Application Note 10464

Multi-Residue Pesticide Analysis in Herbal Juices using GC-MS/MS

Shridhar Gawade[1], Soma Dasgupta[1], Aarti Karkhanis[1], Sunil T. Kumar[1], Hans-Joachim Huebschmann[2]
[1] Thermo Fisher Scientific, Mumbai, India; [2] Thermo Fisher Scientific, Singapore

Keywords
Pesticides, QuEChERS, Aloe Vera, Amla, selectivity in matrix, quantitation, validation

Introduction

Aloe vera (*Aloe barbadensis* Mill.) is a succulent plant species used in herbal medicine since the beginning of the first century A.D. Extracts from Aloe vera are widely used in the cosmetics and alternative medicine industries, having rejuvenating, healing, or soothing properties [1].

Indian gooseberry (*Amla, Phyllanthus emblica*) demonstrates in vitro antiviral, antimicrobial, and anticancer properties [2]. All parts of the plant are used in various Ayurvedic/Unani medicines as herbal preparations, including the fruit, seed, leaves, root, bark and flowers. *Aloe vera* and *Amla* juices are also available in the market for direct consumption. However, there is increasing public concern about health risks from pesticide residues in food leading the strict regulation of maximum residue levels (MRL) and total dietary intake of pesticide residues in foodstuffs. International bodies, such as the Codex Alimentarius Commission [3] and the European Union (EU) [4], exert a major influence on food safety testing globally, with strict legislation in this area.

According to Reg. 396/2005, Article 20 of the EU legislation no specific MRLs for juices are present which means that the MRL applied for juice is the corresponding MRL for the raw agricultural commodity.

The Thermo Scientific™ TSQ™ 8000 Evo triple quadrupole GC-MS is an excellent tool for the control of MRL levels in food commodities. The enhanced velocity optics (EVO) driving EvoCell collision cell technology provide high SRM transition speeds, precision, and sensitivity for even the most complex methods involving several pesticides within a short run time. Other advantages include timed-SRM and AutoSRM for SRM optimization. A method was therefore developed for analysis of more than 200 pesticides in *Aloe vera* and *Amla* within an 11-minute run time.

Sample Preparation

Sample preparation (Figure 1) was based on the QuEChERS protocol [5] and involved the extraction of 10 mL of homogenized juice with 10 mL acetonitrile in the presence of 10 g NaCl. The supernatant (1 mL) was collected after centrifugation, and dispersive cleanup was performed using 200 mg PSA and 10 mg GCB. The extract was centrifuged at 10,000 rpm for 5 min and 2 µL of supernatant was injected via autosampler for analysis. For recovery and validation studies, 10 mL of residue-free juice was injected with appropriate quantities of the pesticide standard mixture and extracted as per the described procedure.

ThermoFisher SCIENTIFIC

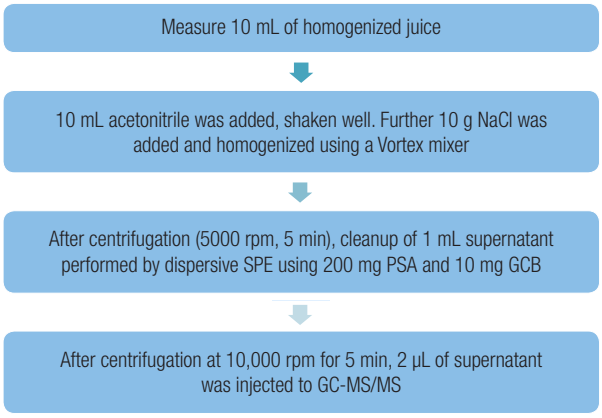

Figure 1. Sample preparation for extraction of pesticides from Aloe vera and Amla juices.

Calibration

Stock standard solutions of each pesticide compound were prepared by weighing 10±0.1 mg and dissolution in 10 mL acetonitrile. The solutions were stored in amber colored glass vials at -20 °C. A total of 10 intermediate mixtures (containing 20–30 compounds each) of 10 mg/L concentration were prepared by diluting adequate quantity of each compound in acetonitrile. A working standard solution (1 mg/L) was prepared by mixing intermediate standard solution and dilution with acetonitrile and stored at -20 °C. The calibration standards ranging from 1 µg/L to 250 µg/L were freshly prepared for measurement of the calibration curves. The calibration graphs for all the compounds were obtained by plotting the individual peak areas against the concentration of the corresponding calibration standards.

Instrument and Method Setup

The analytical method comprised of sample handling using the Thermo Scientific™ TriPlus™ RSH liquid autosampler, Thermo Scientific™ TRACE™ 1300 Series gas chromatograph equipped with a spilt/splitless injector (SSL), and the TSQ™ 8000 Evo GC-MS/MS system.

The Thermo Scientific™ TraceFinder™ software was used for method setup, data acquisition, and data processing. For all pesticides, three SRM transitions were chosen for the MRM acquisition method. The SRM transitions were directly imported from the compound database readily available with TraceFinder. The first transition was used for quantitation, and the other two transitions for confirmation, by checking the ion intensity ratio.

TRACE™ 1310 GC Parameters

Carrier gas	Helium
Injector	SSL
Mode	Splitless
Splitless time	1 min, split flow: 30 mL/min
Oven program	65 °C, 1.5 min (injection), 30 °C/min to 320 °C, hold 1 min
Column	Thermo Scientific™ TraceGOLD™ TG-5SilMS, 15m x 0.25mm x 0.25µm (Part number 26096-1300)
Column flow	1.2 mL/min, constant flow
Injection	2 µL by TriPlus RSH Autosampler

TSQ 8000 Evo MS/MS Parameters

Ion source temperature	280 °C
Interface temperature	310 °C
Acquisition mode	EI, 70 eV
MRM detection	timed SRM mode
MRM parameter	see Table 1

The timed-SRM acquisition method used with the TSQ 8000 Evo GC-MS/MS avoids laborious and time consuming process of segment creation and method maintenance. The scan times are automatically calculated based upon the specified cycle time so that uniform cycle times are obtained for each mass transition, thus reducing the extensive optimization process for scan times and data points across a peak. The dwell times for data acquisition are maximized independent of the number of compounds in the MRM method. Each of the pesticides listed in Table 1 was detected by three SRM transitions, one used for quantitation and two for additional ion ratio confirmation. The data processing and reporting was done using the TraceFinder software suite.

Table 1. MRM transitions and collision energies (CE) of target pesticides.

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
1	3, 5-Dichloroaniline	5.27	161.0 > 90.0	20	161.0 > 98.9	22	161.0 > 125.5	14
2	Acephate	5.46	95.5 > 65.4	8	136.0 > 42.1	8	136.0 > 94.0	12
3	Acetochlor	7.00	131.8 > 117.0	14	146.0 > 117.7	8	146.0 > 131.1	12
4	Acrinathrin	9.13	181.0 > 152.0	22	208.1 > 180.9	8	289.0 > 93.1	8
5	Alachlor	7.06	160.1 > 131.7	10	188.1 > 130.0	32	188.1 > 160.1	8
6	Aldrin	7.40	262.7 > 191.0	30	262.7 > 192.9	32	330.0 > 298.9	10
7	Allethrin (Bioallethrin)	7.62	123.1 > 41.1	24	123.1 > 81.1	8	136.1 > 93.1	12
8	Ametryne	7.14	227.1 > 58.1	12	227.1 > 170.0	10	227.1 > 212.1	8

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
9	Amitraz	9.14	121.0 > 106.1	10	131.9 > 117.1	16	161.9 > 132.0	8
10	Anilofos	8.93	183.7 > 157.0	8	225.9 > 157.0	14	225.9 > 184.0	6
11	Atrazine	6.54	200.0 > 122.1	8	200.0 > 132.0	8	215.1 > 58.1	12
12	Azinphos-ethyl	9.12	132.0 > 51.0	26	132.0 > 77.0	12	160.0 > 77.0	16
13	Azinphos-methyl	9.30	132.0 > 77.0	12	160.0 > 50.9	34	160.0 > 77.0	16
14	Azoxystrobin	10.35	344.1 > 156	34	344.1 > 171.9	36	344.1 > 329.0	14
15	Barban	8.26	153.0 > 62.9	30	153.0 > 90.0	20	153.0 > 125.0	12
16	Benalaxyl	8.45	91.0 > 65.0	12	148.1 > 77.0	30	148.1 > 79.0	22
17	Bendiocarb	6.28	126.0 > 51.9	16	151.0 > 43.0	20	166.1 > 151.1	10
18	Benfluralin	6.19	292.0 > 159.7	20	292.0 > 206.1	10	292.0 > 264.0	8
19	Benfuracarb	7.23	135.1 > 107.1	8	163.1 > 107.1	14	163.1 > 135.1	6
20	Bentazon	7.53	118.8 > 63.7	20	118.8 > 91.8	12	198.0 > 118.8	12
21	BHC, Alpha	6.38	182.8 > 146.7	12	218.8 > 146.6	20	218.8 > 183.0	8
22	BHC, Beta	6.57	180.9 > 145.0	14	218.7 > 146.6	18	218.7 > 183.0	8
23	BHC, delta	6.63	182.8 > 146.7	14	218.8 > 146.5	20	218.8 > 182.9	8
24	BHC, gamma	6.84	180.9 > 109.0	26	180.9 > 145.0	14	218.7 > 183.0	8
25	Bifenazate	8.86	198.9 > 184.1	12	258.0 > 196.1	12	258.0 > 199.1	12
26	Bifenthrin	8.77	165.1 > 163.6	24	181.0 > 165.9	10	181.0 > 179.0	12
27	Bioresmethrin	8.63	123.1 > 81.1	8	143.0 > 128.1	10	171.0 > 128.0	14
28	Bitertanol	9.42	170.0 > 115.1	34	170.0 > 141.1	20	170.0 > 169.1	16
29	Bromacil	7.32	204.8 > 162.0	14	204.8 > 187.8	12	206.8 > 164.0	12
30	Bromophos-ethyl	7.78	96.9 > 65.0	16	96.9 > 78.9	12	302.7 > 284.8	14
31	Bromopropylate	8.84	184.9 > 75.5	30	184.9 > 156.9	12	340.8 > 185.0	14
32	Buprofezin	8.06	105.1 > 50.9	32	105.1 > 77.0	18	175.0 > 132.1	12
33	Butachlor	7.81	160.0 > 131.7	12	176.1 > 146.9	12	188.1 > 160.1	10
34	Cadusafos	6.30	159.0 > 96.9	16	159.0 > 130.9	8	213.0 > 89.1	12
35	Captafol	8.71	150.1 > 77.2	24	150.1 > 79.0	6	183.1 > 79.1	8
36	Captan	7.71	149.0 > 70.0	20	149.0 > 78.8	14	149.0 > 105.0	6
37	Carbaryl	7.16	115.0 > 89.0	16	144.0 > 115.1	22	144.0 > 116.1	10
38	Carbofuran	6.53	149.1 > 77.0	24	149.1 > 121.1	8	164.0 > 149.1	8
39	Carboxin	8.11	87.0 > 43.0	6	143.0 > 43.0	16	143.0 > 87.0	8
40	Carfentrazon-ethyl	8.43	290.0 > 99.9	36	311.9 > 150.7	18	340.1 > 312.1	10
41	Chlordane alpha-cis	7.87	372.8 > 265.8	20	374.7 > 265.8	20	376.6 > 268.0	20
42	Chlordane gamma-trans	7.79	271.7 > 236.8	12	372.7 > 263.7	20	374.7 > 265.9	22
43	Chlordene	6.78	236.7 > 118.9	24	236.7 > 142.9	22	271.8 > 236.8	12
44	Chlorfenapyr	8.16	136.9 > 102.0	12	248.9 > 112.0	24	248.9 > 137.1	18
45	Chlorfenvinphos-E-trans	7.63	266.9 > 159.0	14	268.8 > 161.0	12	322.9 > 267.0	12
46	Chlorfenvinphos-Z-cis	7.70	266.9 > 159.0	14	294.9 > 267.0	8	323.0 > 267.0	12
47	Chloridazon	8.67	220.0 > 165.9	22	220.0 > 193.0	16	220.9 > 77.0	20
48	Chlorobenzylate	9.06	111.0 > 75.1	14	139.0 > 74.9	26	139.0 > 111.0	12
49	Chlorothalonil	6.77	228.8 > 168.0	8	265.8 > 133.0	36	265.8 > 170.0	24
50	Chlorpyrifos oxon	7.35	108.9 > 81.0	8	108.9 > 91.0	6	269.8 > 242.0	8
51	Chlorpyrifos-ethyl	7.33	196.7 > 107.0	36	196.7 > 168.9	12	313.9 > 257.9	12
52	Chlorpyrifos-methyl	7.07	125.0 > 47.0	12	125.0 > 79.0	6	285.9 > 93.0	20
53	Chlorthiamid	6.84	170.0 > 135.1	12	170.0 > 143.0	10	204.9 > 170.0	10
54	Clethodim	8.48	164.1 > 80.8	16	164.1 > 108.1	8	204.9 > 176.1	12
55	Clomazone	6.58	125.0 > 89.0	16	138.0 > 74.9	24	138.0 > 111.0	12

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
56	Cyazofamid	8.53	108.0 > 44.0	6	216.0 > 103.1	16	324.0 > 108.1	10
57	Cyfluthrin peak 1	9.56	163.0 > 65.1	26	163.0 > 91.1	12	163.0 > 127.1	6
58	Cyfluthrin peak 2	9.60	163.0 > 91.1	12	163.0 > 127.0	6	206.0 > 151.1	18
59	Cyfluthrin peak 3	9.62	163.0 > 91.1	12	163.0 > 127.0	6	226.0 > 206.1	12
60	Cyfluthrin peak 4	9.64	163.0 > 91.1	12	163.0 > 127.0	6	226.0 > 206.1	10
61	Cyhalofop butyl	9.09	256.0 > 91.1	24	256.0 > 120.0	10	256.0 > 157.8	30
62	Cyhalothrin-R	9.11	180.9 > 151.9	22	197.0 > 141.1	10	208.1 > 180.9	8
63	Cyhalothrin-S	9.17	181.0 > 151.9	22	208.1 > 151.8	28	208.1 > 180.9	8
64	Cymoxanil	6.00	110.9 > 53.0	12	128.2 > 83.0	12	128.2 > 111.0	6
65	Cypermethrin peak 1	9.68	163.0 > 91.1	12	163.0 > 127.1	6	180.9 > 152.1	20
66	Cypermethrin peak 2	9.71	163.0 > 91.1	12	163.0 > 127.0	6	180.9 > 151.9	18
67	Cypermethrin peak 3	9.76	163.0 > 91.0	12	163.0 > 127.0	6	180.9 > 152.2	20
68	Cypermethrin peak 4	9.78	163.0 > 91.1	12	163.0 > 127.1	6	180.9 > 152.2	20
69	Cyprazine	7.02	170.0 > 109.1	12	212.1 > 109.1	20	212.1 > 170.1	10
70	Cyproconazole	8.18	222.0 > 82.1	10	222.0 > 89.3	38	222.0 > 125.0	20
71	DDD p,p	8.05	235.0 > 165.1	20	235.0 > 199.0	14	236.8 > 165.0	20
72	DDD, o, p	8.28	235.0 > 165.1	20	235.0 > 199.0	14	236.8 > 165.0	20
73	DDE o,p	8.01	246.0 > 176.1	28	317.8 > 246.0	20	317.8 > 248.0	18
74	DDE p, p	7.82	246.0 > 176.1	28	317.8 > 246.0	20	317.8 > 248.0	18
75	DDT o,p	8.28	235.0 > 165.1	22	235.0 > 199.5	10	236.8 > 165.0	22
76	DDT p,p	8.51	235.0 > 165.1	22	235.0 > 199.5	10	236.8 > 165.0	22
77	Deltamethrin	10.24	181.0 > 152.1	22	252.8 > 92.9	16	252.8 > 172.0	8
78	Demeton-S (Disulfoton oxon)	6.44	114.0 > 81.0	14	142.5 > 114.9	6	170.0 > 114.0	8
79	Demeton-S-methyl-sulfone	7.29	169.0 > 79.0	18	169.0 > 109.0	12	169.0 > 125.0	8
80	Diafenthiuron	8.38	296.1 > 262.2	10	311.1 > 254.1	16	311.1 > 296.1	12
81	Dialifos	9.29	208.0 > 89.1	26	208.0 > 180.9	10	209.7 > 182.9	10
82	Diazinon	6.65	137.1 > 54.1	20	137.1 > 84.1	12	179.1 > 121.5	26
83	Diazinon oxon	6.61	137.0 > 54.1	20	137.0 > 84.1	12	273.1 > 137.1	12
84	Dichlobenil	4.9	170.9 > 99.9	24	170.9 > 136.0	14	172.8 > 99.8	24
85	Dichlofluanid	7.32	123.0 > 51.0	32	123.0 > 77.0	18	223.9 > 123.0	10
86	Dichlorobenzophenone, 4, 4	7.46	111.0 > 74.9	12	139.0 > 74.9	26	139.0 > 111.0	12
87	Dichlorvos	4.38	109.0 > 79.0	6	185.0 > 93.0	12	186.9 > 93.0	12
88	Diclofop methyl	8.6	252.9 > 126.9	36	252.9 > 161.9	16	340.0 > 253.0	10
89	Dicofol	8.92	111.0 > 74.9	12	139.0 > 111.0	12	250.9 > 139.0	12
90	Dieldrin	8.05	262.8 > 190.9	30	262.8 > 192.9	30	262.8 > 227.8	16
91	Difenoconazole peak 1	10.19	265.0 > 139.0	36	265.0 > 202.1	16	323.0 > 265.0	14
92	Difenoconazole peak 2	10.21	265.0 > 138.9	36	265.0 > 202.0	18	323.0 > 265.0	16
93	Diflubenzuron	4.62	113.0 > 63.0	12	141.0 > 63.0	26	141.0 > 113.0	12
94	Diflufenican	8.59	266.0 > 238.1	12	266.0 > 246.1	10	394.0 > 266.1	12
95	Dimethoate	6.49	87.0 > 42.1	10	93.0 > 63.0	8	125.0 > 79.0	8
96	Dimethomorph peak 1	10.4	165.0 > 77.0	18	165.0 > 137.0	10	301.0 > 165.1	12
97	Dimethomorph peak 2	10.54	301.0 > 139.0	14	301.0 > 165.1	10	387.1 > 301.1	10
98	Diniconazole	8.26	232.0 > 149.0	14	268.0 > 136.0	34	268.0 > 232.0	10
99	Dioxathion	6.61	96.9 > 65.0	16	125.0 > 97.0	6	153.0 > 96.9	10
100	Disulfoton	6.84	88.0 > 45.0	18	88.0 > 59.8	6	185.9 > 96.9	16
101	Diuron	7.67	124.0 > 73.0	16	186.9 > 124.0	22	186.9 > 159.0	10
102	Edifenphos	8.50	172.9 > 65.1	30	172.9 > 109.0	8	310.0 > 109.0	26

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
103	Endosulfan peak 1	7.89	194.7 > 125.0	22	194.7 > 159.4	8	240.6 > 205.9	14
104	Endosulfan peak 2	8.25	158.9 > 123.0	12	194.7 > 159.0	8	240.6 > 205.8	12
105	Endosulfan sulfate	8.51	238.7 > 203.9	12	271.7 > 234.9	12	271.7 > 236.8	12
106	Endrin	8.29	245.0 > 173.0	22	262.8 > 192.9	30	280.8 > 245.3	8
107	Endrin-Ketone	8.75	209.2 > 138.4	30	316.8 > 208.9	28	316.8 > 281.0	10
108	Epoxiconazole	8.70	165.0 > 138.0	8	192.0 > 111.0	22	192.0 > 138.0	12
109	Esfenvalerate	10.08	125.0 > 89.3	20	167.0 > 125.0	10	225.1 > 119.1	18
110	Ethiofencarb	6.89	107.0 > 77.0	16	168.0 > 77.0	30	168.0 > 107.0	8
111	Ethion	8.29	153.0 > 97.0	10	230.9 > 128.9	22	230.9 > 174.9	12
112	Ethion monoxon	8.08	170.9 > 97.0	22	170.9 > 115.0	12	170.9 > 143.0	6
113	Ethoprophos	6.14	157.9 > 96.9	16	157.9 > 113.9	6	200.0 > 158.0	6
114	Ethoxyquin	6.49	174.1 > 131.2	18	174.1 > 146.1	12	202.1 > 174.1	14
115	Etofenprox	9.81	163.1 > 77.1	32	163.1 > 107.1	16	163.1 > 135.1	10
116	Etrimfos	6.77	153.1 > 56.0	16	153.1 > 98.0	10	167.9 > 153.1	6
117	Famoxadone	10.44	224.1 > 167.2	18	224.1 > 196.1	8	329.8 > 224.1	8
118	Fenamidone	8.89	238.1 > 103.1	22	268.0 > 77.1	34	268.0 > 180.1	18
119	Fenamiphos	7.94	154.0 > 139.0	10	216.9 > 202.0	12	303.1 > 195.2	8
120	Fenarimol	9.26	1390 > 74.9	26	139.0 > 111.0	14	219.0 > 107.0	10
121	Fenazaquin	8.91	145.1 > 91.0	24	145.1 > 117.1	12	160.1 > 145.1	8
122	Fenbuconazol	9.64	129.0 > 77.8	18	129.0 > 102.0	14	198.1 > 129.1	8
123	Fenchlorfos	7.14	124.9 > 47.0	12	124.9 > 79.0	6	169.0 > 110.4	6
124	Fenitrothion	7.24	125.0 > 79.0	8	277.0 > 109.0	16	277.0 > 260.0	6
125	Fenobucarb	5.99	121.1 > 77.0	20	121.1 > 103.1	12	150.1 > 121.1	8
126	Fenoxycarb	8.79	116.0 > 44.1	16	116.0 > 88.0	8	255.1 > 186.1	10
127	Fenpropathrin	8.85	97.1 > 55.1	6	181.0 > 126.8	28	181.0 > 151.9	22
128	Fenthion	7.35	245.3 > 125.0	12	278.0 > 109.0	18	278.0 > 169.0	14
129	Fenthion sulfoxide	8.28	109.0 > 79.0	8	125.0 > 47.0	14	125.0 > 79.0	8
130	Fenvalerate	10.00	125.0 > 89.0	18	167.0 > 89.0	32	167.0 > 125.0	10
131	Flonicamid	6.08	146.0 > 126.0	8	174.0 > 69.0	36	174.0 > 146.0	10
132	Fluchloralin	6.64	264.0 > 159.5	14	264.0 > 206.1	8	306.0 > 264.0	8
133	Flucythrinate peak 1	9.75	157.0 > 107.1	12	199.1 > 107.1	22	199.1 > 157.1	8
134	Flucythrinate peak 2	9.81	157.0 > 107.0	12	199.0 > 107.0	22	199.0 > 157.1	8
135	Flufenacet	7.37	122.7 > 122.0	8	151.1 > 95.0	24	151.1 > 136.1	10
136	Flufenoxuron	6.74	267.9 > 135.0	34	267.9 > 169.9	24	267.9 > 241.0	12
137	Flusilazole	8.04	206.0 > 151.3	14	233.0 > 151.9	14	233.0 > 164.9	16
138	Fluvalinate peak 1	10.04	180.8 > 152.1	22	250.0 > 55.1	16	250.0 > 199.9	18
139	Fluvalinate peak 2	10.07	180.8 > 152.1	20	250.0 > 55.1	16	250.0 > 200.0	16
140	Folpet	7.75	104.0 > 76.0	10	130.0 > 102.0	12	259.9 > 130.1	14
141	Heptachlor	7.11	99.8 > 39.0	26	99.8 > 65.0	12	271.8 > 236.9	12
142	Heptachlor epoxide	7.65	262.9 > 192.9	30	352.8 > 262.9	16	354.7 > 264.9	12
143	Hexaconazole	7.94	213.9 > 123.5	28	213.9 > 159.0	18	231.0 > 175.0	10
144	Hexazinone	8.60	127.7 > 83.0	10	171.1 > 71.1	14	171.1 > 85.1	12
145	Imazalil	7.95	172.8 > 109.0	26	174.7 > 147.0	16	215.0 > 173.0	8
146	Imiprothrin	8.33	123.0 > 41.1	22	123.0 > 55.9	12	123.0 > 81.0	8
147	Indoxacarb	10.20	133.9 > 106.0	8	203.0 > 106.1	22	203.0 > 134.0	12
148	Iprobenfos	6.88	91.1 > 65.0	16	203.9 > 91.9	8	203.9 > 121.0	28
149	Isazophos	6.75	118.9 > 76.0	18	161.0 > 119.0	8	161.0 > 146.0	6

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
150	Isodrin	7.59	146.8 > 111.1	10	192.9 > 123.0	28	192.9 > 157.2	20
151	Isoprothiolane	7.96	204.0 > 85.0	28	204.0 > 118.0	8	290.0 > 118.0	12
152	Isoproturon	7.20	146.1 > 128.0	10	191.1 > 146.1	8	206.1 > 72.1	18
153	Kresoxim-methyl	8.02	116.0 > 62.9	24	116.0 > 89.0	14	130.9 > 130.1	10
154	Malaoxon	7.00	99.0 > 71.0	8	127.0 > 99.0	6	127.0 > 109.0	12
155	Malathion	7.26	92.8 > 63.0	8	125.0 > 79.0	8	173.1 > 99.0	12
156	Metalaxyl	7.14	131.9 > 117.0	12	160.1 > 130.0	18	160.1 > 144.8	10
157	Methamidophos	4.55	141.0 > 64.0	18	141.0 > 79.0	20	141.0 > 94.8	8
158	Methidathion	7.79	145.0 > 58.0	14	145.0 > 85.0	6	302.6 > 284.9	14
159	Methiocarb	7.25	153.0 > 45.0	12	153.0 > 109.1	6	168.1 > 153.0	10
160	Methomyl	5.87	87.8 > 44.0	10	104.7 > 58.0	10	104.7 > 88.0	6
161	Methoxychlor	8.85	227.1 > 141.1	32	227.1 > 169.1	22	227.1 > 212.1	12
162	Metolachlor	7.37	162.1 > 132.9	14	238.1 > 132.8	26	238.1 > 162.2	10
163	Metoxuron	7.74	167.9 > 140.0	8	183.0 > 167.9	10	228.2 > 183.0	6
164	Metribuzin	7.03	198.0 > 55.0	26	198.0 > 82.1	16	198.0 > 110.0	10
165	Mevinphos	5.32	127.0 > 95.0	14	127.0 > 109.0	10	192.0 > 127.0	10
166	Monocrotophos	6.52	96.9 > 82.0	10	127.0 > 95.0	16	127.0 > 109.0	10
167	Monolinuron	6.56	125.8 > 99.0	12	214.0 > 94.0	20	214.0 > 172.0	8
168	Myclobutanil	8.05	179.0 > 90.0	28	179.0 > 125.0	14	179.0 > 151.7	8
169	Ortho-phenylphenol	5.65	141.1 > 115.1	14	170.1 > 115.0	34	170.1 > 141.1	22
170	Oxadiazon	7.97	174.9 > 76.0	28	174.9 > 112.0	12	174.9 > 147.2	6
171	Oxamyl	5.75	145.1 > 61.0	8	145.1 > 72.0	16	162.0 > 115.0	10
172	Oxychlordane	7.68	115.0 > 50.9	22	184.9 > 84.9	26	184.9 > 121.0	12
173	Oxyfluorfen	8.04	252.0 > 146.0	30	252.0 > 169.8	28	252.0 > 224.0	10
174	Paclobutrazol	7.84	125.0 > 89.0	18	236.0 > 125.0	12	236.0 > 167.0	10
175	Paraoxon-ethyl	7.21	109.0 > 81.0	10	149.0 > 91.1	10	149.0 > 102.0	16
176	Paraoxon-methyl	6.77	95.9 > 65.0	12	109.0 > 79.0	6	230.0 > 105.9	16
177	Parathion (ethyl)	7.39	109.0 > 81.0	10	124.9 > 97.0	6	291.0 > 109.0	12
178	Parathion-methyl	7.07	124.9 > 79.0	6	263.0 > 109.0	12	158.9 > 89.0	28
179	Penconazole	7.62	248.0 > 157.0	22	248.0 > 192.0	12	125.0 > 62.8	28
180	Pencycuron	6.58	125.0 > 89.0	16	125.0 > 99.0	16	252.1 > 161.0	14
181	Pendimethalin	7.55	252.1 > 162.0	8	252.1 > 191.3	8	263.9 > 164.9	26
182	Pentachlorophenol	6.62	267.8 > 166.9	26	267.8 > 168.9	28	163.0 > 91.1	12
183	Permethrin peak 1	9.40	183.1 > 153.0	12	183.1 > 168.0	12	183.0 > 153.0	14
184	Permethrin peak 2	9.60	183.0 > 165.1	10	183.0 > 168.1	10	123.1 > 41.1	24
185	Phenothrin	8.96	123.1 > 79.1	14	123.1 > 81.1	8	121.0 > 77.0	22
186	Phenthoate	7.64	246.0 > 121.0	8	274.0 > 121.0	10	75.0 > 47.0	8
187	Phorate	6.31	121.0 > 65.0	8	260.0 > 75.0	8	109.0 > 81.0	10
188	Phorate oxon sulfone	7.38	138.9 > 111.0	6	183.0 > 111.0	10	109.0 > 63.0	30
189	Phorate oxon sulfoxide	7.31	109.0 > 81.0	10	109.0 > 91.0	6	125.0 > 97.0	5
190	Phorate sulfone	7.36	153.0 > 96.9	10	199.0 > 143.0	10	96.9 > 65.0	16
191	Phorate sulfoxide	7.31	125.0 > 97.0	6	153.0 > 97.0	10	121.1 > 65.0	10
192	Phosalone	9.04	182.0 > 74.8	30	182.0 > 111.0	14	160.0 > 50.9	38
193	Phosmet	8.81	160.0 > 76.9	22	160.0 > 133.0	10	127.0 > 94.9	16
194	Phosphamidon	6.99	127.0 > 109.0	12	264.1 > 127.0	12	135.2 > 77.1	14
195	Phoxim	7.88	135.2 > 94.0	8	135.2 > 134.5	6	145.1 > 102.1	25
196	Picoxystrobin	7.81	145.1 > 115.1	15	145.1 > 130.0	15	166.1 > 55.0	18

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
197	Pirimicarb	6.86	166.1 > 96.0	12	238.1 > 166.1	10	304.0 > 168.1	12
198	Pirimiphos-ethyl	7.48	318.1 > 166.1	12	318.1 > 182.1	10	290.1 > 125.0	20
199	Pirimiphos-methyl	7.17	290.1 > 233.0	8	305.1 > 180.1	8	202.1 > 145.5	14
200	Pretilachlor	7.95	202.1 > 174.2	8	238.1 > 146.1	10	69.9 > 42.0	8
201	Prochloraz	9.52	180.1 > 138.1	12	308.0 > 147.1	12	95.9 > 53.0	16
202	Procymidone	7.69	95.9 > 67.1	8	283.0 > 96.1	8	296.7 > 268.9	10
203	Profenofos	7.98	336.9 > 266.9	12	336.9 > 308.9	8	210.1 > 112.0	10
204	Prometon	6.54	210.1 > 168.1	10	225.0 > 168.1	10	58.1 > 42.0	20
205	Propamocarb	5.00	129.1 > 58.1	12	188.2 > 58.1	8	160.9 > 99.0	24
206	Propanil	7.06	160.9 > 125.7	16	217.0 > 161.0	8	135.1 > 77.1	26
207	Propargite	8.59	135.1 > 107.1	12	150.1 > 135.1	8	138.0 > 64.0	15
208	Propetamphos	6.60	138.0 > 110.0	10	193.9 > 165.9	10	172.9 > 74.0	38
209	Propiconazole peak 1	8.51	172.9 > 109.0	26	172.9 > 145.0	16	172.9 > 74.0	38
210	Propiconazole peak 2	8.55	172.9 > 109.0	24	172.9 > 145.0	14	110.0 > 62.9	24
211	Propoxur	6.02	110.0 > 64.1	16	152.1 > 110.0	8	132.0 > 51.1	35
212	Pyraclostrobin	10.08	132.0 > 77.0	20	164.0 > 132.1	10	1070 > 91.1	10
213	Pyridalyl	9.79	204.0 > 148.1	18	204.0 > 176.1	10	198.1 > 117.9	30
214	Pyrimethanil	6.74	198.1 > 157.6	18	198.1 > 182.9	14	136.1 > 78.0	20
215	Pyriproxyfen	9.08	136.1 > 96.0	10	226.1 > 186.1	12	146.0 > 118.1	10
216	Quinalphos	7.66	157.1 > 102.0	22	157.1 > 129.0	14	213.8 > 141.9	28
217	Quintozene	6.57	213.8 > 178.9	14	294.8 > 236.9	14	163.0 > 99.9	20
218	Quizalofop-ethyl	9.77	163.0 > 136.0	10	372.1 > 299.0	10	123.1 > 81.1	8
219	Simazine	6.55	172.7 > 172.2	8	186.0 > 91.0	8	213.0 > 152.1	12
220	Simetryn	7.11	213.0 > 170.1	10	213.0 > 185.1	8	99.0 > 57.1	6
221	Spiromesifen	8.70	254.1 > 209.1	10	272.1 > 254.2	8	100.1 > 41.0	20
222	Spiroxamine peak 1	7.21	100.1 > 58.0	10	100.1 > 72.1	8	100.1 > 41.0	20
223	Spiroxamine peak 2	7.33	100.1 > 58.0	10	100.1 > 72.1	8	125.0 > 89.0	16
224	Tebuconazole	8.63	125.0 > 99.0	16	250.0 > 125.0	20	125.0 > 47.0	12
225	Temephos	10.98	125.0 > 79.1	8	466.1 > 203.0	12	230.9 > 128.9	22
226	Terbufos	6.62	230.9 > 174.9	12	230.9 > 203.0	8	125.0 > 97.0	6
227	Terbufos sulfone	7.74	153.0 > 97.0	10	199.0 > 143.0	10	100.9 > 51.0	10
228	Tetraconazole	7.41	159.0 > 123.4	16	336.0 > 204.0	28	159.0 > 74.8	32
229	Tetradifon	9.02	159.0 > 111.0	20	159.0 > 131.0	10	151.0 > 77.1	30
230	Thiabendazole	7.78	174.0 > 130.1	10	201.0 > 174.0	14	72.0 > 44.0	6
231	Thiobencarb	7.34	100.1 > 44.0	10	100.1 > 72.0	6	88.0 > 59.8	6
232	Thiometon	6.53	125.0 > 47.0	14	125.0 > 79.0	8	160.1 > 130.0	18
233	Thiophanate-methyl	7.12	160.1 > 144.8	10	192.0 > 160.1	6	265.0 > 219.9	20
234	Tolclofos-methyl	7.06	265.0 > 250.0	12	266.8 > 252.0	12	109.0 > 57.1	6
235	Tralkoxydim	9.12	137.0 > 57.0	10	137.0 > 109.1	6	127.0 > 91.1	8
236	Transfluthrin	7.04	163.0 > 91.1	12	163.0 > 143.0	14	208.0 > 111.0	20
237	Triadimefon	7.41	208.0 > 126.7	12	208.0 > 180.8	8	112.0 > 57.6	8
238	Triadimenol	7.76	128.0 > 65.0	18	168.2 > 70.0	10	86.1 > 43.3	6
239	Triallate	6.79	268.0 > 183.9	18	268.0 > 226.0	12	91.0 > 65.0	12
240	Triazophos	6.89	161.0 > 105.7	12	161.0 > 134.1	8	92.9 > 65.0	6
241	Trichlorfon	7.38	109.0 > 63.0	10	109.0 > 81.0	6	162.0 > 84.9	18
242	Tricyclazole	8.00	162.0 > 133.9	8	189.0 > 161.9	10	116.1 > 63.0	24
243	Trifloxystrobin	8.40	116.1 > 89.0	14	145.0 > 95.0	14	179.0 > 144.0	14

No.	Compound Name	RT [min]	Quantitation [m/z]	CE [V]	Qualifier 1 [m/z]	CE [V]	Qualifier 2 [m/z]	CE [V]
244	Triflumizole	7.70	206.0 > 179.0	14	206.0 > 186.0	8	306.1 > 159.7	20
245	Trifluralin	6.16	306.1 > 206.0	10	306.1 > 264.1	8	215.0 > 168.1	16
246	Triphenylphosphate (TPP)	8.62	326.1 > 168.6	28	326.1 > 325.3	10	217.0 > 167.0	18
247	Triticonazole	9.07	235.1 > 181.9	12	235.1 > 217.1	8	186.8 > 124.0	18

Results

The multiresidue pesticide analysis of juices for routine target analyte detection and quantitation is described using QuEChERS and GC-MS/MS detection with the TSQ 8000 Evo GC-MS/MS system.

All standards and samples were processed using the TraceFinder software with high speed and throughput. Linearity of the calibration curves of all the test compounds in both matrices was established with R^2 > 0.98. Detection of false positives in the control sample extracts for each matrix was < 1% indicating the specificity and sensitivity of the method.

The LOQs for 152 compounds were ≤ 1 µg/kg, whereas for 75 compounds the LOQs ranged between 1 and 5 µg/kg. For 20 compounds the LOQs ranged between 5 and 10 µg/kg. In general, the LOQ of individual compounds followed the order *Aloe vera* < *Amla*.

When using calibration standards prepared in solvent, comparatively higher matrix enhancement was noted for few compounds in aloe vera juice as compared to *Amla* juice. Moderate enhancement in signals was observed for *Amla*. Some examples are presented in Figure 2.

The recovery for the test compounds at 2, 5, and 10 µg/kg was within 70–120% with the associated relative standard deviations < 20% in both *Aloe vera* and *Amla*.

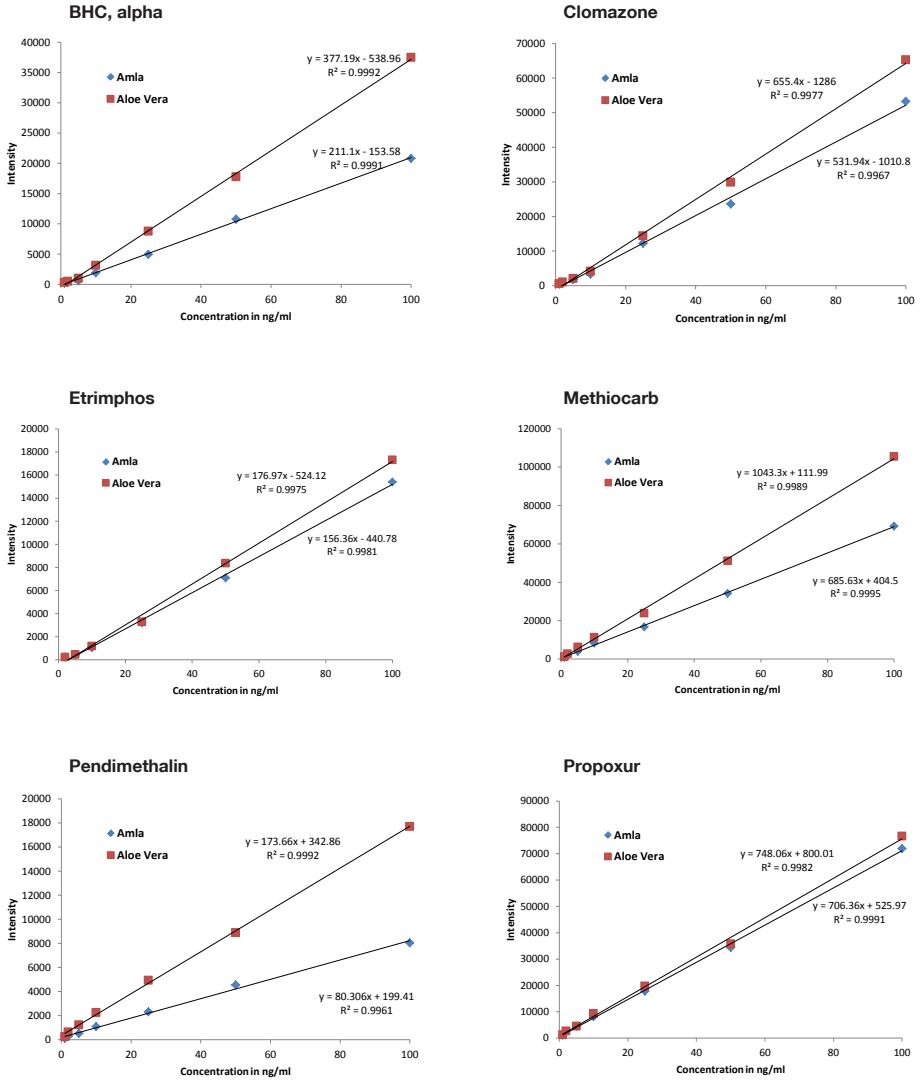

Figure 2. Calibration curves of selected compounds in *Amla* and *Aloe vera*.

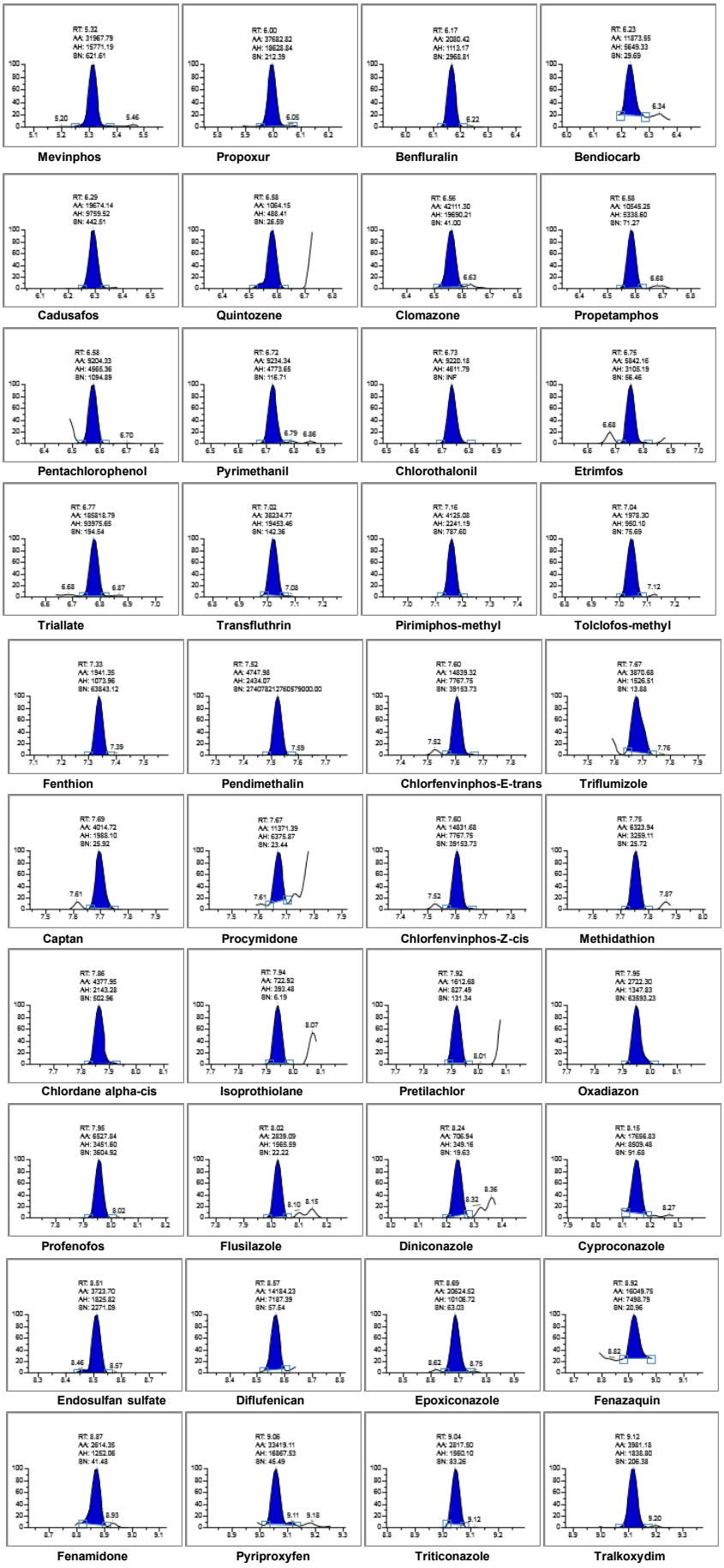

Figure 3. Peaks of selected compounds at 5 µg/kg in *Aloe vera* matrix.

Conclusions

The method was successfully validated for the analysis of 247 compounds in two different herbal juices with good precision and accuracy, demonstrating the potential of the method for analysis of pesticides for both regulatory and routine residue monitoring.

The TSQ 8000 Evo system with TraceFinder™ data processing software suite increased sample throughput and reduced the after-run processing time due to its high target compound selectivity, short GC run time, and excellent automated peak integration.

This method can be utilized for detection and confirmation of trace amounts of pesticides in herbal juices and has potential to detect trace level compounds at concentrations as low as 1-2 ng/g.

References

1. Kunkel. G. (1984) *Plants for Human Consumption*. Koeltz Scientific Books.
2. Ngamkitidechakul, C.; Jaijoy, K.; Hansakul, P.; Soonthornchareonnon, N.; Sireeratawong, S. (2010). "Antitumour effects of phyllanthus emblica L.: Induction of cancer cell apoptosis and Inhibition of in vivo tumour promotion and in vitro invasion of human cancer cells". Phytotherapy Research 24 (9): 1405–1413. doi:10.1002/ptr.3127
3. Codex Alimentarius Commission. (http://www.codexalimentarius.net/web/index en.jsp)
4. Commission Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC Text with EEA relevance.
5. Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J. J.; AOAC Int. 2003, 86, 412.

www.thermoscientific.com/TSQ8000Evo

Thermo Fisher Scientific, Austin, TX USA is ISO 9001:2008 Certified.

Africa +43 1 333 50 34 0
Australia +61 3 9757 4300
Austria +43 810 282 206
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China 800 810 5118 (free call domestic) 400 650 5118
Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland +358 9 3291 0200
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9494
Italy +39 02 950 591
Japan +81 45 453 9100
Korea +82 2 3420 8600
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
Norway +46 8 556 468 00
Russia/CIS +43 1 333 50 34 0
Singapore +65 6289 1190
Spain +34 914 845 965
Sweden +46 8 556 468 00
Switzerland +41 61 716 77 00
UK +44 1442 233555
USA +1 800 532 4752

Thermo SCIENTIFIC
A Thermo Fisher Scientific Brand

AN10464-EN 0615S