	20	276.92	206.93
Dieldrin	7.83	10	276.92	240.92
Diethofencarb	6.83	8	267.15	225.12
Diethofencarb	6.83	10	267.15	168.09
Difenoconazole 1+2	10.75	15	323.05	265.04
Difenoconazole 1+2	10.75	20	325.05	267.04
Diflufenican	8.48	10	266.05	246.05
Diflufenican	8.48	10	394.07	266.05
Dimethoate	5.92	15	125.00	79.00
Dimethoate	5.92	5	229.01	87.01
Dimethomorph 1+2	11.04	10	301.10	165.05
Dimethomorph 1+2	11.04	12	387.12	301.10
Diniconazole	8.02	15	268.06	232.05
Diniconazole	8.02	15	270.06	234.05
Dinitramine	6.17	15	305.08	244.07
Dinitramine	6.17	15	307.08	216.06
Diphenamid	7.04	20	167.09	165.09
Diphenamid	7.04	10	239.13	167.09
Diphenylamine	5.51	25	167.10	166.09
Diphenylamine	5.51	20	169.10	168.09
Disulfoton	6.20	10	142.01	109.01
Disulfoton	6.20	5	186.02	153.02
Ditalimfos	7.51	5	271.03	243.03
Ditalimfos	7.51	10	299.04	243.03
Endosulfan A+B	7.54	15	273.88	238.89
Endosulfan A+B	7.54	15	271.88	236.89
Endrin	8.07	5	280.91	244.92
Endrin	8.07	8	344.88	280.90
Epoxiconazole	8.26	10	192.04	138.03
Epoxiconazole	8.26	10	192.04	111.02
EPTC	4.35	5	128.08	86.05
EPTC	4.35	5	189.12	128.08
Etaconazole 1+2	8.00	15	245.04	173.03
Etaconazole 1+2	8.00	10	245.04	191.03
Ethion	8.03	20	230.99	129.01
Ethion	8.03	15	230.99	174.99
Ethoxyquin	5.91	20	202.14	145.10
Ethoxyquin	5.91	15	202.14	174.12
Etofenprox	10.21	10	163.09	135.07
Etofenprox	10.21	16	163.09	107.06
Etoprofos	5.53	10	158.04	130.03
Etoprofos	5.53	10	200.05	158.04
Etridiazole (Terrazole)	4.78	15	210.93	182.94
Etridiazole (Terrazole)	4.78	15	210.93	139.95
Etrimfos	6.21	10	292.06	153.03
Etrimfos	6.21	10	292.09	181.04
Fenamidone	8.88	20	238.08	209.07
Fenamidone	8.88	20	238.08	237.08
Fenamiphos	7.54	10	288.10	260.09
Fenamiphos	7.54	15	303.11	260.09

Pesticide	Retention Time	CE	Precursor	Product
Fenarimol	9.38	15	139.01	111.01
Fenarimol	9.38	15	251.03	139.01
Fenazaquin	8.97	15	145.08	117.07
Fenazaquin	8.97	20	160.09	117.07
Fenbuconazole	9.91	15	129.04	102.03
Fenbuconazole	9.91	10	198.07	129.04
Fenchlorphos (VS)	6.61	12	284.82	269.97
Fenchlorphos (VS)	6.61	12	286.72	272.08
Fenhexamid	8.39	15	177.04	113.02
Fenhexamid	8.39	15	301.06	97.02
Fenitrothion	6.72	8	277.02	109.01
Fenitrothion	6.72	10	277.02	260.02
Fenpropathrin	8.86	10	265.13	89.04
Fenpropathrin	8.86	15	265.13	210.10
Fenpropidin	6.72	10	145.13	117.11
Fenpropidin	6.72	10	274.25	98.09
Fenpropimorph	6.89	15	128.11	70.06
Fenpropimorph	6.89	15	128.11	110.09
Fenson	7.03	20	267.98	77.00
Fenson	7.03	10	267.98	141.00
Fensulfothion	7.97	10	293.03	125.01
Fensulfothion	7.97	16	293.03	97.01
Fenthion	6.88	18	278.02	109.01
Fenthion	6.88	20	278.02	169.01
Fenvalerate 1+2	10.52	10	167.05	125.04
Fenvalerate 1+2	10.52	10	419.13	225.07
Fipronil	7.03	15	419.94	350.95
Fipronil	7.03	15	421.94	352.95
Fluazifop-P-butyl	7.85	20	383.13	254.09
Fluazifop-P-butyl	7.85	15	383.13	282.10
Fluazinam	7.72	12	388.90	352.20
Fluazinam	7.72	12	388.90	354.20
Flubenzimine	7.52	15	167.00	77.00
Flubenzimine	7.52	25	186.00	77.00
Flucitrinate 1+2	10.14	22	199.07	107.04
Flucitrinate 1+2	10.14	10	199.07	157.06
Fludioxonil	7.60	20	248.04	154.02
Fludioxonil	7.60	15	248.04	182.03
Flufenacet	6.89	10	211.04	183.03
Flufenacet	6.89	10	211.04	123.02
Fluopicolide	8.36	26	346.95	171.93
Fluopicolide	8.36	26	346.95	176.02
Fluorocloridone I+II	6.96	15	313.01	174.01
Fluorocloridone I+II	6.96	15	313.01	187.01
Fluquinconazole	9.73	25	340.01	286.01
Fluquinconazole	9.73	22	340.01	298.01
Flusilazole	7.72	20	233.07	152.05
Flusilazole	7.72	20	233.07	165.05
Flutriafol	7.55	15	123.04	75.03
Flutriafol	7.55	15	219.07	123.04
Fluvalinate tau	10.57	20	250.06	200.05
Fluvalinate tau	10.57	20	252.06	200.05
Folpet	7.35	15	261.60	129.80
Folpet	7.35	5	261.60	234.40
Folpet met.	4.86	15	146.98	103.24
Folpet met.	4.86	15	146.98	104.39
Fonofos	6.11	10	137.02	109.01
Fonofos	6.11	10	246.03	137.02
Formothion	6.34	15	224.01	125.01
Formothion	6.34	10	224.01	196.01
Furalaxyl	7.26	15	242.11	95.04
Furalaxyl	7.26	10	301.13	225.1

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

Pesticide	Retention Time	CE	Precursor	Product
Haloxyfop-methyl	7.33	10	375.05	316.04
Haloxyfop-methyl	7.33	20	375.05	288.04
Heptachlor	6.63	15	273.87	238.88
Heptachlor	6.63	15	271.87	236.89
Heptachlor epoxide B	7.26	15	182.91	154.93
Heptachlor epoxide B	7.26	15	134.93	98.95
Heptachlor epoxide A	7.23	15	352.83	262.87
Heptachlor epoxide A	7.23	16	352.83	281.86
Heptenophos	5.26	10	124.01	89.01
Heptenophos	7.62	25	250.02	89.01
Hexachlorobenzene (HCB)	7.62	20	283.81	213.86
Hexachlorobenzene (HCB)	7.47	20	283.81	248.84
Hexaconazole	7.47	20	214.05	172.04
Hexaconazole	5.26	15	214.05	187.04
Hexythiazox	7.62	10	184.05	149.04
Hexythiazox	7.62	10	227.07	149.04
Imazalil	10.79	20	173.00	145.00
Imazalil	10.79	16	175.00	147.00
Indoxacarb	8.72	20	203.03	106.01
Indoxacarb	8.72	20	203.03	134.02
Iprodione	8.00	15	314.03	245.03
Iprodione	8.00	15	316.03	247.03
Iprodione degr.	6.08	16	243.88	187.00
Iprodione degr.	6.08	16	243.88	188.00
Isofenphos	7.05	17	213.07	121.04
Isofenphos	7.05	10	213.07	185.06
Isopropalin	7.72	15	280.15	180.10
Isopropalin	7.72	10	280.15	238.13
Kresoxim-methyl	8.34	20	131.06	116.05
Kresoxim-methyl	8.34	15	206.09	131.06
Lenacil	5.00	15	153.09	82.05
Lenacil	5.00	15	153.09	136.08
Lufenuron 1	4.60	20	175.99	120.99
Lufenuron 1	4.60	20	175.99	147.99
Lufenuron 2	6.77	25	352.99	173.99
Lufenuron 2	6.77	25	352.99	202.99
Malathion	8.60	10	173.02	99.01
Malathion	8.60	10	173.02	127.01
Mefenpyr-diethyl	7.49	20	253.04	190.03
Mefenpyr-diethyl	7.49	20	253.04	189.03
Mepanipyrim	6.58	15	222.11	207.10
Mepanipyrim	6.58	15	223.11	208.10
Metalaxyl	7.81	10	234.11	174.11
Metalaxyl	7.81	10	249.13	190.10
Metamitron	7.11	5	202.09	174.07
Metamitron	7.11	10	202.09	186.08
Metazachlor	5.71	20	133.05	117.04
Metazachlor	5.71	12	209.07	132.05
Methabenzthiazuron	7.38	20	164.05	136.04
Methabenzthiazuron	7.38	20	164.05	135.04
Methidathion	8.48	15	144.98	57.99
Methidathion	8.48	10	144.98	84.99
Methoxychlor I	6.85	20	227.01	169.01
Methoxychlor I	6.85	15	227.01	212.01
Metolachlor	6.48	15	162.08	133.06
Metolachlor	6.48	15	238.11	162.08
Metribuzin	4.64	20	198.08	82.03
Metribuzin	4.64	20	198.08	110.05
Mevinphos	9.37	10	127.04	109.02
Mevinphos	9.37	12	192.04	127.03
Mirex	5.18	15	269.81	234.84
Mirex	5.18	15	271.81	236.84

Pesticide	Retention Time	CE	Precursor	Product
Molinate (Ordram)	5.67	10	126.07	55.03
Molinate (Ordram)	5.67	10	187.10	126.07
Monocrotophos	7.72	20	127.03	95.03
Monocrotophos	7.72	10	192.05	127.03
Myclobutanil	3.82	15	179.07	125.05
Myclobutanil	7.58	30	179.07	90.00
Naled	7.58	12	109.00	79.00
Napropamide	7.91	10	128.07	72.04
Napropamide	7.91	5	271.16	128.07
Nitrofen	8.48	21	201.99	138.99
Nitrofen	8.48	15	282.98	252.98
Nuarimol	5.09	15	235.05	139.03
Nuarimol	5.09	15	314.06	139.03
Ortho-phenylphenol	7.68	20	170.07	115.05
Ortho-phenylphenol	7.68	20	170.07	141.06
Oxadiazon	8.02	10	258.05	175.04
Oxadiazon	8.02	10	304.06	260.05
Oxadixyl	7.71	40	163.07	117.05
Oxadixyl	7.71	10	163.07	132.06
Oxyfluorfen	7.46	10	300.03	223.02
Oxyfluorfen	7.46	12	361.03	300.03
Paclobutrazol	7.01	15	236.10	125.06
Paclobutrazol	7.01	15	236.10	167.07
Paraoxon-ethyl	6.19	10	149.03	119.02
Paraoxon-ethyl	6.19	10	220.05	174.04
Paraoxon-methyl	6.92	10	230.02	136.01
Paraoxon-methyl	6.92	10	230.02	200.02
Parathion-ethyl	6.53	15	291.03	109.01
Parathion-ethyl	6.53	10	291.03	137.02
Parathion-methyl	7.18	15	262.99	109.00
Parathion-methyl	7.18	15	262.99	246.00
Penconazole	5.75	25	248.06	157.04
Penconazole	5.75	15	248.06	192.04
Pencycuron	7.12	12	125.05	89.04
Pencycuron	7.12	12	180.07	125.05
Pendimethalin	9.64	12	252.13	162.08
Pendimethalin	9.64	12	252.13	191.09
Permethrin 1+2	7.24	15	183.04	153.03
Permethrin 1+2	7.24	15	183.04	165.03
Phenthoate	5.75	10	274.03	246.02
Phenthoate	5.75	7	274.03	121.01
Phorate	9.11	10	231.01	203.01
Phorate	9.11	5	260.01	75.01
Phosalone	8.79	15	181.99	111.00
Phosalone	8.79	10	366.99	181.99
Phosmet	6.40	20	160.01	77.01
Phosmet	6.40	15	160.01	133.01
Phosphamidon I+II	6.29	15	227.05	127.03
Phosphamidon I+II	6.29	15	264.06	127.03
Pirimicarb	7.00	10	166.10	137.08
Pirimicarb	7.00	15	238.14	166.10
Pirimiphos-ethyl	6.68	15	304.12	168.06
Pirimiphos-ethyl	6.68	15	333.13	318.12
Pirimiphos-methyl	9.76	10	290.09	233.07
Pirimiphos-methyl	9.76	15	305.10	290.09
Prochloraz	7.29	15	180.01	138.01
Prochloraz	7.29	10	308.03	70.01
Procymidone	7.66	10	283.02	255.02
Procymidone	7.66	10	285.02	257.02
Profenofos	6.01	20	336.94	266.95
Profenofos	6.01	20	338.94	268.95
Profluralin	5.91	15	318.10	198.05

Pesticide	Retention Time	CE	Precursor	Product
Profluralin	5.91	5	330.10	302.10
Prometon	6.60	10	225.16	183.13
Prometon	6.60	10	225.16	210.15
Prometryn	5.43	12	226.13	184.10
Prometryn	5.43	15	241.15	184.10
Propachlor	6.44	10	176.06	120.04
Propachlor	6.44	10	196.07	120.04
Propanil	8.49	10	217.01	161.00
Propanil	8.49	10	219.01	163.00
Propargite	6.03	15	135.06	107.05
Propargite	6.03	12	173.08	105.05
Propetamphos	4.79	15	236.07	166.05
Propetamphos	4.79	5	236.07	194.06
Propham	8.30	8	137.07	93.05
Propham	8.30	15	179.09	93.05
Propiconazole 1+2	5.41	20	259.02	173.02
Propiconazole 1+2	5.41	20	261.02	175.02
Propoxur	6.10	10	110.00	64.00
Propoxur	6.10	10	152.00	110.00
Propyzamide	7.63	15	145.01	109.01
Propyzamide	7.63	18	173.01	109.01
Prothiofos	10.56	10	266.97	238.97
Prothiofos	10.56	5	308.97	238.97
Pyraclostrobin	9.33	15	132.03	77.02
Pyraclostrobin	9.33	20	325.08	132.03
Pyrazophos	9.74	10	221.05	193.04
Pyrazophos	9.74	10	232.05	204.05
Pyridaben	8.69	20	147.06	117.04
Pyridaben	8.69	15	309.12	147.06
Pyridaphenthion	7.20	10	340.06	109.02
Pyridaphenthion	7.20	10	340.06	199.04
Pyrifenox 1+2	6.16	20	262.03	192.02
Pyrifenox 1+2	6.16	20	262.03	200.02
Pyrimethanil	7.25	35	198.11	118.07
Pyrimethanil	7.25	15	198.11	183.10
Quinalphos	8.34	15	146.03	91.02
Quinalphos	8.34	15	146.03	118.02
Quinoxyfen	6.03	20	237.05	208.00
Quinoxyfen	6.03	20	272.01	237.00
Quintozene (PCNB)	6.68	15	292.84	234.87
Quintozene (PCNB)	6.68	20	294.84	236.87
S421	8.53	22	129.93	94.95
S421	8.53	22	131.93	96.95
Sethoxydim	5.65	24	178.01	81.00
Sethoxydim	5.65	21	178.01	107.95
Sulfotep	7.31	15	202.01	146.01
Sulfotep	7.31	15	322.02	202.01
Sulphur	8.50	12	255.78	159.87
Sulphur	8.50	24	255.78	95.83
Tebuconazole	8.97	20	250.12	125.06
Tebuconazole	8.97	20	252.12	127.06
Tebufenozide	8.91	10	145.00	117.00
Tebufenozide	8.91	15	160.00	145.00
Tebufenpyrad	5.35	15	276.13	171.08
Tebufenpyrad	5.35	15	318.15	145.07
Tecnazene	6.19	15	260.88	202.90
Tecnazene	6.19	15	258.88	200.90
Tefluthrin	6.07	20	177.02	127.02
Tefluthrin	6.07	15	197.03	141.02
Terbufos	6.02	15	231.04	175.03
Terbufos	6.02	10	231.04	203.03
Terbuthylazine	6.70	10	214.10	104.05
Terbuthylazine	6.70	10	214.10	132.06
Terbutryn	7.42	10	241.14	185.10
Terbutryn	7.42	15	241.14	170.10
Tetrachlorvinphos	6.89	22	328.91	108.97
Tetrachlorvinphos	6.89	22	330.91	108.97
Tetraconazole	9.06	20	336.02	218.01
Tetraconazole	9.06	20	336.02	204.01
Tetradifon	8.72	18	226.93	198.94
Tetradifon	8.72	10	355.88	228.93
Tetramethrin	6.55	17	164.09	107.06
Tetramethrin	6.55	10	164.09	135.07
Tolclofos-methyl	7.20	20	264.96	92.99
Tolclofos-methyl	7.20	15	264.96	249.96
Tolylfluanid	6.93	15	238.09	137.05
Tolylfluanid	6.93	15	240.09	137.05
Triadimefon	7.28	25	208.07	111.04
Triadimefon	7.28	10	208.07	181.06
Triadimenol	8.15	10	128.05	100.04
Triadimenol	8.15	10	168.06	70.03
Triazophos	3.82	13	161.03	105.02
Triazophos	3.82	10	257.05	162.03
Triciclazole	7.69	8	161.94	160.93
Triciclazole	7.69	20	188.98	160.93
Trifloxystrobin	8.24	15	116.04	89.03
Trifloxystrobin	8.24	10	131.04	130.04
Trifluralin	5.61	15	306.10	160.05
Trifluralin	5.61	15	306.10	264.09
Vamidothion	7.43	10	145.02	87.01
Vamidothion	7.43	10	145.02	112.02
Vinclozolin	6.51	15	284.97	212.00
Vinclozolin	6.51	15	286.97	214.00
Zoxamide	7.67	15	187.01	159.01
Zoxamide	7.67	15	258.02	187.01
Zoxamide-metab.	7.30	15	187.02	159.01
Zoxamide-metab.	7.30	15	242.01	214.01

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. Data elaboration was performed using Thermo Scientific QuanLab Forms software.

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.

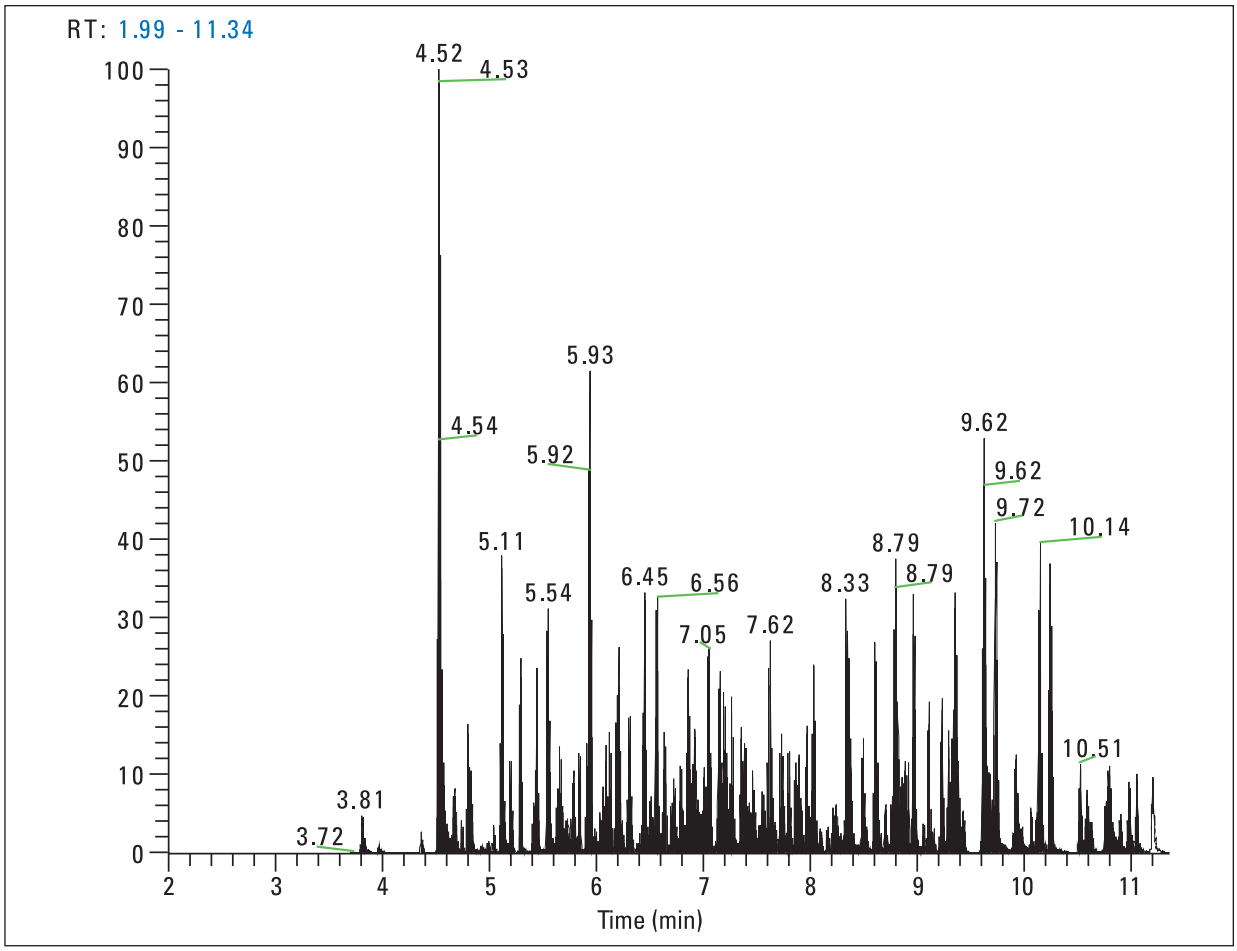

Figure 1: Chromatogram showing the coelutions of compounds in a single run

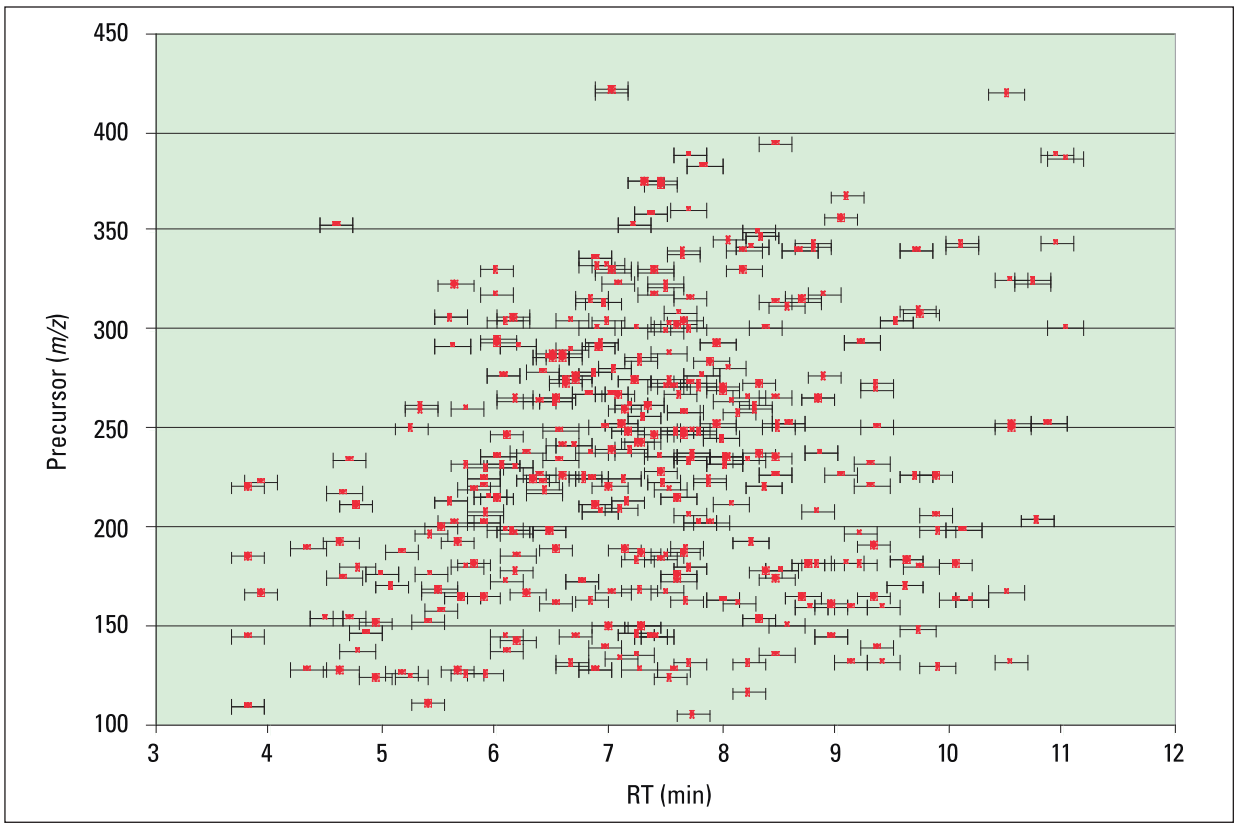

Figure 2: Timed-SRM distribution during the Fast GC chromatography

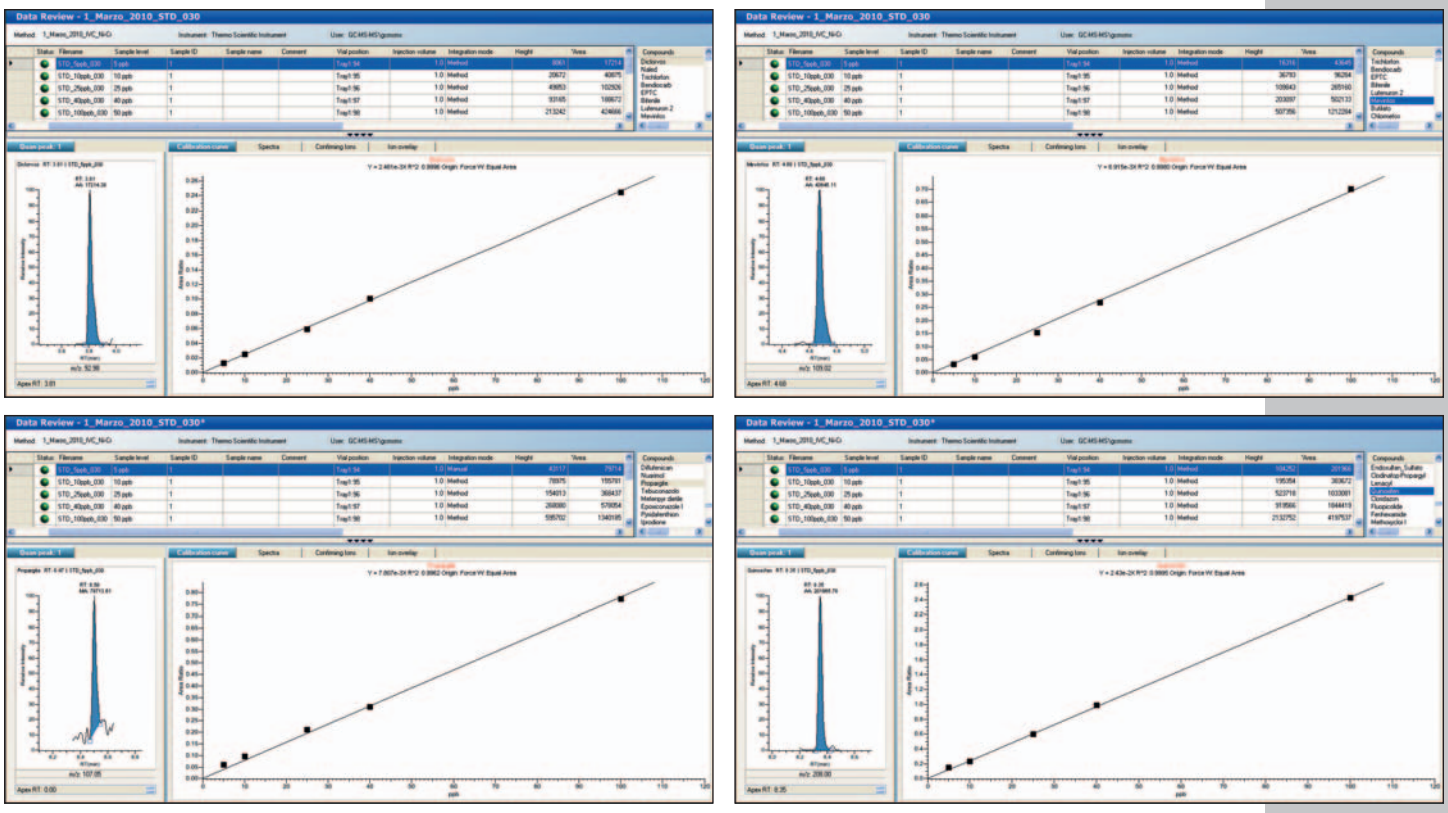

Figure 3: Calibration curve and integrated peak area of the lowest level (5 ppb) in apple matrix (Dichlorvos, Mevinphos, Propargite, Quinoxifen)

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° bent 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.

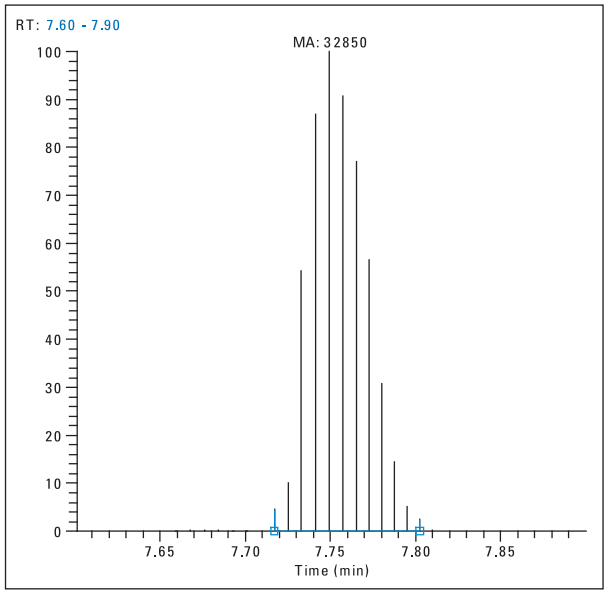

Figure 4: Flusilazole at 5 ppb in apple matrix

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.

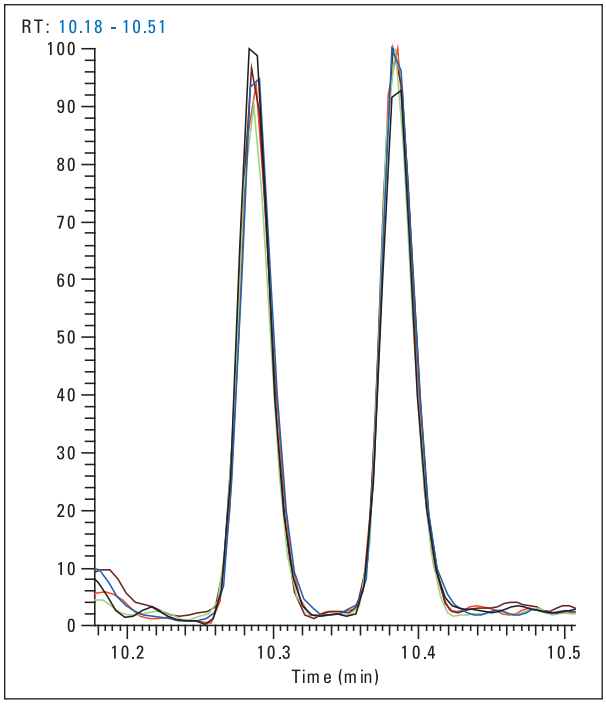

Figure 5: 5 injections of Flucythrinate at 5 ppb in apricot matrix

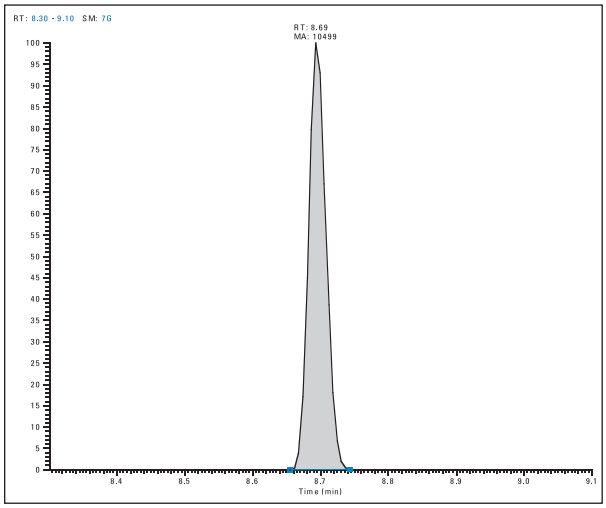

Figure 6: Iprodione at 15 ppb in onion sample

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 Scientific 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.

References

1. Efficient sample preparation and clean-up using the QuEChERS Method, Thermo Scientific Product Information, BRO-GSC-QUECHERS-1108, 2008.
2. QuEChERS, European Standard, EN 15662
3. M. Anastassiades, S. J. Lehotay, D. Stajnbaher, F. J. Schenck: Fast and Easy Multiresidue Method Employing Acetonitile Extraction/Partitioning and “Dispersive Solid-Phase Extraction” for the Determination of Pesticide Residues in Produce, J. AOAC Int., 86 (2003) 412-431
4. M. Hetmanski, High sensitivity multi-residue pesticide analyses in foods using the TSQ Quantum GC-MS/MS, presented at RAFA conference, Prague, Nov 2009.
5. B. Chen, A. Huang, et al., Timed SRMs method on a GC triple quad mass spectrometer for pesticides, presented at the CRC Conference, Sydney, Oct 2009.
6. Commission Directive of 12 August 2002, implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results, Official Journal of the European Communities L 221/9, 17.8.2002.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa-Other
+27 11 570 1840
Australia
+61 3 9757 4300
Austria
+43 1 333 50 34 0
Belgium
+32 53 73 42 41
Canada
+1 800 530 8447
China
+86 10 8419 3588
Denmark
+45 70 23 62 60
Europe-Other
+43 1 333 50 34 0
Finland/Norway/Sweden
+46 8 556 468 00
France
+33 1 60 92 48 00
Germany
+49 6103 408 1014
India
+91 22 6742 9434
Italy
+39 02 950 591
Japan
+81 45 453 9100
Latin America
+1 561 688 8700
Middle East
+43 1 333 50 34 0
Netherlands
+31 76 579 55 55
New Zealand
+64 9 980 6700
Russia/CIS
+43 1 333 50 34 0
South Africa
+27 11 570 1840
Spain
+34 914 845 965
Switzerland
+41 61 716 77 00
UK
+44 1442 233555
USA
+1 800 532 4752

www.thermoscientific.com

AN52027_E 12/10M