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Method Validation for Qualitative and Quantitative Analysis of Pesticide Residues in Tomato with GC-MS/MS (TQD) for Food Safety Testing

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Abstract

Pesticide residues analysis in fruits and fresh vegetables is a challenge for food safety as the gap between pesticide sprays and harvests is very less in vegetables. A multi residue method was developed for qualitative and quantitative analysis of 64 pesticides (insecticides, fungicides and herbicides) using QuEChERS extraction method and GC-MS/MS (Triple Quadrupole) for analysis. Eight different concentrations of certified reference materials from 0.05 ppm to 0.30 ppm were injected in GC-MS/MS with MRM method, in six replications, and R^2 ranged from 0.990-0.999 with RSD of 0.55 to 11.24. The sample preparation approach is through adoption of QuEChERS method, untreated control tomato samples were fortified with mixture of pesticides at 0.05, 0.25, 0.5 mg/kg, each is five replications, and the recovery of pesticides is in the range of 80-95%, and hence method can be used for qualitative and quantitative analysis of 64 pesticides in/on tomato for monitoring studies.

Highlights

- The sample preparation and analytical method validated in this study for multiple pesticide residues analysis in Tomato is useful for qualitative and quantitative analysis of residues at 0.05 ppm level for 64 pesticides

Keywords: Method validation, pesticide residues, tomato, GC-MS/MS (TQD)

Vegetables are the important ingredient of the human diet for the maintenance of the health and prevention of diseases. Tomato (*Lycopersicon esculentum* Mill.) is widely consumed vegetable in India usually in the form of curry, and also in raw form as salad, home-cooked, or processed as juice, paste, or sauce. As per the National Sample survey conducted during 2011-2012 in India, per capita consumption of tomato in rural and urban area is 586 and 806 grams per month, respectively (Anonymous, 2014), and the total Indian meal constitutes about 150-250 g of vegetables per day (Mukherjee and Gopal, 2003). A wide range of pesticides are used for crop protection against pest infection during the cultivation of vegetables (Agnihotri 1999; Kalra, 2003), and the literature reveals that vegetables contain the residues of pesticides above their respective maximum residue limit (Taneja, 2005; Ashutosh K Srivatsava

Table 1: MRM parameters for qualitative and quantitative analysis of pesticides on GC-MS/MS (TQD)

Name of the Pesticide	Retention Time (min)	Molecular Weight	Monitoring Ions	Precursor Ion	Qualifier Ion	Quantifier Ion
Methamidophos	8.54	141.34	141, 94	141	141>64, 141>79, 141>95	141>95
Dichlorvos	8.62	220.98	237, 235	185	185>63, 185>93, 185>109	185>93
Monocrotophos	15.45	223	192, 127, 164	127	127>109, 127>95, 127>79	127>109
Phorate	15.71	276	260, 231, 121	260	260>175, 260>231, 121>93	121>93
Alpha HCH	15.84	290.82	219, 181, 183	219, 181	219>183, 219>147, 181>145	181>145
Dimethoate	16.45	229.28	125, 229, 93, 87	125, 229	125>79, 125>93, 125>125, 125>87	125>125
Beta HCH	17.00	290.82	219, 181, 183	181, 219	181>145, 219>183	181>145
Atrazine	17.09	215.68	215, 200	215	215>200, 215>172, 215>138	215>200
Lindane	17.36	290.8	181, 219, 183	181, 219	181>145, 219>183	181>145
Chlorthalanil	18.14	265.91	266	266	266>133, 266>168, 266>231	266>231
Diazinon	18.15	304.3	304, 779, 179	304, 179	304>137, 304>164, 304>179, 179>137	179>137, 304>137
Delta HCH	18.80	290.82	219,183, 181	181, 219	181>145, 219>183	181>145
Phophomidon	20.04	299	264, 127	264	264>72, 264>127, 264>193	264>127
Chlorpyrifos methyl	20.35	322.53	286, 125	286	286>208, 286>241	286>241
Methyl parathion	20.71	263.21	263, 223, 125	263	263>109, 263>127, 263>246	263>109
Alachlor	20.81	269.76	188, 369, 238, 240	188, 269	188>160, 188>130, 269>160, 269>188	188>160, 269>160
Heptachlor	20.97	373.32	337, 274, 272	272	272>237, 272>141, 272>117	272>237
Metalaxyl	21.25	279	206	206	206>132, 206>162, 206>206	206>206
Demeton-S-methyl sulfone	21.70	290.34	142, 109, 169	169	169>109, 169>125	169>125
Fenitrothion	22.11	277	277, 260	260,277	260>109, 260>125, 260>151, 277>109, 277>260	260>109, 277>109
Malathion	22.79	330.36	173, 127, 125	173	173>99, 173>117, 173>127	173>99
Aldrin	22.83	364.91	263,286, 314, 293	263	263>193, 263>228	263>193
Chlorpyrifos	22.99	350.62	314, 286, 197	314,286	314>166, 314>258, 314>286, 286>93, 286>271	314>258
Fenthion	23.24	278	278, 169	278	278>109, 278>125, 278>245	278>109
Parathion	23.43	291.3	291, 261, 235	291	291>109, 291>137	291>109
Dicofol	23.71	370.48	250, 251, 759	251	251>139, 251>111	251>139
Dieldrin	23.71	380.9	277,263	277,263	277>241,277>206,277>170,263>193, 263>228	263>193

Fipronil	25.27	437.15	367, 369, 351, 213	367	367>178, 367>213, 367>255	367>213
Chlorfenvinphos	25.51	359.57	323, 267	267, 323	267>159, 323>267	323>267
Quinolphos	25.76	298	298, 146, 157, 118	298, 146, 157	298>129, 298>156, 298>190, 146>118, 157>129	146>118
Allethrin-a	26.00	302.41	125,135,169,107	125	125>81, 123>95	125>81
Allethrin-b	26.00	346.42	125,135,169,107	125	125>81, 123>95	125>81
2,4 DDE	26.70	318.03	237, 235	246,318,163, 226	246>176,318>318,318>246, 163>127, 226>206	246>176
Alpha endosulfan	27.05	406.93	241, 265, 277, 243	241, 265	241>206, 241>170, 265>229, 265>195, 265>193	241>206
Butachlor	27.21	311.9	237, 323, 240, 266	237, 323	237>160, 237>188, 176>134, 176>146, 188>130	176>146
Hexaconazole	28.01	314.21	214, 175	214	214>124, 214>152, 214>172	214>172
Fenamiphos	28.47	303.3	303,288, 154	303	303>139, 303>154, 303>180	303>154
Profenophos	28.47	372	339, 139, 559, 759	339, 139	339>188, 339>251, 339>269, 139>97	139>97
4,4 DDE	28.61	318.03	318, 246	318, 246	318>176, 318>246, 246>176, 318>318	318>318
2,4 DDD	28.91	320.05	237, 235	235	235>165, 235>200, 235>139	235>165
Endrin	29.72	380.93	281, 263, 317, 245	281, 263	281>173, 281>209, 281>245, 263>193, 263>228	263>193
Beta endosulfan	30.42	406.93	241, 195	195, 241	195>159, 241>206	195>159
4,4 DDD	31.02	320.05	237, 235	235	235>165, 235>199, 235>200	235>165
2,4DDT	31.02	354.49	237, 235	235, 141	235>200, 235>235, 141>95	141>95
Ethion	31.25	384.48	231, 384, 257, 153	231	231>129, 231>175, 231>203	231>129
Triazophos	32.15	313	257, 161	257	257>119, 257>134, 257>162	257>162
Endosulfansulphate	32.67	422.92	274, 272, 387	272, 387	272>141, 272>165, 272>237, 387>253	272>237
4,4 DDT	33.18	354.49	237, 235	235	235>165, 235>199, 235>200, 235>235, 235>199	235>165
Trifloxystrobin	33.33	408.37	222, 116, 190	222, 116, 190	222>190, 222>162, 222>130, 116>89, 190>130	116>89
Tebuconazole	34.20	307.8	250, 125	250	250>125, 250>153, 250>163	250>125
Bifenithrin	36.71	422.87	181, 165, 166	181, 165	181>115, 181>165, 181>166, 165>115	181>166
Methoxychlor	36.83	345.7	228, 227	227	227>169, 227>184	227>169

Fenpropathrin	37.30	349	265, 165, 181,125	265,165,181	265>210, 265>181, 165>153, 181>152	181>152
Phosalone	38.66	367	367, 182	367, 182	367>111, 367>138, 367>182, 182>138, 182>111	367>111, 182>111
Lambda cyhalothrin	40.97	449.9	181, 797	181, 797	181>127, 181>152	181>152
Azinphos ethyl	41.28	345.4	160, 134, 155, 127	160,134,155, 127	160>102, 160>105, 160>132	160>132
Permethrin-I	42.9	390	183, 163	163, 183	163>127, 183>153	183>153
Permetrin-II	43.21	390	183, 163	163, 183	163>127, 183>153	163>127
Cyfluthrin	44.48	434.3	226, 206, 163	206, 163, 226	206>151,206>177,206>179, 163>127, 226>206	206>177
Cypermethrin	44.64	416.32	163, 181, 165, 127	163, 181	163>127, 181>152	163>127
Alpha cypermethrin	44.92	406.93	241, 265, 277, 243	241, 265	241>206,241>170,265>229, 265>195, 265>193	241>206
Fenvalarate	46.04	419	225, 167	225	225>91, 225>119, 225>147	225>119
Fluvalinate-I	46.30	502.93	250, 199, 157	250	250>55, 250>200	250>200
Fluvalinate-II	46.30	502.93	250, 199, 157	250	250>55, 250>200	250>200
Deltamethrin	47.38	505.24	253, 181, 172	253,172	253>172, 253>199, 172>93	172>93

Table 2. Linearity parameters for different pesticides on GC-MS/MS (TQD) with MRM method

S.No	Name of the Pesticide	Coefficient of variation (R^2)	RSD	S.No	Name of the Pesticide	Coefficient of variation (R^2)	RSD
1.	Dichlorvos	0.995	2.91-4.21	36.	Hexaconazole	0.998	2.67-4.98
2.	Methamidophos(1ppm)	0.991	2.61-4.18	37.	Fenamiphos	0.996	2.88-5.01
3	Monocrotophos(1ppm)	0.99	3.66-4.19	38.	Profenophos	0.997	3.08-7.02
4	Phorate	0.992	1.99-3.88	39.	Dieldrin	0.998	1.23-5.10
5.	Alpha HCH	0.994	0.89-2.06	40.	4,4 DDE	0.997	1.31-1.98
6.	Dimethoate	0.995	1.31-4.77	41.	2,4 DDD	0.997	2.01-2.66
7.	Beta HCH	0.996	0.85-2.90	42.	Endrin	0.994	1.66-3.78
8.	Atrazine	0.997	2.01-4.88	43.	Beta endosulfan	0.999	0.55-3.71
9.	Lindane	0.999	1.01-4.0	44.	4,4 DDD	0.998	1.77-5.10
10.	Chlorthalanil	0.998	2.86-5.11	45.	2,4 DDT	0.996	2.57-4.05
11.	Diazinon	0.997	1.44-3.89	46.	Ethion	0.995	3.09-4.42
12.	Delta HCH	0.996	0.89-4.44	47.	Triazophos	0.996	1.11-4.21
13.	Phophomidon	0.998	1.99-4.88	48.	Endosulfansulphate	0.996	1.23-8.11
14.	Chlorpyrifos methyl	0.996	0.99-2.07	49.	4,4 DDT	0.998	1.42-4.70
15.	Methyl parathion	0.997	2.39-3.24	50.	Trifloxtstrobin	0.999	1.02-4.89
16.	Alachlor	0.998	2.02-4.77	51.	Tebuconazole (0.1ppm)	0.993	0.97-4.32
17.	Heptachlor	0.999	1.05-3.6	52.	Bifenithrin	0.999	1.44-4.89
18.	Metalaxyl	0.991	1.20-5.00	53.	Methoxychlor	0.997	0.96-3.88
19.	Demeton-S-methyl sulfone	0.99	0.77-4.87	54	Fenpropathrin	0.996	2.29-4.04
20.	Fenitrothion	0.992	3.09-3.81	55	Phosalone	0.998	1.86-4.89
21.	Malathion	0.993	0.98-3.87	56	Lambda cyhalothrin	0.994	1.34-7.51
22.	Aldrin	0.994	4.01-4.89	55	Azinphos ethyl	0.993	2.09-3.99
23.	Chlorpyrifos	0.996	2.04-4.70	58	Permethrin –I	0.992	2.77-4.89
24.	Fenthion	0.994	1.44-4.99	59	Permetrin-II	0.993	1.98-4.33
25.	Parathion	0.998	1.28-4.77	60	Cyfluthrin	0.995	0.88-4.69
26.	Dicofol	0.995	1.08-4.70	61	Cypermethrin	0.996	1.44-4.89
27.	Dieldrin	0.998	1.66-5.42	62	Alpha cypermethrin	0.997	3.71-8.99
28.	Fipronil	0.994	2.04-4.08	63	Fenvalarate	0.996	2.78-10.54
29.	Chlorfenvinphos	0.996	0.66-3.89	64	Fluvalinate-I	0.998	2.81-11.24
30.	Quinalphos	0.997	1.66-2.63	65	Fluvalinate-II	0.998	3.77-8.91
31.	Allethrin-a	0.993	2.67-5.02	66	Deltamethrin	0.995	
32.	Allethrin-b	0.992	1.89-4.07				
33.	2,4 DDE	0.997	1.33-2.49				
34.	Alpha endosulfan	0.994	1.99-4.10				
35.	Butachlor	0.998	1.99-4.10				

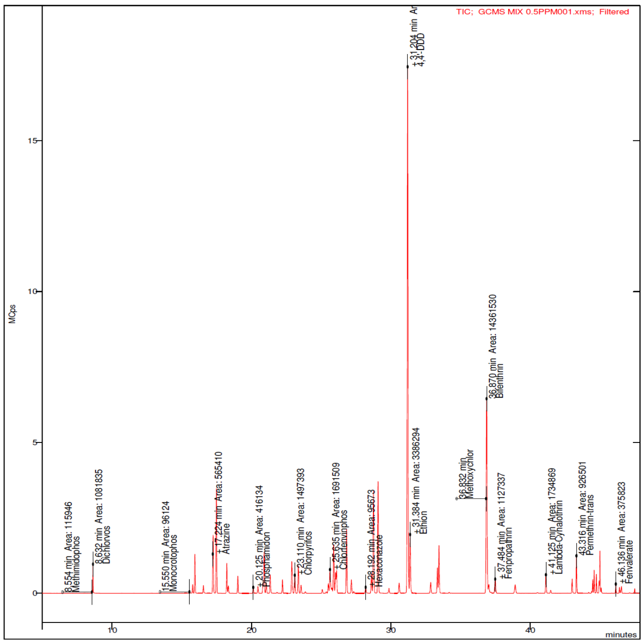

Figure 1. Chromatogram of 64 pesticides on GC-MS/MS (TQD) in MRM method

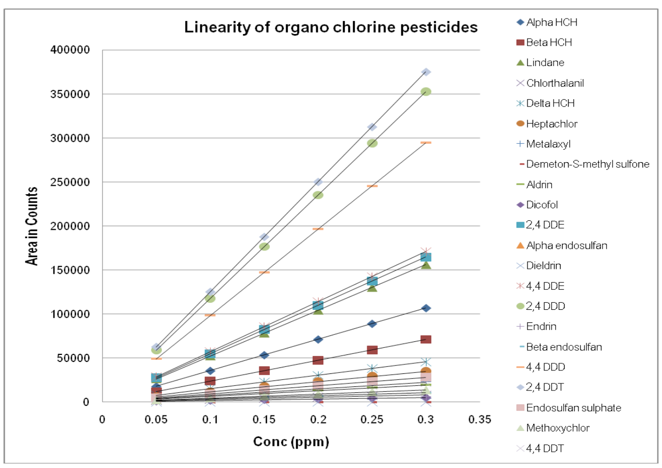

Figure 2. Linearity of organochlorines pesticides on GC-MS/MS (TQD) in MRM method

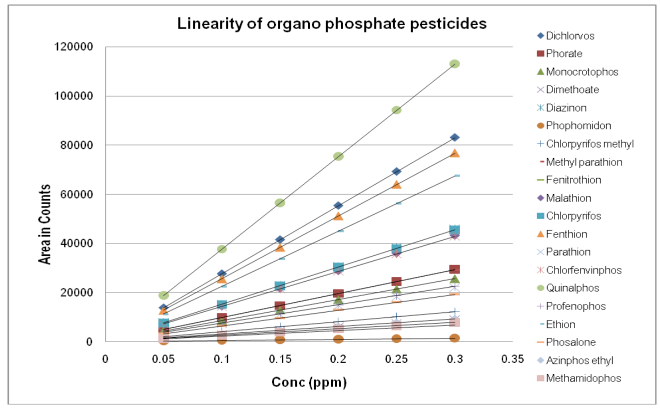

Figure 3. Linearity of organophosphate pesticides on GC-MS/MS (TQD) in MRM method

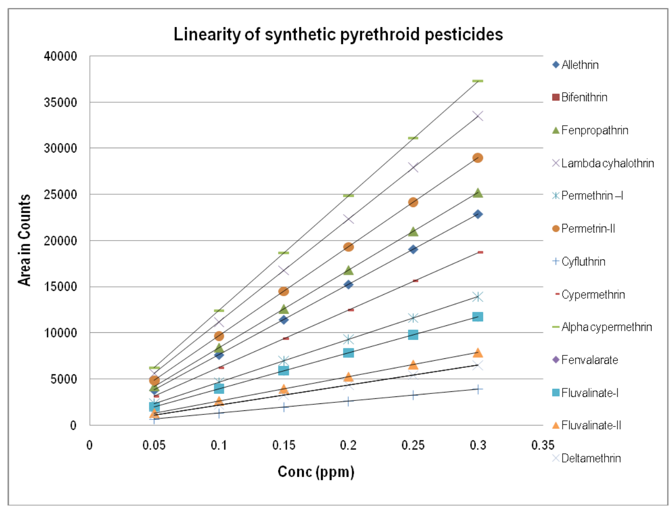

Figure 4. Linearity of synthetic pyrethroid pesticides on GC-MS/MS (TQD) in MRM method

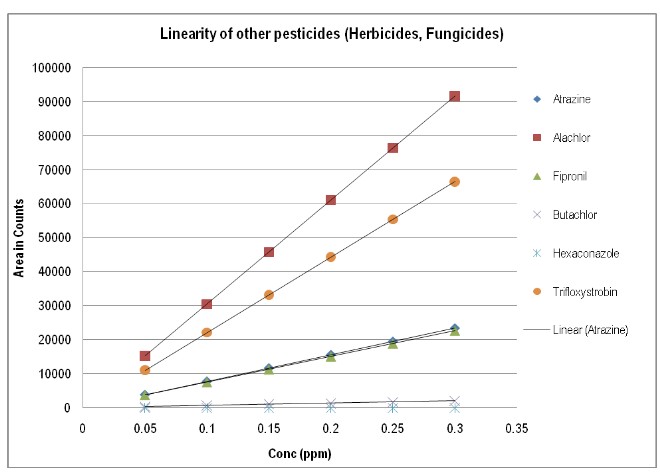

Figure 5. Linearity of other pesticides on GC-MS/MS (TQD) in MRM method

et al. 2011) may pose health hazards to consumers (Elliion *et al*. 2000; Mukherjee and Gopal, 2003). The determination of pesticide residues in vegetables and fruits is of great concern for all countries to study the risk analysis and take up food safety measures for both export and domestic trade purposes. The aim of this work is to develop procedures for the analysis of multi class pesticides and its metabolites through best extraction methods, and by gas chromatography mass spectroscopy. The studies focus on sample preparation, sample extraction following QuEChERS method and instrumental analysis using MRM methods in GC-MS/MS.

Materials and Methods

Chemicals and Reagents

Solvents like *n*-hexane, acetone, toluene and acetonitrile (HPLC grade) were purchased from M/S Merck India. Anhydrous sodium sulfate (Na_2SO_4) and anhydrous magnesium sulfate ($MgSO_4$) were purified with acetone and baked for 4 h at 600°C in muffle Furnace to remove possible phthalate impurities. Primary secondary amine (PSA) bondasil 40 µm was purchased from M/S Agilent. Certified Reference Materials (CRMs) of high purity (≥98%) were procured from M/S Sigma Aldrich, USA.

Calibration standards and Linearity studies

Primary (500-1000 ppm) and intermediary standards (50 ppm) of pesticides (Table 1) were prepared in calibrated volumetric flasks from the CRMs using GC PR grade acetone and hexane solvents. Six calibration pesticide solutions (working standards) were prepared in the range of 0.01 ppm to 0.5 ppm in calibrated graduated volumetric flasks using distilled n-hexane as solvent. Each concentration level was injected (1 µL) six times in Bruker Scion 436 GC-MS/MS Triple Quadrupole Detector (EI) using Multiple Reaction Monitoring (MRM) method (Table 1). Standards were injected in split mode (1: 10) at 260°C injector temp at column flow of 1 ml/min (Helium 99.99% purity) using Zebron MR 2 capillary column (30 mm length, 0.25 mm ID, 0.20 µm film coated with 1% phenyl-methyl polysiloxane) maintained the column temperatures starting from 50°C to 290°C with four ramps with a total program of 50 minutes. Mass spectra detector (Triple Quadrupole) with mass range 50 to 400 was operated at 250°C of transfer line, 220°C of source, and 40°C of manifold temperatures. Limit of detection (LOD), LOQ (Limit of Quantification) and%RSD (Relative standard deviation) values were calculated for each pesticide under the standard conditions.

Field samples and extraction methods

Tomatoes (untreated) were collected from the supervised fields of Student farm, College of Agriculture. QuEChERS (Quick Easy Cheap Effective Rugged Safe) method for extraction and clean up was validated as per SANCO/12571/2013 guidelines. Tomato fruits (5 kg) collected from control plots were homogenized with Robot Coupe Blixer, from which 15 g was taken in to 50 mL centrifuge tubes. The required quantities of 64 pesticides intermediary standards are added to each 15 g sample to get fortification levels of 0.05 mg kg^{-1}, 0.25 mg kg^{-1}, and 0.5 mg kg^{-1}, in three replications each. Acetonitrile (30 ± 0.1 mL) was added to tube, homogenized for 1-3 min using Heidolph silent crusher (low volume homogenizer). Then 3±0.1 g sodium chloride was added to tube and mixed by shaking gently, and centrifuged for 3 min at 2500-3000 xg with Remi R-238 to separate the organic layer. The top organic layer of about 16 mL was taken into the 50 mL centrifuge tube to which 9 ± 0.1 g anhydrous sodium sulphate was added to remove the moisture content. Extract (9 mL) was taken in to 15 mL tube containing 0.4 ± 0.1 g PSA sorbent (for dispersive solid phase d-SPE cleanup) and 1.2 ± 0.01 g anhydrous magnesium sulphate, and the sample tube was vortexed for 30 sec followed by centrifugation for 5 min at 2500-3000 xg. The extract of (2 mL) was transferred into test tubes and evaporated to dryness using concentration work station (Turbovap LV of Capiler life sciences) with nitrogen gas and reconstituted with 1mL n-Hexane:Acetone (9:1) for analysis. The mean recovery of the residues was calculated to judge the

Table 3. Recovery results for different pesticides in/on Tomato

S.No	Name of the Pesticide	% Recovery at different fortification levels				S.No	Name of the Pesticide	% Recovery at different fortification levels			
		0.05 mg/ kg	0.25 mg/ kg	0.5 mg/kg	LOD			0.05 mg/ kg	0.25 mg/ kg	0.5 mg/ kg	LOD
1.	Dichlorvos	81.02	84.09	86.02	0.005	34.	Alpha endosulfan	87.62	88.12	89.01	0.001
2.	Methamidophos(1ppm)	80.09	81.11	82.64	0.005	35.	Butachlor	91.69	92.14	93.14	0.001
3	Monocrotophos(1ppm)	83.86	85.12	86.09	0.005	36.	Hexaconazole	87.02	88.14	89.92	0.001
4	Phorate	84.16	85.66	86.88	0.001	37.	Fenamiphos	81.22	82.02	82.99	0.005
5.	Alpha HCH	91.02	91.99	92.09	0.001	38.	Profenophos	89.77	88.66	85.62	0.005
6.	Dimethoate	80.08	80.14	80.99	0.005	39.	Dieldrin	80.12	81.48	82.01	0.005
7.	Beta HCH	90.60	91.89	91.22	0.001	40.	4,4 DDE	90.62	91.84	90.09	0.001
8.	Atrazine	81.18	81.42	82.64	0.001	41.	2,4 DDD	91.44	92.00	91.89	0.001
9.	Lindane	84.66	85.12	85.99	0.001	42.	Endrin	83.12	82.62	81.69	0.001
10.	Chlorthalanil	85.69	86.44	87.12	0.001	43.	Beta endosulfan	91.22	92.89	94.62	0.001
11.	Diazinon	81.24	81.69	87.88	0.005	44.	4,4 DDD	87.62	88.14	89.20	0.001
12.	Delta HCH	84.69	84.01	84.12	0.001	45.	2,4 DDT	86.42	85.19	84.68	0.001
13.	Phophomidon	83.21	84.10	83.04	0.005	46.	Ethion	89.04	90.68	88.14	0.005
14.	Chlorpyrifos methyl	88.02	89.14	88.89	0.005	47.	Triazophos	86.62	85.19	87.19	0.005
15.	Methyl parathion	90.09	91.24	92.66	0.005	48.	Endosulfansulphate	88.14	85.02	86.88	0.001
16.	Alachlor	91.22	91.39	92.02	0.001	49.	4,4 DDT	82.62	83.14	84.82	0.001
17.	Heptachlor	92.04	94.62	93.82	0.001	50.	Trifloxtstrobin	87.88	86.92	88.14	0.005
18.	Metalaxyl	88.62	88.91	87.62	0.001	51.	Tebuconazole (0.1ppm)	81.62	82.12	83.09	0.005
19.	Demeton-S-methyl sulfone	79.91	80.42	79.86	0.005	52.	Bifenithrin	91.02	92..08	93.62	0.001
20.	Fenitrothion	82.42	83.64	84.01	0.005	53.	Methoxychlor	86.12	85.04	84.88	0.001
21.	Malathion	84.82	85.21	85.99	0.005	54	Fenpropathrin	81.92	82.12	83.04	0.005
22.	Aldrin	81.96	82.04	82.92	0.001	55	Phosalone	85.44	84.46	83.22	0.005
23.	Chlorpyrifos	87.62	86.14	87.99	0.005	56	Lambda cyhalothrin	81.86	82.22	83.09	0.005
24.	Fenthion	90.66	91.88	89.51	0.005	55	Azinphos ethyl	79.96	79.02	80.04	0.005
25.	Parathion	86.42	81.44	82.99	0.005	58	Permethrin –I	81.02	82.04	84.99	0.005
26.	Dicofol	89.08	89.92	91.46	0.001	59	Permetrin-II	84.64	85.02	86.42	0.005
27.	Dieldrin	80.44	81.24	82.14	0.005	60	Cyfluthrin	81.86	82.62	84.09	0.005
28.	Fipronil	91.94	92.01	93.82	0.005	61	Cypermethrin	82.12	80.86	81.89	0.005
29.	Chlorfenvinphos	90.01	91.62	90.89	0.005	62	Alpha cypermethrin	83.24	84.62	86.12	0.005
30.	Quinalphos	89.88	89.02	88.61	0.005	63	Fenvalarate	84.11	85.69	86.82	0.005
31.	Allethrin-a	80.62	81.88	81.22	0.005	64	Fluvalinate-I	81.80	82.14	84.14	0.005
32.	Allethrin-b	80.62	81.88	81.22	0.005	65	Fluvalinate-II	85.42	86.12	87.70	0.005
33.	2,4 DDE	89.16	88.17	87.12	0.001	66	Deltamethrin	88.62	87.29	88.24	0.005

efficiency of the method for qualitative and analysis of selected pesticides in/on tomato for national monitoring studies.

Results and Discussion

The standard chromatogram with 64 pesticides at 500 ppb on GC-MS/MS was presented in Figure 1 and the data on retention time (RT), MRM papmeters was presented in Table 1. Eight point linearity curve was drawn by injecting mixture of various pesticides (Figure 2,3,4,5) and data on regression values including% RSD from linearity for each pesticide was given in Table 2. It is seen that the R^2 value (Coefficient of Determination: a measure of goodness of fit of linear regression) ranged from 0.990-0.999 and percentage of Relative Standard Deviation is in between 0.55-8.11 explains that the instrument has wide linearity for quantitation purposes. Limit of detection of organo chlorine pesticides is in the range of 0.001 to 0.005 mg/kg, with recovery of 79.91% to 92.00% at 0.05 mg/kg, 81.24 to 94.62% at 0.25 mg/kg and 79.86 to 94.62% at 0.5 mg/kg levels (Table 3). Limit of detection for organo phosphate are in the range of 0.001 to 0.005 mg/kg and recovery is in the range of 79.96 to 90.66% at 0.05 mg/kg, 79.02 to 91.88% at 0.25 mg/kg and 80.99 to 93.82% at 0.5 mg/kg fortification levels. The percent recovery of synthetic pyrethroid pesticides is in the range of 81.02 to 91.02% at 0.05 mg/kg, 80.86 to 92.08% at 0.25 mg/kg and 81.89 to 93.62% at 0.5 mg/kg fortification level. The recovery of other pesticides such at herbicides and fungicides is in the range of 88.81 to 91.69% at 0.05 mg/kg 81.42 to 92.12% at 0.25 mg/kg and 82.64 to 93.14% at 0.5 mg/kg fortification levels. The extraction and cleanup methodology followed proved to be rapid and highly effective for extraction of 64 pesticides from tomato with a recovery of various pesticides in the range of 80-120% and the method used for estimation of pesticides using MRMs method in GC-MS/MS (TQD) is highly useful for identification of pesticides at very low levels, as the coefficient of determination is very high in the linear range of 0.01 ppm to 0.50 ppm, which is very useful for monitoring studies are the MRLs (Maximum Residue Limits) for the targeted pesticides are > 0.01 mg/kg in tomato. The method developed by Anastassiades M *et al*. (2003) for fast and easy extraction procedures for analysis of multiple pesticides in foods has been followed wordwide in various matrices, and during the present investigation, it was known that the method is good for tomato matrix also as there were no matrix interferences. Sample preparation is an important step for better extraction and cleanup for MS analysis and in the present investigation the method described by Lehotey SJ (2011) was followed with some modifications, and based on the results obtained the present study, it can be recommended to be used in the national residue monitoring programs as the method is validated as per the internationally followed "Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed" of Health and Consumer Protection Directorate General, European Commission (SANCO/12571/2013 (2013).

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