Analysis of Multiresidue Pesticides Present in Ayurvedic Churna by GC-MS/MS

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Overview

Purpose

Analysis of Herbal powders or 'churnas' using an optimized GC-MS/MS method is described. As they have high amount of matrix co-extractives, they pose critical analytical problems. The purpose of this work was overcome the effect of the matrix and develop a reliable method.

Methods

Ayurvedic churna samples were extracted by liquid-liquid extraction and cleanup with dispersive solid phase extraction. The analysis was performed by GC-MS/MS using a timed-SRM detection method on Thermo Scientific TSQ 8000™ triple quadrupole GC-MS/MS instrument, employing two SRM transitions for each pesticide compound in a typical MRM method setup. Data processing and reporting are performed by using the Thermo Scientific TraceFinder™ software with one SRM transition used for quantitation and the second one for ion ratio confirmation.

Results

The results show good correlation factors with satisfactory recoveries. Real life samples were analyzed demonstrating the robustness and productivity of the applied method.

Introduction

Ayurveda is a Sanskrit term, made up of the words "ayus" and "veda." meaning life and science; together translating to 'science of life'. A blend of several herbs and spices make up the powdered mixture known as churna. Depending on its intended use for medicinal, beauty, or culinary purpose, the recipe varies. Avipittakara churna is a traditional Ayurvedic formula used widely and almost daily to control vitiated pitta dosha, remove heat in the digestive system, control indigestion, constipation, vomiting and anorexia. A major analytical challenge for these type of samples is mainly addition of multiple herbs with sugar and the natural color of herbs.

The dried leaves result in highly complex extracts from the sample preparation due to the rich content of active ingredients, essential oils and the typical high boiling natural polymer compounds.

Owing to the use of pesticides in the fresh herbs the churna may contain residual pesticides. Analysis of pesticide residues is thus important. Strict quality parameters, have been implemented to preserve the quality and efficacy of these churnas.

Key Feature
Trace GC1300 series
•Instant connect modularity GC injector & detector ports
The new Trace 1300 Series offers the most **versatile** GC platform in the market, with unique "**instant connect" modularity** for ground-breaking **ease of use** and **performance**, setting a new era in GC technology
GCMS/MS-TSQ-8000
•ExtractaBright Ion source cartidrige
•Ion source removal without venting vacuum
•Timed SRM acquisition

FIGURE 1. TSQ™ 8000 GC-MS/MS system with Thermo Scientific TriPlus RSH auto sampler with automated tool/syringe changer

Methods

Sample Preparation

Weigh 15g of *Churna*

↓

For recovery studies Pesticide stock solution was added in calculated quantities and kept for 30 min

↓

15mL of Acetonitrile (with 1% acetic acid) was added, shaken well. Further 3g $MgSO_4$ + 1.5g NaOAc + 10g NaCl was added and homogenized using Vortex mixer

↓

After centrifugation (5000 rpm, 5 min), cleanup of 1 mL supernatant performed by DSPE using 200 mg PSA and 10 mg GCB

↓

3 µL of supernatant injected to GC-MS/MS

TSQ 8000 GC-MS/MS Method Setup

The analytical method comprises the sample handling using the Triplus™ RSH liquid auto sampler, Thermo Scientific TRACE 1300 Series gas chromatograph equipped with a temperature programmable PTV injector, and the TSQ 8000 triple quadrupole MS.

TRACE™ 1310 Gas Chromatograph

Column oven program

Ramp rate	Temperature	Hold time
	70°C	2min
10°C/min	200°C	1min
10°C/min	285°C	8.5min

Carrier gas :Helium

Injection mode : PTV Splitless mode

Injection temp: :87°C (0.30 min)-285°C(Rate- 14.5°C/sec) (2.5min), Cleaning Phase - 290°C (20 min)

Splitless time :3 min, Split flow: 30 ml/min

Column Flow :1.2 ml/min

Column :TG-5 (30 mm x 0.25 mm I.D.x0.25 µm)

TSQ-8000 GCMS/MS

Ion source temp :230°C

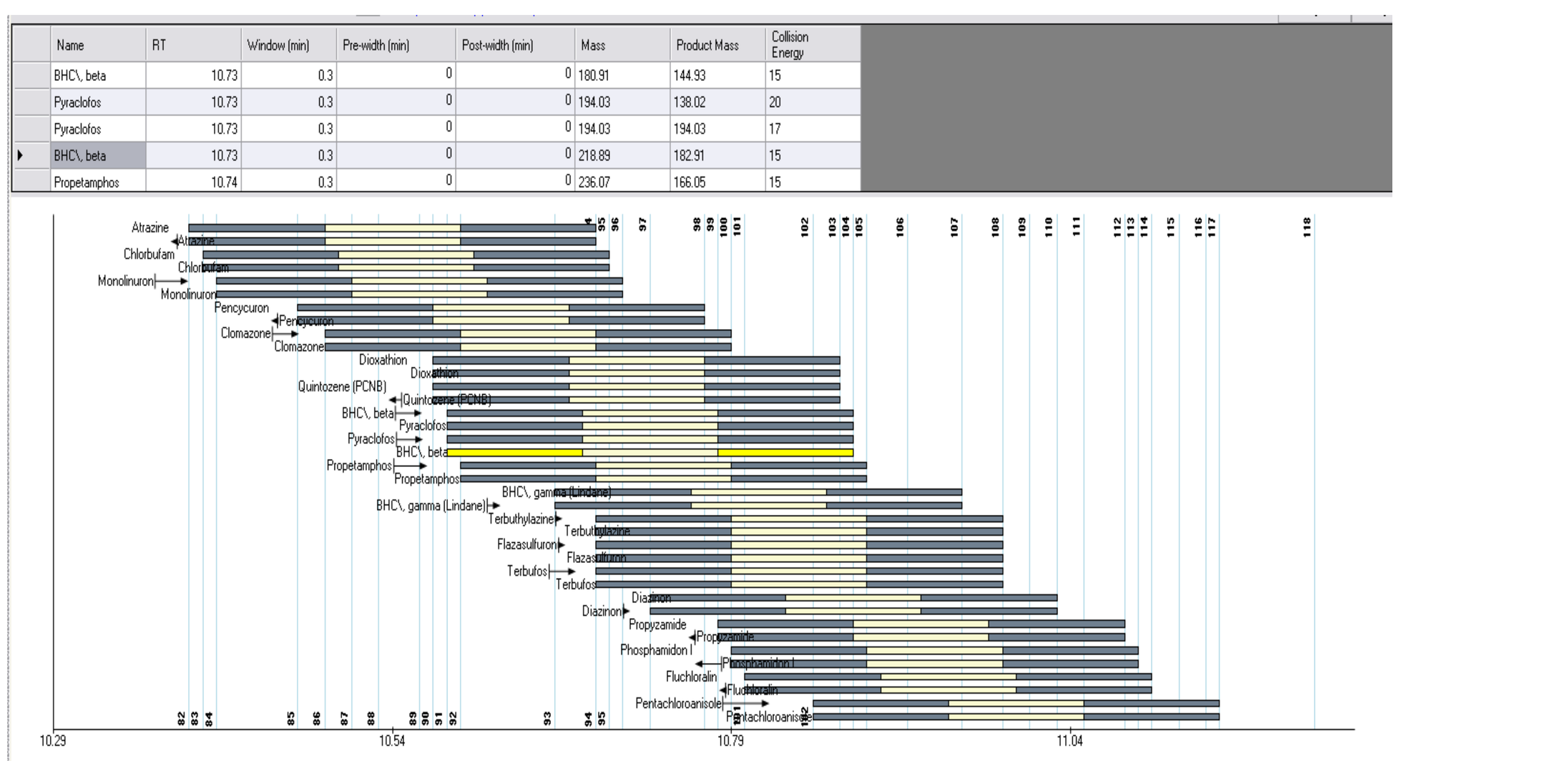
Interface temp :285°C

Acquisition mode :EI

MRM detection :timed SRM mode

Triplus RSH Auto sampler

Injection Volume :3µL



Data Analysis

The data processing and reporting was done using the Trace Finder™ quantitation and reporting software suite.

Results

Multi-residue pesticide analysis of Ayurvedic churnas using liquid-liquid extraction with GC-MS/MS detection by TSQ 8000 GC-MS/MS system for routine target analyte detection and quantitation is described. Software features of TraceFinder™ software was employed to quickly create the processing method from the ready database of compounds. All standards and samples were processed with high throughput. Around 200 pesticide compounds were considered for this study and included into a routine screening method with ≈28 min run time which was applied for analyzing market samples.

Calibration, Linearity, Recovery and Repeatability

All test compounds had correlation coefficients > 0.99 for the concentration range 2.5 to 50 ng/g. Obtained recoveries were within 70-120% with <20% associated RSDs.

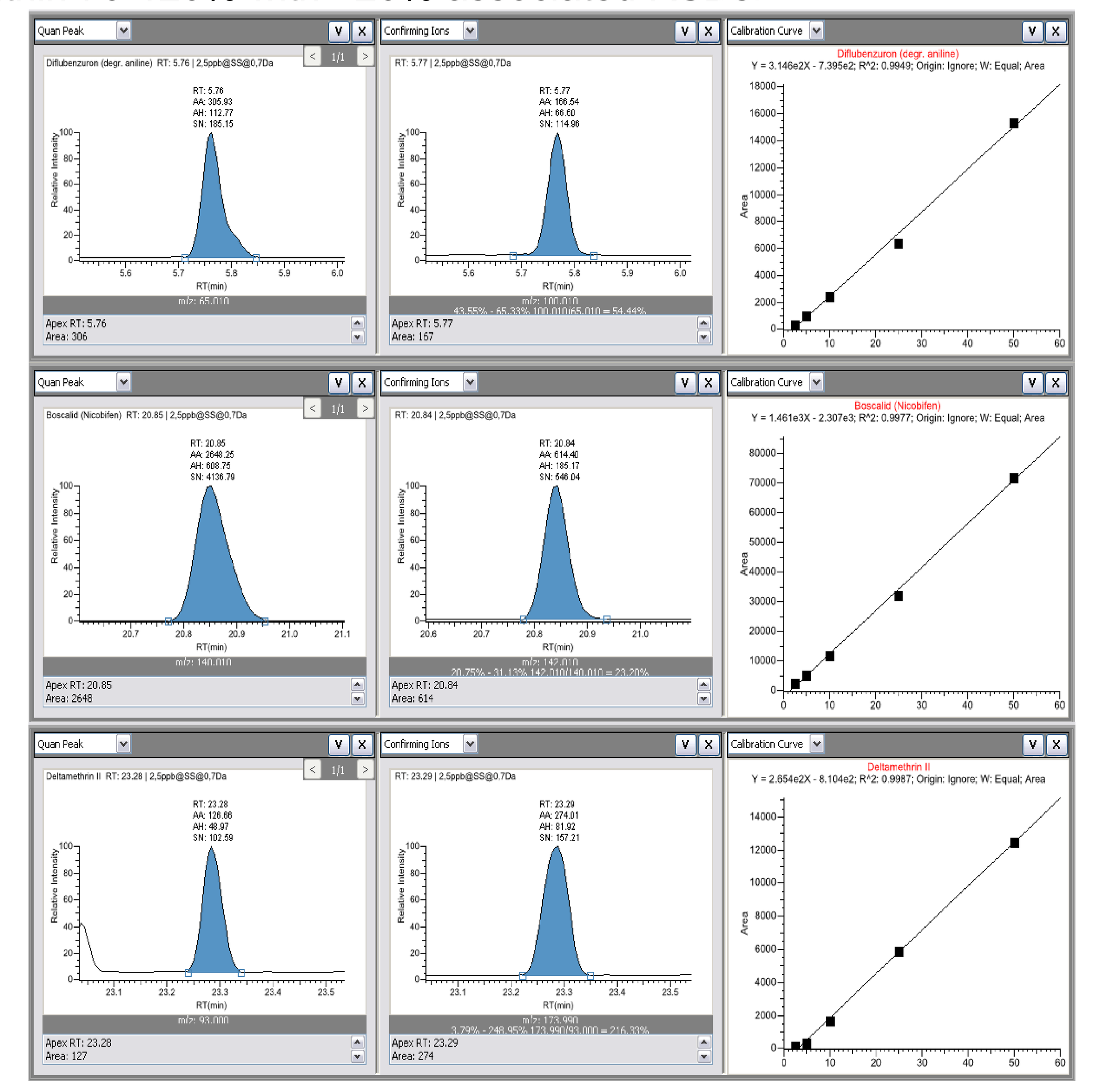


FIGURE 3. Selected chromatograms at 2.5 ng/g and calibration curves of few pesticides.

TABLE 1. MRM transitions, CE, slope, intercept and R2 of matrix standards

S. No.	Compound Name	RT (min)	Q1>Q3			CE	Q1>Q3			CE	Slope	Intercept	R2
1	Diflubenzuron (degr. i-cyanat)	5.24	153.02	>	90.01	20	153.02	>	125.01	20	7.98E+02	-1.19E+03	0.9969
2	Diflubenzuron (degr. aniline)	5.75	127.01	>	65.01	30	127.01	>	100.01	30	3.15E+02	-7.40E+02	0.9949
3	Methamidophos	5.87	141.00	>	95.00	10	141.00	>	126.00	5	1.28E+03	-3.18E+03	0.993
4	Dichlorphos (DDVP)	5.94	184.95	>	92.98	17	219.95	>	184.95	10	2.21E+02	-9.97E+00	0.996
5	Dichlobenil	6.82	135.97	>	99.98	10	170.96	>	135.97	15	8.45E+02	-6.43E+02	0.996
6	Mevinphos	7.39	127.03	>	109.02	10	192.04	>	127.03	12	1.59E+03	-2.46E+03	0.9964
7	Acephate	7.50	136.01	>	42.00	10	136.01	>	94.01	15	7.19E+02	-4.31E+03	0.9904
8	Dichloraniline\, 3\,5-	7.61	160.98	>	89.99	25	160.98	>	98.99	25	3.11E+02	-2.47E+02	0.9989
9	Molinate (Ordram)	8.58	126.07	>	55.03	10	187.10	>	126.07	10	6.48E+02	1.25E+03	0.9941
10	TEPP	8.60	263.06	>	179.04	15	263.06	>	235.06	5	5.71E+02	-2.52E+03	0.9946
11	Omethoate	9.00	110.01	>	79.01	15	156.02	>	110.01	10	8.09E+02	-5.42E+03	0.9969
12	Fenobucarb	9.11	121.07	>	77.05	15	150.09	>	121.07	10	1.13E+03	1.68E+03	0.9977
13	Propoxur	9.13	110.06	>	64.03	10	152.08	>	110.06	10	7.90E+02	-6.00E+02	0.9981
14	Propachlor	9.16	176.06	>	120.04	10	196.07	>	120.04	10	3.51E+02	5.42E+02	0.998
15	Ethoprophos	9.38	158.00	>	80.90	15	158.00	>	114.00	5	5.75E+01	-3.77E+01	0.9949
16	Trifluralin	9.58	264.09	>	160.05	15	306.10	>	264.09	15	1.37E+02	1.78E+02	0.9944
17	Chlorpropham	9.62	213.00	>	127.00	5	213.00	>	171.00	5	2.90E+02	-8.39E+02	0.9981
18	Benfluralin	9.63	292.10	>	160.05	21	292.10	>	264.09	10	3.91E+01	1.36E+02	0.9923
19	Sulfotep	9.70	322.02	>	202.01	15	322.02	>	294.02	10	2.58E+02	1.13E+03	0.9943
20	Bendiocarb	9.72	166.06	>	151.06	15	166.06	>	166.06	15	2.84E+03	-7.27E+02	0.9996
21	Monocrotophos	9.80	127.03	>	95.03	20	127.03	>	109.03	25	9.47E+02	-6.71E+03	0.9971
22	Methabenzthiazuron	9.82	164.05	>	136.04	12	164.05	>	164.05	10	1.07E+03	-3.59E+03	0.9974
23	BHC\, alpha	10.15	180.91	>	144.93	15	218.89	>	182.91	15	3.06E+02	-1.40E+02	0.997
24	Metamitron	10.36	202.09	>	174.07	5	202.09	>	186.08	10	1.61E+03	-8.25E+03	0.9969
25	Atrazine	10.54	215.09	>	173.08	10	215.09	>	200.09	10	6.38E+02	-1.36E+03	0.9945
26	Pencycuron	10.62	125.05	>	89.04	12	180.07	>	125.05	12	5.09E+02	2.76E+01	0.9914
27	Dioxathion	10.72	125.00	>	97.00	15	125.00	>	141.00	15	9.17E+02	-3.03E+02	0.9936
28	BHC\, beta	10.73	180.91	>	144.93	15	218.89	>	182.91	15	1.14E+03	-3.43E+03	0.9933
29	Propetamphos	10.74	236.07	>	166.05	15	236.07	>	194.06	5	1.49E+02	5.14E+01	0.9918
30	BHC\, gamma (Lindane)	10.81	180.91	>	144.93	15	218.89	>	180.91	5	1.15E+03	-3.65E+03	0.9939
31	Terbuthylazine	10.84	214.10	>	132.06	10	229.11	>	173.08	10	5.86E+02	-2.51E+02	0.9935
32	Diazinon	10.88	137.05	>	84.03	10	304.10	>	179.06	15	2.28E+02	4.48E+02	0.9987
33	Propyzamide	10.93	173.01	>	145.01	15	175.02	>	147.01	15	4.60E+03	-5.02E+03	0.9939
34	Fluchloralin	10.95	264.04	>	206.03	10	306.05	>	264.04	10	1.90E+02	-8.73E+02	0.9967
35	Pyroquilon	11.07	173.08	>	130.06	20	173.08	>	145.07	20	2.25E+03	-2.77E+02	0.9974
36	Pyrimethanil	11.11	198.11	>	158.09	30	198.11	>	183.10	15	8.18E+02	-2.68E+03	0.9953
37	Tefluthrin	11.16	177.02	>	127.02	20	197.03	>	141.02	15	1.27E+03	3.14E+03	0.9991
38	Etrimfos	11.29	292.06	>	153.03	10	292.06	>	181.04	10	1.36E+04	-1.23E+02	0.9935
39	Pirimicarb	11.50	166.10	>	96.06	10	238.14	>	166.10	15	4.37E+02	3.47E+02	0.9937
40	BHC\, delta	11.54	180.91	>	144.93	15	204.07	>	91.03	15	7.51E+02	-2.99E+03	0.9949
41	Iprobenfos	11.54	204.07	>	122.04	15	218.89	>	182.91	15	3.37E+03	-7.26E+03	0.9997
42	Formothion	11.74	126.00	>	93.00	8	172.00	>	93.00	5	2.55E+03	-7.33E+03	0.9982
43	Phosphamidon II	11.83	227.05	>	127.03	15	264.06	>	193.04	15	3.32E+02	-2.10E+03	0.9977
44	Dichlofenthion	11.90	222.98	>	204.98	10	278.97	>	222.98	15	3.32E+02	4.94E+01	0.9946
45	Dimethachlor	11.94	197.08	>	148.06	10	199.08	>	148.06	10	3.85E+03	1.37E+03	0.9992
46	Dimethenamid	11.95	230.06	>	154.04	10	232.06	>	154.04	10	3.93E+03	-2.33E+03	0.9953
47	Propazine	12.02	214.09	>	172.08	12	214.09	>	214.09	10	3.77E+02	-9.45E+02	0.997
48	Propanil	12.06	217.01	>	161.00	10	219.01	>	163.00	10	1.49E+03	-4.04E+02	0.9934
49	Malaoxon	12.07	127.02	>	99.02	10	127.02	>	109.02	20	4.87E+03	-2.13E+04	0.9978
50	Chlorpyrifos-methyl	12.08	124.96	>	78.97	10	285.91	>	92.97	20	3.76E+03	-1.25E+02	0.9945
51	Metribuzin	12.13	198.08	>	82.03	20	198.08	>	110.05	20	1.05E+03	-2.16E+03	0.9997
52	Spiroxamine I	12.15	100.09	>	58.05	15	100.09	>	72.06	15	5.98E+02	-2.21E+02	0.9909
53	Vinclozolin	12.16	212.00	>	172.00	15	285.00	>	212.00	15	1.90E+02	3.40E+02	0.9957
54	Carbofuran\, 3-Hydroxy	12.21	137.06	>	81.03	18	180.08	>	137.06	15	1.05E+03	-2.93E+02	0.9974
55	Parathion-methyl	12.22	263.00	>	109.00	15	263.00	>	246.00	15	1.93E+03	-2.45E+03	0.9966
56	Alachlor	12.23	161.07	>	146.06	12	188.08	>	160.07	10	5.06E+02	-2.20E+02	0.9997
57	Tolclofos-methyl	12.25	264.96	>	92.99	20	264.96	>	249.96	15	2.38E+02	4.77E+02	0.9932
58	Propisochlor	12.31	162.08	>	144.07	10	223.11	>	147.07	10	6.03E+02	-9.86E+02	0.9983
59	Metalaxyl	12.37	249.13	>	190.10	10	249.13	>	249.13	5	1.73E+03	-1.45E+03	0.9911
60	Carbaryl	12.41	144.06	>	115.05	20	144.06	>	116.05	20	3.02E+03	-6.15E+03	0.9919
61	Fuberidazol	12.41	183.80	>	156.10	10	183.80	>	183.10	20	1.79E+03	-3.27E+03	0.9902
62	Fenchlorfos (Ronnel)	12.47	284.91	>	269.92	13	286.91	>	271.91	20	1.88E+03	6.66E+02	0.9994
63	Prosulfocarb	12.63	100.00	>	72.00	10	128.00	>	43.10	5	-5.89E+01	2.91E+03	0.9938
64	Pirimiphos-methyl	12.66	290.09	>	233.07	10	305.10	>	290.09	15	6.26E+02	-3.69E+02	0.9911
65	Spiroxamine II	12.75	100.09	>	58.05	15	100.09	>	72.06	15	7.48E+02	6.32E+03	0.9916
66	Ethofumesate	12.80	207.08	>	161.06	10	277.02	>	109.01	8	1.31E+03	-4.50E+01	0.9907
67	Fenitrothion Confirming 1	12.80	277.02	>	260.02	10	286.11	>	207.08	12	1.66E+02	-2.68E+02	0.9997
68	Methiocarb	12.84	168.06	>	109.04	15	168.06	>	153.06	15	8.86E+02	-2.04E+03	0.9971
69	Malathion	12.92	127.01	>	99.01	10	173.02	>	127.01	10	3.28E+03	-4.34E+03	0.9951
70	Dichlofluanid	12.95	223.97	>	122.99	15	225.97	>	122.99	15	9.42E+02	-9.53E+02	0.9971
71	Phorate sulfone	13.01	153.00	>	125.00	5	199.00	>	143.00	10	5.89E+03	-2.71E+04	0.9942
72	Dipropetryn	13.02	241.90	>	149.80	20	254.90	>	180.30	20	7.60E+01	-3.88E+02	0.9906
73	Chlorpyrifos (-ethyl)	13.12	198.96	>	170.96	15	313.93	>	285.94	12	3.17E+03	-7.87E+03	0.9995
74	Fenthion oxon	13.22	277.80	>	109.10	25	329.60	>	298.90	10	2.60E+02	-9.79E+02	0.9927
75	Chlorthal-dimethyl (DCPA)	13.24	300.91	>	300.91	15	331.90	>	300.91	15	9.92E+03	8.30E+02	0.9986
76	Flufenacet	13.26	211.04	>	123.02	10	211.04	>	183.03	10	5.72E+02	-4.17E+02	0.9959
77	Endosulfan I (alpha)	13.43	240.89	>	205.91	20	264.88	>	192.91	22	1.24E+00	3.61E+01	0.9942
78	Imazethapyr	13.49	201.90	>	133.00	15	252.00	>	145.90	20	6.80E+02	8.31E+01	0.9944
79	Butralin	13.50	266.14	>	190.10	15	266.14	>	220.11	15	4.05E+02	-2.24E+02	0.9996
80	Pirimiphos (-ethyl)	13.54	304.12	>	168.06	15	333.13	>	318.12	15	1.20E+03	-2.03E+03	0.9992
81	Pendimethalin	13.86	252.12	>	162.08	12	252.12	>	191.09	12	7.48E+02	1.43E+02	0.9912
82	Fipronil	13.87	212.97	>	177.98	16	366.95	>	212.97	25	5.46E+02	-2.17E+03	0.9938
83	Cyprodinil	13.91	224.13	>	208.12	20	225.13	>	210.12	18	1.21E+03	-4.88E+03	0.9959
84	Metazachlor	13.92	133.05	>	117.04	20	209.07	>	132.05	12	3.44E+02	-4.82E+01	0.9939
85	Penconazole	14.01	248.06	>	157.04	25	248.06	>	192.04	15	7.21E+02	-1.29E+03	0.9977
86	Tolylfluanid	14.05	137.05	>	91.03	20	238.09	>	137.05	15	1.20E+03	-2.69E+03	0.9922
87	Chlorfenvinphos-Z	14.05	266.98	>	158.99	15	322.97	>	266.98	15	1.88E+03	-3.40E+03	0.9904
88	Allethrin	14.06	123.08	>	81.05	10	136.08	>	93.06	10	2.31E+03	-1.42E+03	0.9923
89	Mecarbam	14.09	226.04	>	198.03	5	329.05	>	160.03	10	2.83E+02	5.56E+02	0.9979
90	Phenthoate	14.18	146.01	>	118.01	10	274.03	>	246.02	10	3.93E+03	-1.10E+04	0.9951
91	Mephosfolan	14.20	196.02	>	140.02	15	196.02	>	168.02	10	2.14E+03	-8.14E+03	0.9973
92	Quinalphos	14.21	146.03	>	118.02	15	157.03	>	129.02	13	4.05E+03	-4.04E+03	0.9943
93	Triflumizole	14.31	179.04	>	144.04	15	206.05	>	179.04	15	1.11E+03	-2.46E+03	0.9925
94	Procymidone	14.31	283.02	>	96.01	15	283.02	>	255.02	10	2.88E+02	-1.32E+03	0.9983
95	Bromophos-ethyl	14.50	358.89	>	302.91	20	358.89	>	330.90	10	7.85E+02	-6.52E+02	0.9985
96	Methidathion	14.60	124.98	>	98.99	22	144.98	>	84.99	10	1.14E+03	-4.03E+03	0.9945
97	Chlordane\, alpha (cis)	14.62	372.81	>	265.87	18	374.81	>	267.87	15	-1.50E+01	3.59E+03	0.9967
98	DDE o\,p	14.63	245.95	>	175.97	25	317.94	>	245.95	20	9.58E+02	-8.14E+02	0.9946
99	Sulfallate	14.68	188.02	>	132.02	22	188.02	>	160.02	16	1.39E+02	2.56E+02	0.9945
100	Paclobutrazol	14.72	236.10	>	125.06	15	236.10	>	167.07	15	4.12E+03	-1.66E+03	0.9926
101	Disulfoton sulfone	14.74	213.01	>	125.01	10	213.01	>	153.01	5	4.26E+02	-5.26E+02	0.9912
102	Picoxystrobin	14.77	303.09	>	157.04	20	335.09	>	303.09	10	4.71E+02	-8.30E+02	0.9937
103	Endosulfan II (beta)	14.88	271.88	>	236.89	18	338.85	>	265.88	15	6.75E+02	-1.81E+02	0.9973
104	Mepanipyrim	14.89	222.11	>	207.10	15	223.11	>	208.10	15	1.13E+03	-6.30E+03	0.9965
105	Chlordane\, gamma (trans)	14.89	372.81	>	265.87	18	374.81	>	267.87	15	1.19E+03	-1.10E+03	0.9991
106	Flutriafol	14.97	123.04	>	75.03	15	219.07	>	123.04	15	1.63E+02	-6.37E+02	0.9915
107	Napropamide	15.00	128.07	>	72.04	10	271.16	>	128.07	5	2.81E+03	-1.30E+02	0.9972
108	Flutolanil	15.03	173.06	>	145.05	15	173.06	>	173.06	15	1.04E+04	-1.03E+03	0.9988
109	Pretilachlor	15.13	162.09	>	147.08	15	216.05	>	174.04	20	2.00E+02	-9.70E+02	0.9935
110	Hexaconazole Confirming 1	15.13	231.06	>	175.04	10	262.14	>	202.11	15	3.14E+03	-5.50E+03	0.9962
111	Isoprothiolane	15.14	290.06	>	118.03	15	290.06	>	204.05	15	2.44E+02	-8.60E+02	0.9961
112	Profenofos	15.21	138.98	>	96.98	8	338.94	>	268.95	20	1.21E+03	-4.61E+03	0.9939
113	Oxadiazon	15.26	258.05	>	175.04	10	304.06	>	260.05	10	2.66E+03	-5.04E+03	0.9927
114	DDE p\,p	15.32	245.95	>	175.97	25	317.94	>	245.95	20	7.92E+02	9.03E+01	0.9964
115	Myclobutanil	15.40	179.07	>	125.05	15	179.07	>	152.06	15	1.79E+03	-3.43E+03	0.9912
116	Buprofezin	15.43	172.09	>	57.03	10	249.13	>	193.10	10	1.22E+02	-1.70E+02	0.9906
117	Kresoxim-methyl	15.44	206.09	>	116.05	15	206.09	>	131.06	15	9.50E+02	-1.87E+02	0.9921
118	DDT o\,p	15.47	234.94	>	164.96	15	234.97	>	164.98	20	3.32E+03	-7.13E+03	0.9935
119	DDT o\,p Confirming 1	15.47	236.94	>	164.96	20	236.97	>	164.98	20	2.08E+03	-2.57E+03	0.9963
120	Aramite-1	15.48	185.06	>	63.02	15	319.10	>	185.06	15	6.67E+02	-2.69E+03	0.9959
121	Aramite-2	15.69	185.06	>	63.02	15	319.10	>	185.06	15	1.50E+03	-4.46E+03	0.9971
122	Carpropamid	15.78	139.00	>	103.10	10	222.00	>	125.00	18	1.66E+03	-5.53E+03	0.9982
123	Cyproconazole	15.79	222.09	>	125.05	20	224.09	>	127.05	20	1.68E+03	-2.37E+03	0.9989
124	Nitrofen	15.85	201.99	>	138.99	21	282.98	>	252.98	15	8.64E+02	-3.08E+03	0.9997
125	Chlorobenzilate	15.98	251.02	>	139.01	20	253.03	>	141.01	15	4.90E+03	-5.42E+03	0.9978
126	Oxadiargyl	15.99	149.90	>	122.90	15	285.00	>	255.00	14	4.35E+02	-2.11E+03	0.9963
127	Fenthion sulfoxide	16.05	279.01	>	153.01	15	294.02	>	279.01	8	5.29E+02	-1.76E+03	0.9958
128	Diniconazole	16.11	268.06	>	232.05	15	270.06	>	234.05	15	1.39E+03	-2.54E+03	0.9949
129	Ethion	16.12	230.99	>	202.99	15	383.99	>	230.99	10	1.30E+03	-2.03E+03	0.9973
130	Oxadixyl	16.16	132.06	>	117.05	15	163.07	>	132.06	10	8.13E+02	-8.69E+02	0.9985
131	DDT p\,p	16.20	234.94	>	164.96	20	234.94	>	164.96	20	1.40E+03	-2.70E+03	0.9979
132	DDD\, p\,p	16.20	234.97	>	164.98	20	236.97	>	164.98	20	3.85E+03	-8.78E+03	0.9959
133	Chlorthiophos1	16.20	324.96	>	268.97	15	324.96	>	296.97	10	4.82E+03	-5.03E+03	0.9969
134	Imiprothrin	16.36	123.00	>	81.00	5	324.90	>	269.20	14	2.18E+03	-1.11E+04	0.9967
135	Mepronil	16.45	269.14	>	119.06	10	269.14	>	210.11	10	1.79E+03	-3.67E+03	0.9945
136	Triazophos	16.46	161.03	>	134.03	10	257.05	>	162.03	10	2.15E+03	-4.89E+03	0.9936
137	Ofurace	16.58	186.05	>	158.05	10	232.07	>	186.05	10	2.66E+03	-2.54E+03	0.9973
138	Carfentrazone-ethyl	16.59	330.03	>	310.03	20	340.03	>	312.03	10	1.20E+03	-2.17E+03	0.9919
139	Benalaxyl	16.63	234.12	>	174.09	10	266.14	>	148.08	10	4.85E+02	-2.25E+03	0.9951
140	Trifloxystrobin	16.65	116.04	>	89.03	15	190.06	>	130.04	10	2.02E+03	-2.76E+03	0.9962
141	Propiconazole peak 1	16.77	259.02	>	69.01	20	259.02	>	173.02	20	2.24E+03	-3.36E+03	0.9989
142	Edifenphos	16.78	173.01	>	109.01	15	310.03	>	173.01	10	6.11E+03	-1.86E+04	0.9904
143	Quinoxyfen	16.84	272.00	>	237.00	20	307.00	>	272.00	10	3.67E+03	-3.83E+03	0.9982
144	Endosulfan sulfate	16.85	271.88	>	236.89	15	273.88	>	238.89	15	3.21E+03	-2.64E+03	0.9929
145	Clodinafop-propargyl	16.87	349.05	>	238.04	15	349.05	>	266.04	15	4.22E+02	-1.17E+03	0.9991
146	Flupicolide	16.90	208.80	>	182.00	20	261.00	>	175.00	24	2.06E+03	-4.90E+03	0.9988
147	Hexazinone	17.02	171.00	>	71.00	10	171.00	>	85.00	10	2.37E+03	-5.04E+02	0.9998
148	Propargite	17.16	135.06	>	107.05	15	350.16	>	201.09	10	1.58E+03	-1.64E+03	0.9991
149	Diflufenican	17.21	266.05	>	246.05	10	394.07	>	266.05	10	8.05E+02	-1.34E+03	0.9981
150	Triphenylphosphate (TPP)	17.26	325.07	>	169.04	25	326.07	>	325.07	10	8.99E+02	-1.73E+03	0.9995
151	Iprodione	17.65	187.02	>	124.01	20	187.02	>	159.02	40	2.74E+02	-1.87E+03	0.9979
152	Bifenthrin	17.77	181.05	>	153.05	6	181.05	>	166.05	15	4.18E+02	-1.67E+03	0.9922
153	Picolinafen	17.90	376.08	>	238.05	15	376.08	>	239.05	15	4.11E+02	-2.66E+02	0.9981
154	Bromopropylate	17.91	184.98	>	156.98	20	342.96	>	184.98	20	2.07E+03	7.95E+02	0.9967
155	Fenoxycarb	17.93	186.08	>	186.08	10	255.11	>	186.08	10	4.54E+03	-2.04E+03	0.9933
156	Fenpropathrin	18.01	181.09	>	152.07	23	265.13	>	210.10	15	9.64E+02	-3.89E+03	0.9956
157	Fenamidone	18.10	238.08	>	237.08	20	268.09	>	180.06	20	3.28E+03	-3.12E+03	0.9994
158	Tebufenpyrad	18.11	276.13	>	171.08	15	333.16	>	276.13	10	4.29E+03	-4.74E+03	0.9997
159	Fenazaquin	18.23	145.08	>	117.07	15	160.09	>	117.07	20	7.41E+03	-2.41E+03	0.9951
160	Imazalil	18.25	173.03	>	145.02	20	215.04	>	173.03	15	9.79E+02	3.21E+03	0.9954
161	Furathiocarb	18.27	163.07	>	107.04	10	325.13	>	194.08	10	1.15E+03	-3.88E+03	0.9989
162	Flurtamone	18.38	199.06	>	157.05	20	333.10	>	120.04	15	4.32E+02	3.09E+03	0.9945
163	Tetradifon	18.46	226.93	>	198.94	18	353.88	>	158.95	15	4.71E+02	1.84E+03	0.9973
164	Phosalone	18.54	181.99	>	111.00	15	181.99	>	138.00	10	1.89E+03	-2.79E+03	0.9985
165	Triticonazole	18.57	217.09	>	182.07	10	235.10	>	217.09	10	7.08E+02	-2.99E+03	0.9945
166	Pyriproxyfen	18.68	136.06	>	78.03	15	136.06	>	96.04	15	1.23E+03	-4.43E+02	0.9941
167	Cyhalofop butyl	18.70	256.10	>	120.05	10	256.10	>	256.10	10	2.62E+03	-3.21E+03	0.9969
168	Tralkoxydim	18.80	137.00	>	57.20	10	181.04	>	152.03	23	1.73E+03	-9.82E+02	0.9995
169	Cyhalothrin\, lambda	18.80	197.04	>	141.03	15	234.90	>	217.20	15	3.78E+02	2.34E+03	0.9997
170	Lactofen	18.83	344.04	>	223.02	15	344.04	>	300.03	15	6.64E+02	-2.06E+03	0.9975
171	Benfuracarb	19.03	164.08	>	149.07	10	190.09	>	144.07	10	6.04E+01	9.28E+02	0.9975
172	Pyrazophos	19.05	221.05	>	193.04	10	232.05	>	204.05	10	5.68E+03	-1.07E+04	0.993
173	Fenarimol	19.15	139.01	>	111.01	15	219.02	>	107.01	15	2.13E+03	-3.27E+03	0.9993
174	Azinphos-ethyl	19.20	132.01	>	77.01	20	160.02	>	132.01	5	2.51E+03	-2.51E+03	0.9944
175	Fenoxaprop-P	19.41	288.03	>	260.03	10	361.04	>	288.03	10	1.77E+02	2.25E+01	0.9998
176	Bitertanol1	19.59	170.09	>	115.06	25	170.09	>	141.07	20	5.81E+02	-2.02E+03	0.9993
177	Permethrin peak 1	19.68	183.04	>	165.03	15	183.04	>	168.03	15	1.02E+03	-2.78E+03	0.9973
178	Bitertanol2	19.71	170.09	>	115.06	25	170.09	>	141.07	20	5.81E+02	-2.02E+03	0.9993
179	Permethrin peak 2	19.81	183.04	>	165.03	15	183.04	>	168.03	15	1.03E+03	-3.45E+03	0.9909
180	Prochloraz	19.88	180.01	>	138.01	15	310.03	>	268.02	10	4.07E+02	-9.53E+02	0.9932
181	Cafenstrole	20.21	100.04	>	72.03	15	188.08	>	119.05	15	3.24E+03	-9.67E+02	0.9991
182	Cyfluthrin peak 1	20.26	163.02	>	91.01	12	163.02	>	127.02	10	-2.82E+00	1.14E+02	0.9915
183	Fenbuconazole	20.34	129.04	>	102.03	15	198.07	>	129.04	10	1.80E+03	-1.06E+03	0.9996
184	Cypermethrin I	20.65	163.03	>	127.02	10	181.03	>	152.03	25	1.43E+03	-1.06E+04	0.9996
185	Boscalid (Nicobifen)	20.84	342.03	>	140.01	15	344.03	>	142.01	15	1.46E+03	-2.31E+03	0.9977
186	Flucythrinate peak 1	20.85	199.07	>	107.04	22	199.07	>	157.06	10	5.91E+02	-5.19E+02	0.9958
187	Quizalofop-Ethyl	20.92	299.07	>	255.06	20	372.09	>	299.07	15	4.23E+02	5.20E+02	0.9969
188	Etofenprox	21.08	163.09	>	107.06	16	163.09	>	135.07	10	3.36E+03	-5.78E+03	0.9987
189	Flucythrinate peak 2	21.12	199.07	>	107.04	22	199.07	>	157.06	10	5.66E+02	-9.77E+02	0.9989
190	Fenvalerate peak 1	21.94	167.05	>	125.04	10	419.13	>	225.07	10	2.27E+03	2.29E+01	0.9978
191	Fluvalinate peak 1	22.09	250.06	>	200.05	20	252.06	>	200.05	20	4.67E+02	-1.82E+03	0.9973
192	Pyraclostrobin	22.17	132.03	>	77.02	15	325.08	>	132.03	20	1.20E+03	-3.04E+03	0.9936
193	Fluvalinate peak 2	22.20	250.06	>	200.05	20	252.06	>	200.05	20	4.65E+02	-1.73E+03	0.9977
194	Fenvalerate peak 2	22.28	167.05	>	125.04	10	419.13	>	225.07	10	4.91E+03	-2.59E+03	0.9996
195	Difenoconazole peak 1	22.76	323.05	>	265.04	15	325.05	>	267.04	20	2.82E+03	-2.99E+03	0.9995
196	Indoxacarb	22.95	203.03	>	106.01	20	203.03	>	134.02	20	6.46E+01	-3.09E+02	0.9996
197	Deltamethrin II	23.28	252.99	>	93.00	18	252.99	>	173.99	18	2.65E+02	-8.10E+02	0.9987
198	Azoxystrobin	23.63	344.10	>	329.10	20	388.11	>	345.10	15	1.30E+03	-1.16E+03	0.9991
199	Dimethomorph-1	23.91	301.10	>	165.05	10	387.12	>	301.10	12	7.18E+02	-1.39E+03	0.9992
200	Dimethomorph-2	24.60	301.10	>	165.05	10	387.12	>	301.10	12	6.61E+02	-8.51E+02	0.999

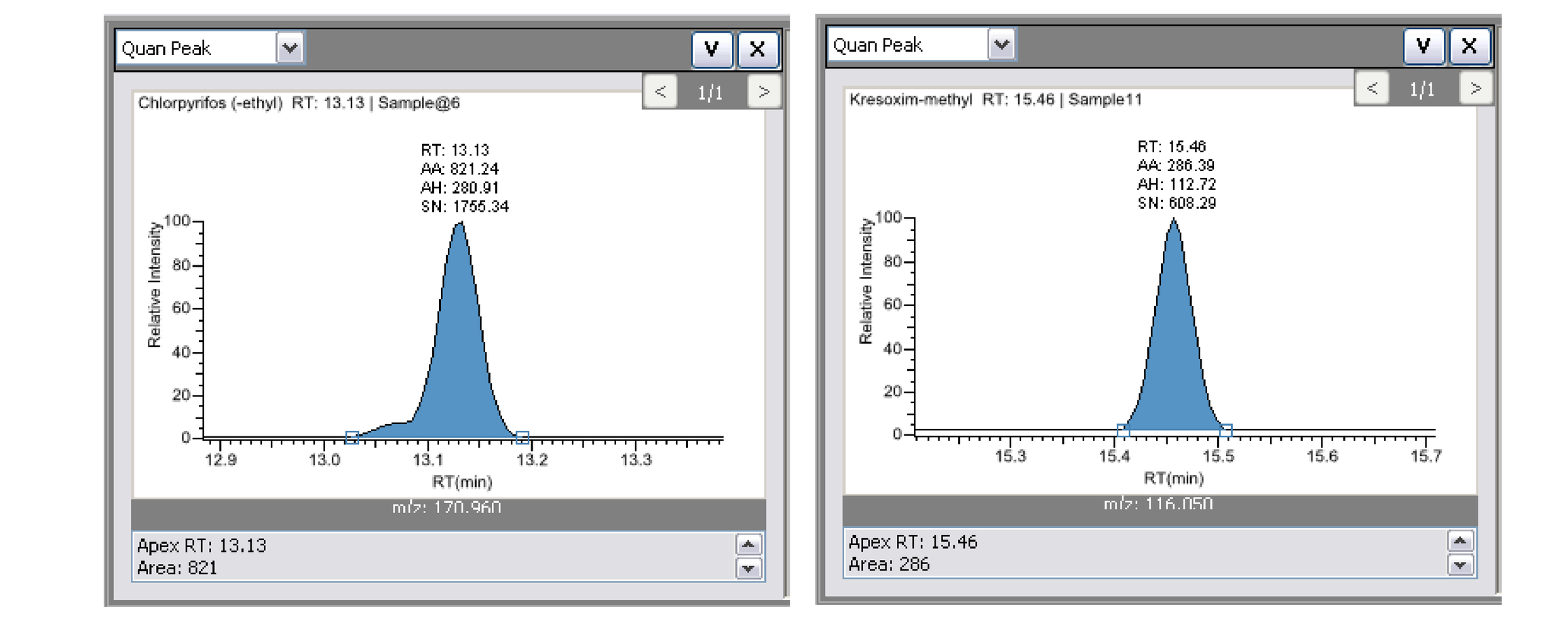


FIGURE 4. Traces of Chlorpyrifos ethyl and Kresoxim Methyl were detected at 2.3 and 2.7 µg/Kg respectively.

TABLE 2. Summary of pesticide detections in real samples

Pesticide Sr.No. (from Table 1)	Detected Pesticide	Amount (in mg/kg)
73	Chlorpyrifos –ethyl	0.0023
117	Kresoxim methyl	0.0027

Conclusion

A rapid and sensitive quantitative method is always a major goal for analytical laboratories involved in pesticide analysis. Within 28 minutes 200 pesticides were determined using the same method. Triple quadrupole mass analyzer TSQ 8000™ GC-MS/MS system with TraceFinder™ was used for data processing to reduce the processing time thereby resulting in a high throughput method.

- Linearity, specificity, recovery and repeatability of the method was established with minimal sample preparation time.
- This method can be utilized for detection and confirmation of trace amount of pesticides in difficult matrices such as herbal churnas. The method has potential to detect trace level compounds at concentration as low as 2.5 ng/g.
- As per the available guidelines, the concentration of the detected pesticides (0.0023 and 0.0027 mg/Kg) were below the prescribed limit of Unani Guidelines

References

1. http://www.myyog.com
2. ttp://www.ashtangayurveda.com/pages/History-of-Ayurveda.asp
3. http://www.plimism.nic.in/Protocol_For_Testing.pdf
4. Protocol for testing guideline for Ayurvedic, Siddha and Unani medicines Chapter 2.5.1

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