SHIMADZU
Excellence in Science

Application Note

No. GC-06-ADI-006

GCMS-TQ8030

Analysis of 126 residual pesticides in salad using triple quadrupole GCMS/MS system

❑ Introduction

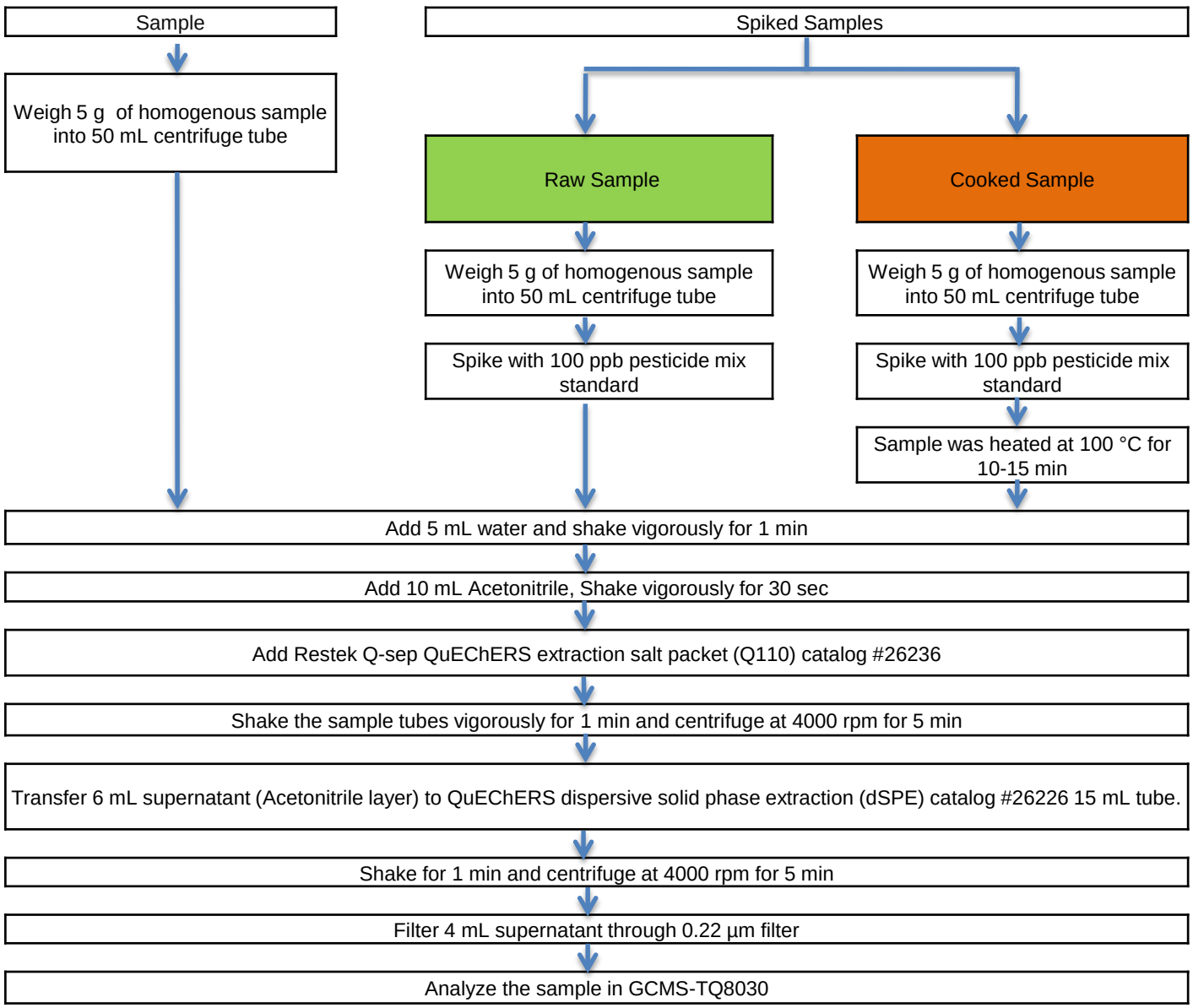
Pesticides are used to protect crops from insects, fungi, weeds, etc. and to improve the productivity. Different countries have different regulations to control usage and residual content of pesticides. So, it has become essential to analyze multiple pesticides in a single run to ensure fast and reliable testing method. Generally most of the cooked products have low risk of pesticides contamination as they get degraded at high temperature. Salad is usually consumed directly without being cooked and this increases the risk of exposure to multi pesticide residues.

The objective of the current study is to develop a fast, sensitive, selective, accurate and reliable method for analysis of 126 pesticide residues in pre-cooked and post-cooked salad separately by using Shimadzu GCMS-TQ8030, employing QuEChERS method for extraction, so as to determine the risk of pesticides in salad.

❑ Experimental:

Extraction of Pesticides from Salad

Extraction of pesticides was done using QuEChERS method, described as follows[1][2][3]



Application Note **No. GC-06-ADI-006**

GC/MS/MS Analytical conditions

The analysis was carried out on Shimadzu GCMS-TQ8030 as per the conditions given below:

Chromatographic parameters

Column	Rxi-5Sil MS (30 m x 0.25 mm x 0.25 µm)		
Injection Mode	Split		
Split ratio	5.0		
Carrier gas	Helium		
Flow Control Mode	Linear Velocity		
Linear Velocity	40.2 cm/sec		
Column Flow	1.2 mL/min		
Injection Volume	2.0 µL		
PTV Temp. Program	Rate ˚C /min	Temperature ˚C	Hold time (min)
		150.0	0.0
	300.0	290.0	41.0

Column Temp. Program :	Rate ˚C /min	Temperature ˚C	Hold time (min)
		70.0	2.0
	25.0	150.0	0.0
	3.0	200.0	0.0
	8.0	280.0	10.0

Mass Spectrometry parameters

Ion Source Temp	230.0 ˚C
Interface Temp	280.0 ˚C
Ionization Mode	EI
Acquisition Mode	MRM

❑ Results and Discussion:

For MRM optimisation, well resolved pesticides were grouped together. Standard solution mixture of about 1ppm concentration was prepared and injected using programmable temperature vaporization (PTV) technique to determine precursor ions for individual pesticide. Further, product ion scan was performed for individual pesticides followed by optimization of collision energy to obtain their characteristic MRM transitions. Based on MRM transitions, mixture of 126 pesticides was analyzed in a single run (Figure 3)[4] .

Linearity was plotted from LOQ concentration of 10 ppb to 200 ppb (represented in Figure 5 and 6) and recovery was studied by spiking known pesticides concentration of 100 ppb as depicted in Table 3 to 5.
Reproducibility studies of 100 ppb mix pesticides standards was carried out and results are shown in Table 2.

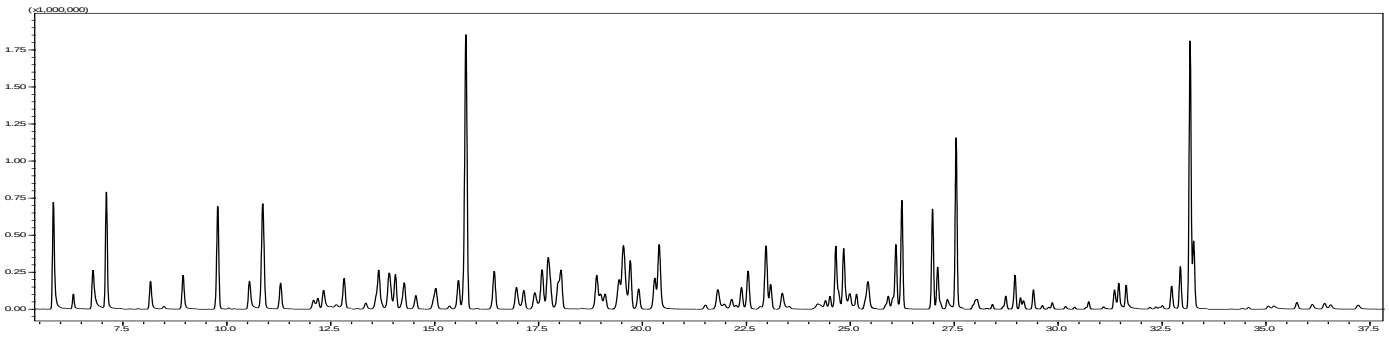


Figure 3: TIC for Pesticides Standard mixture (200 ppb)

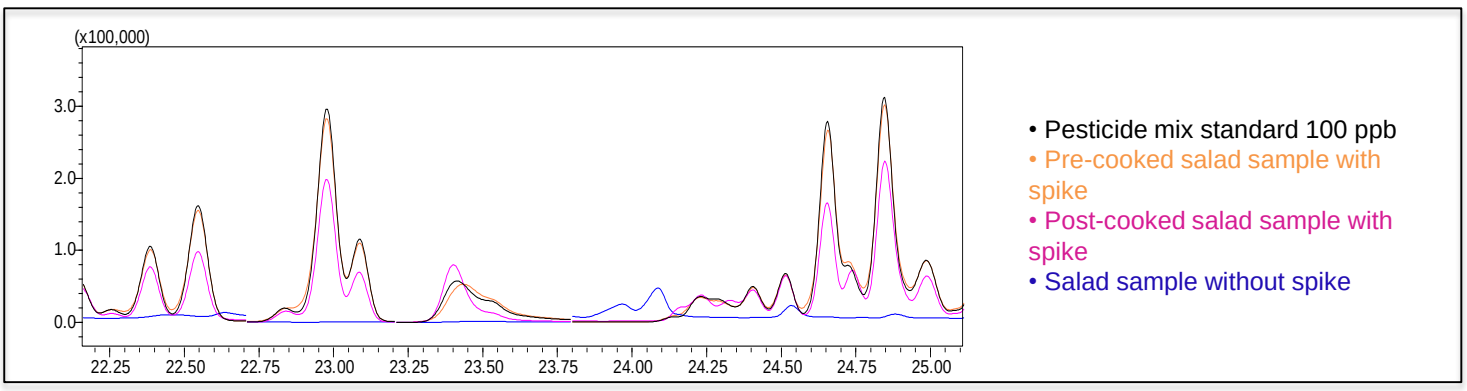


Figure 4: Overlay chromatogram

Table 1: List of pesticides

Sr. No	Compound Name	Sr. No	Compoud Name	Sr. No	Compound Name
1	3-Chloroaniline	43	Methiocarb	84	Cyproconazole-1 & 2
2	Novaluron	44	Dichlofluanid	85	Endrin
3	Diflubenzuron	45	Chlorpyriphos oxon	86	Beta-endosulfan
4	Dichlobenil	46	Malathion	87	Fenthion
5	3,4-Dichloraniline	47	Metholachlor-s	88	Oxadiargyl
6	Trichlorfon	48	Aldrin	89	Fenthion sulphone
7	cis 1,2,3,6-	49	Thiobencarb	90	o,p-DDT
	Tetrahydrophthalimide	50	Chlorpyriphos ethyl	91	Benalaxyl
8	Molinate	51	Fenthion	92	Carfentrazone
9	Omethoate	52	Triadimefon	93	Edifenfos
10	Fenobucarb	53	Flufenacet	94	Endosulfan sulphate
11	Propoxur	54	4,4-Dichlorobenzophenone	95	Trifloxystrobin
12	Diphenylamine	55	Tetraconazole	96	Chloridazon
13	Trifluralin	56	Pendimethalin	97	Fluopicolide
14	Benfluralin	57	Penconazole	98	Triphenyl phosphate
15	Monocrotophos	58	Fipronil	99	Diclofop
16	Alpha-HCH	59	Chlorfenvinphos	100	Captafol
17	Pencycuron DEG.	60	Captan	101	Diflufenican
18	Dimethoate	61	Quinalphos	102	Oxycarboxin
19	Carbofuran	62	Folpet	103	Spiromesifen
20	Simazine	63	Procymidone	104	Iprodione
21	Beta-HCH	64	Triflumizole	105	Carbosulfan
22	Atrazine	65	Methidathion	106	Phosmet
23	Monolinuron	66	Chlordane-trans	107	Bromopropylate
24	Clomazone	67	Bromophos-ethyl	108	Bifenthrin
25	Lindane	68	Alpha-endosulfan	109	Methoxychlor
26	Terbufos	69	Fenamiphos	110	Dicofol
27	Diazinon	70	Hexaconazole	111	Fenazaquin
28	Chlorothalonil	71	Isoprothiolane	112	Phenothrin-1
29	Paraoxon methyl	72	Profenofos	113	Tetradifon
30	Delta-HCH	73	p,p-DDE	114	Phenothrin-2
31	Etrimfos	74	Fipronil sulphone	115	Lambda-cyhalothrin
32	Tri-allate	75	Oxadiazon	116	Acrinathrin
33	Fenchlorphos oxon	76	Myclobutanyl	117	Permethrin-1
34	Fenchlorphos	77	Iprovalicarb-1	118	Permethrin-2
35	Metribuzin	78	Flusilazole	119	Cyfluthrin-1
36	Vinclozolin	79	Buprofezin	120	Cyfluthrin-2
37	Parathion methyl	80	Oxyfluorfen	121	Cyfluthrin-3
38	Alachlor	81	Kresoxim-methyl	122	Boscalid
39	Carbaryl	82	Iprovalicarb-2	123	Etofenprox
40	Heptachlor	83	Chlorfenapyr	124	Fenvalerate
41	Metalaxyl	84	Cyproconazole-1 & 2	125	Dimethomorph-1
42	Chlorpyriphos methyl	85	Endrin	126	Dimethomorph-2

Application N0. GC-06-ADI-006
Note

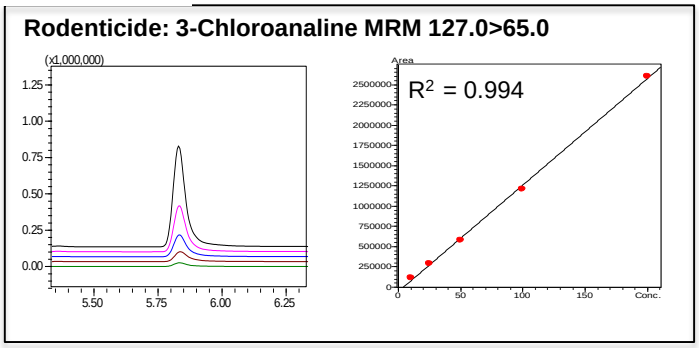


Figure 5: Linearity Plot for 3-Chloroaniline

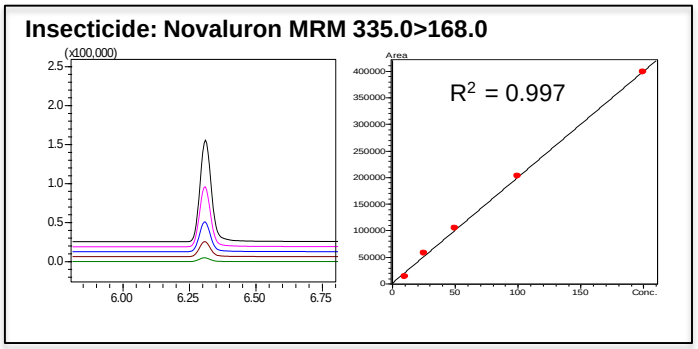


Figure 6: Linearity Plot for Novaluron

Table 2: Reproducibility (100 ppb)

Sr. No.	%RSD Range	Number of pesticides
1	1 - 2	15
2	2 - 5	75
3	5 - 10	25
4	10 - 20	11

Table 3: Linearity (10 ppb to 200 ppb)

Sr. No.	R^2	Number of pesticides
1	0.99 to 1.00	114
2	Less than 0.99	12

Table 4: Recovery

Sr. No.	%Recovery Range	Number of pesticides
1	90 – 110%	60
2	80 – 120%	84
3	70 – 130%	113
4	Less than 70%	13

Table 5: LOD/LOQ

Sr. No.	LOD Range	Number of pesticides	S/N Ratio range
1	0.4 - 5 ppb	99	8 - 91
2	5 - 10 ppb	15	94 - 185
3	10 - 20 ppb	10	197 - 327
4	20 - 30 ppb	02	380 & 484
Sr. No.	**LOQ Range**	**Number of pesticides**	**S/N Ratio range**
1	1 - 10 ppb	68	24 - 182
2	10 - 20 ppb	40	186 - 361
3	20 - 30 ppb	06	377 - 441
4	30 - 80 ppb	12	560 - 1466

❑ Conclusion

1. A highly sensitive method was developed for quantification of 126 pesticides in salad matrix sample by using GCMS/MS technique with QuEChERS method.
2. Advance features of GCMSMS TQ-8030 such as Ultra fast scanning, UFsweeper® and advance scanning speed protocol (ASSP) enabled sensitive, selective, fast, reproducible, linear and accurate pesticides analysis.

❑ References

1. EURL-FV Multi residue Method using QuEChERS followed by GC-QqQ/MS/MS and LC-QqQ/MS/MS for Fruits and Vegetables (European Reference Laboratory, 2010-M1).
2. Simultaneous analysis of Residual Pesticides in Foods via the QuEChERS Method utilizing GC-MS/MS Application Data sheet No-71, January, 2013.
3. Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate, AOAC official Method 2007.01.
4. Scan/MRM Analysis of Residual Pesticides in Food using GC-MS/MS (3) Shimadzu Application Data sheet No 72, January, 2013.

SHIMADZU
Excellence in Science

Shimadzu Analytical (India) Pvt.Ltd.
1 A/B, Rushabh Chambers, Makwana Road,
Marol, Andheri (East), Mumbai- 400059, India.
Tel: +91 22 29204741 Fax: +91 22 29205679
www.shimadzu.in

Related Solutions

- Environment
- Food Contamination

- Price Inquiry
- Product Inquiry
- Technical Service / Support Inquiry
- Other Inquiry