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Analysis of multiple pesticide residues in salad using triple quadrupole GCMS/MS system

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1. Introduction

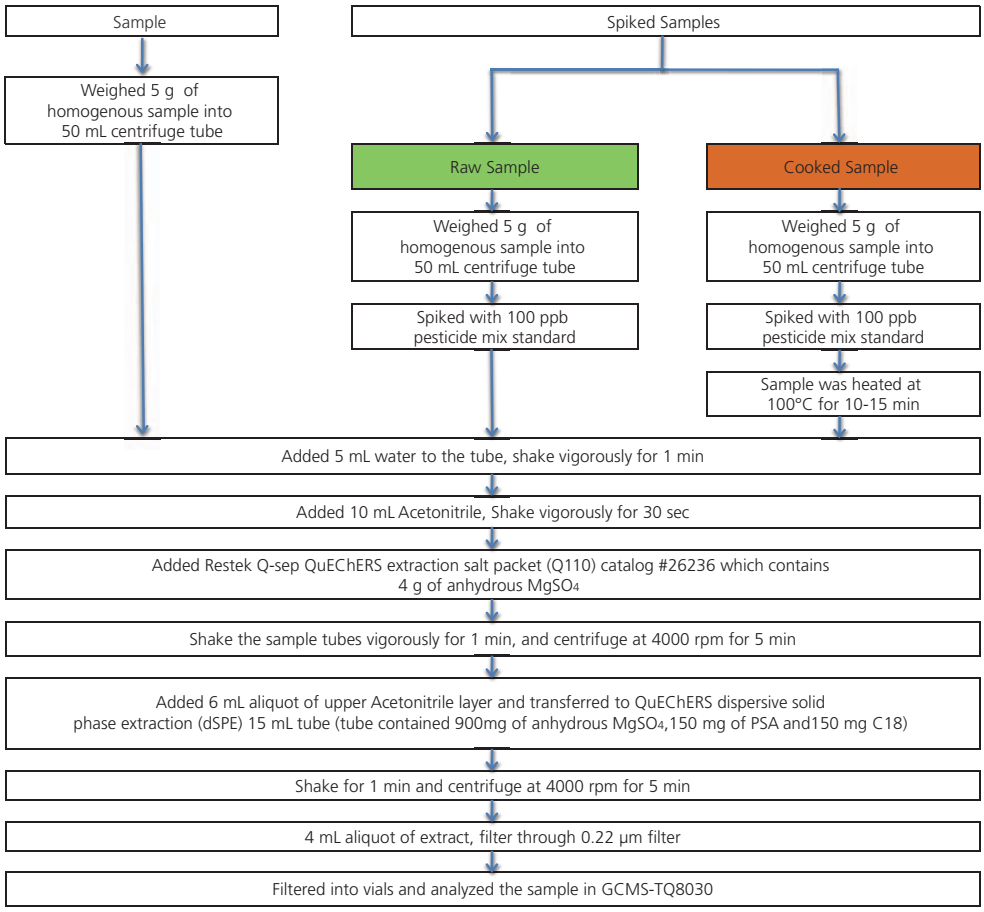
Pesticides are used in agriculture to protect crops from insects, fungi and weeds. Exposures to pesticides in different countries have different regulations to control usage and its content in consumer products. So it has become essential to analyze multiple pesticides in a single run to ensure fast 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 multi 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.

Fig. 1 Salad

2. Extraction of Pesticides from Salad

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



2-1. GCMS/MS Analytical conditions

The analysis was carried out on Shimadzu GCMS-TQ8030 as per the condition given below,

Fig. 2 GCMS-TQ8030 with Triple quadrupole system by Shimadzu

Key Features of GCMS-TQ8030

High-speed scan and data acquisition for accurate quantitation at 20,000 u/seconds.
Capable of performing simultaneous Scan/MRM
Ufsweeper® technology efficiently sweeps residual ions from the collision cell for fast, efficient ion transport and no cross-talk
Two overdrive lenses reduce random noise from helium, high-speed electrons, and other Factors to improve S/N ratio.
Flexible platform with EI, CI, and NCI ionization techniques
Full complement of acquisition modes including MRM, Scan/MRM and Neutral Loss Scan.

GCMS/MS analytical conditions[4]

Chromatographic parameters

Column	: Rxi-5Sil MS (30 m × 0.25 mm × 0.25 µm)		
Injection Mode	: Split		
Split ratio	: 5.0		
arrier 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
Mode	: MRM

2-2. List of pesticides

Table 1

Sr. No.	Pesticides	Sr. No.	Pesticides	Sr. No.	Pesticides
1	3-Chloroaniline	11	Propoxur	21	Beta hch
2	Novaluron	12	Diphenylamine	22	Atrazine
3	Diflubenzuron	13	Trifluralin	23	Monolinuron
4	Dichlobenil	14	Benfluralin	24	Clomazone
5	3,4-Dichloraniline	15	Monocrotophos	25	Lindane
6	Trichlorfon	16	Alpha hch	26	Terbufos
7	cis 1,2,3,6-Tetrahydrophthalimide	17	Pencycuron DEG.	27	Diazinon
8	Molinate	18	Dimethoate	28	Chlorothalonil
9	Omethoate	19	Carbofuran	29	Paraoxon methyl
10	Fenobucarb	20	Simazine	30	Delta hch

Sr. No.	Pesticides	Sr. No.	Pesticides	Sr. No.	Pesticides
31	Etrimfos	63	Procymidone	95	Trifloxystrobin
32	Tri-allate	64	Triflumizole	96	Chloridazon
33	Fenchlorphos oxon	65	Methidathion	97	Fluopicolide
34	Fenchlorphos	66	Chlordane trans	98	Triphenyl phosphate
35	Metribuzin	67	Bromophos-ethyl	99	Diclofop
36	Vinclozolin	68	Alpha endosulfan	100	Captafol
37	Parathion methyl	69	Fenamiphos	101	Diflufenican
38	Alachlor	70	Hexaconazole	102	Oxycarboxin
39	Carbaryl	71	Isoprothiolane	103	Spiromesifen
40	Heptachlor	72	Profenofos	104	Iprodione
41	Metalaxyl/ Metalaxyl M	73	p,p-DDE	105	Carbosulfan
42	Chlorpyriphos methyl	74	Fipronil sulphone	106	Phosmet
43	Methiocarb	75	Oxadiazon	107	Bromopropylate
44	Dichlofluanid	76	Myclobutanyl	108	Bifenthrin
45	Chlorpyriphos oxon	77	Iprovalicarb	109	Methoxychlor
46	Malathion	78	Flusilazole	110	Dicofol
47	Metholachlor-s	79	Buprofezin	111	Fenazaquin
48	Aldrin	80	Oxyfluorfen	112	Phenothrin
49	Thiobencarb	81	Kresoxim-methyl	113	Tetradifon
50	Chlorpyriphos ethyl	82	Iprovalicarb-1 & 2	114	Phenothrin
51	Fenthion	83	Chlorfenapyr	115	Lambda-cyhalothrin
52	Triadimefon	84	Cyproconazole-1 & 2	116	Acrinathrin
53	Flufenacet	85	Endrin	117	Permethrin-1
54	4,4- Dichlorobenzophenone	86	Beta endosulfan	118	Permethrin-2
55	Tetraconazole	87	Fenthion	119	Cyfluthrin-1
56	Pendimethalin	88	Oxadiargyl	120	Cyfluthrin-2
57	Penconazole	89	Fenthion sulphone	121	Cyfluthrin-3
58	Fipronil	90	o,p-DDT	122	Boscalid
59	Chlorfenvinphos	91	Benalaxyl /benalaxyl M	123	Etofenprox
60	Captan	92	Carfentrazone	124	Fenvalerate
61	Quinalphos	93	Edifenfos	125	Dimethomorph
62	Folpet	94	Endosulfan sulphate	126	Dimethomorph

3. Results

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

Linearity was plotted from LOQ concentration of 10 ppb to 100 ppb and recovery was carried out by spiking known pesticides concentration of 100 ppb as depicted in Table 2 to 5.

Reproducibility of all the listed pesticides was studied and results found were as follows

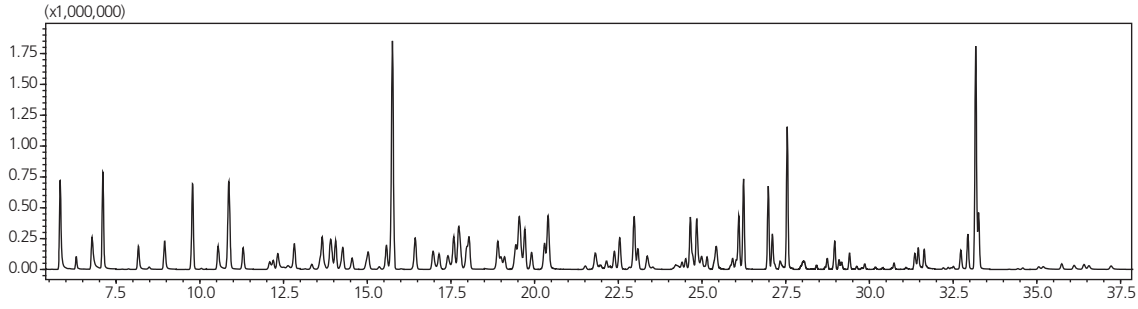


Fig. 3 TIC for Pesticides Standard mixture.

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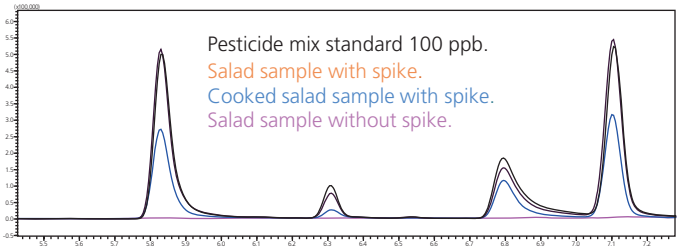

Fig. 4 Overlay chromatogram

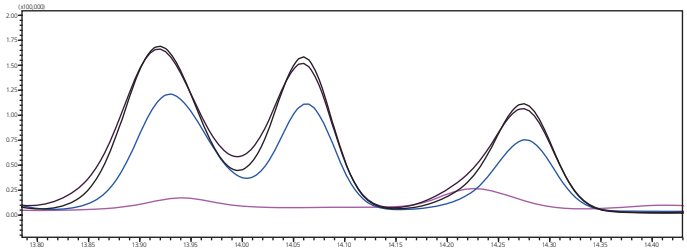

Fig. 5 Overlay chromatogram

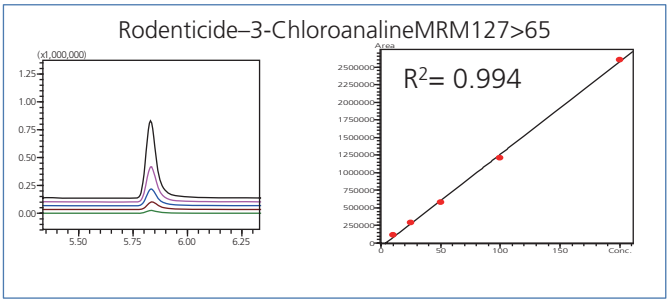

Fig. 6 Linearity Plot for 3-Chloroaniline

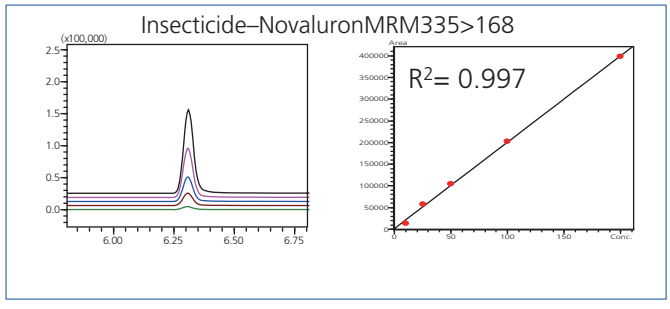

Fig. 7 Linearity Plot for Novaluron

Table 2 Reproducibility

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

Sr. No.	R^2	Number of pesticides
1	Above 0.99	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
	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

4. Conclusion

- A method is developed for quantification of more than100 pesticides at very low concentration level in Salad matrix sample by using GCMS/MS technique with QuEChERS method.
- Ultra fast scanning, sweeper and advance scanning speed protocol (ASSP) technique enabled sensitive, selective, fast, reproducible, linear and accurate pesticides analysis.
- It is safe to consume post-cooked salad rather than the pre-cooked, as the pesticide concentration levels were found to be greatly reduced in cooked salad sample.

5. 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, Jan uary, 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, Jan uary, 2013.

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