

Multiresidue analysis of pesticides in Turmeric (*Curcuma longa*) powder by GCMS/MS using QuEChERS' extraction method

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1. Introduction

Turmeric is a plant indigenous to south Asia, with majority of its production coming from India. The rhizome of the plant is used to produce powdered turmeric (Figure 1), which is used in food, cosmetics and some medicines. It is one of the most essential spices used extensively in Indian cooking.

The intensive use of agrochemicals during its cultivation has given rise to concerns over consumer's exposure to pesticide residues and associated health risks. Hence, it is important for turmeric producers and regulators to ensure that presence of residual pesticides meet compliance criteria. The Minimum Residual Limit (MRL) as per EU guideline ranges from 5 ppb to 5000 ppb level.

This study reports a sensitive and reliable analytical method for quantitative analysis of multi-pesticide residues in commercially available turmeric powder by using GCMS/MS triple quadrupole system.



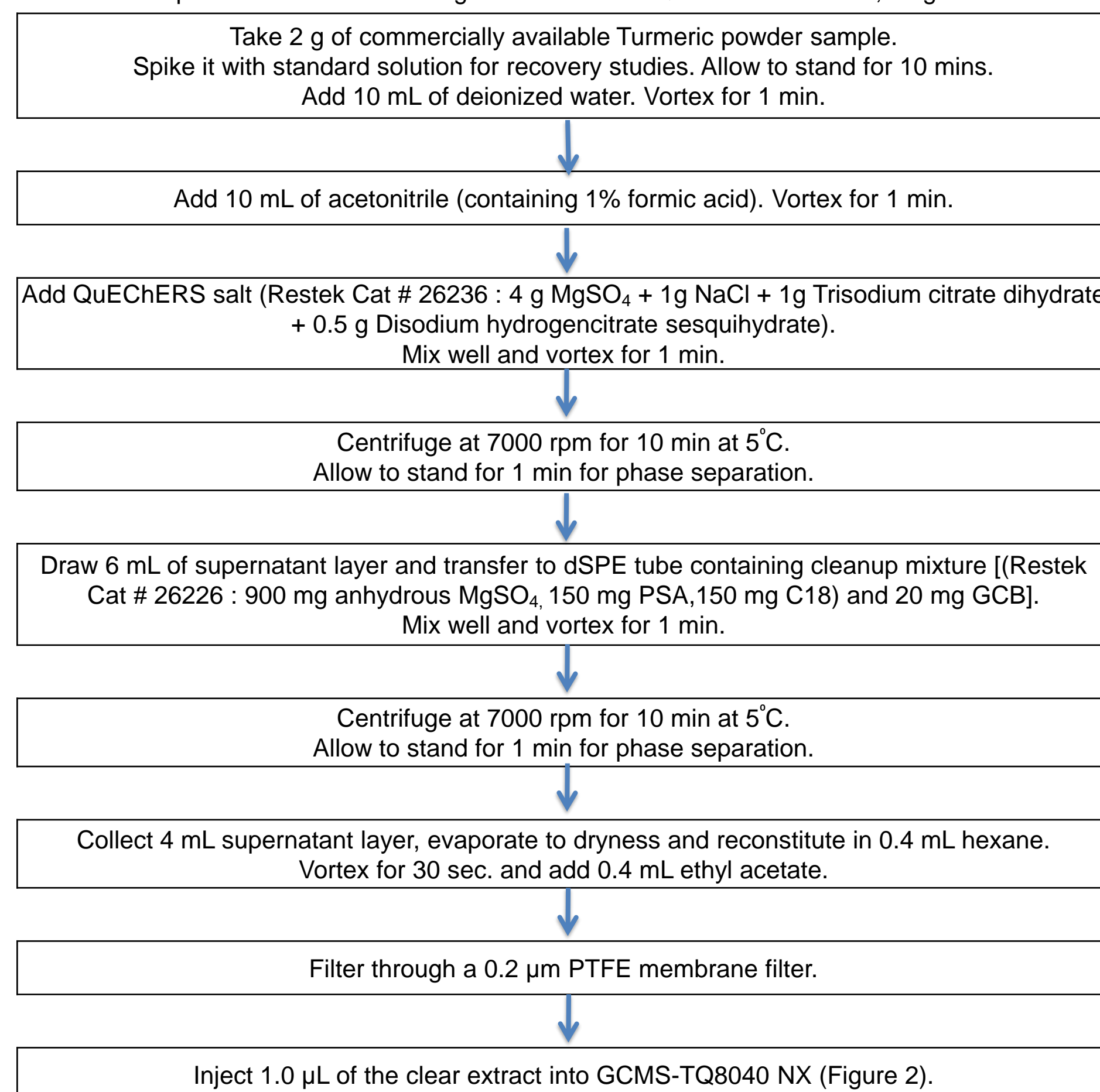
Figure 1. Turmeric powder

2. Method of analysis

2-1. Sample preparation

• Sample extraction

Extraction of pesticides was done using modified AOAC QuEChERS method, as given below.



• Preparation of solvent standard concentration levels

GC multi-residue pesticides mixture obtained from Restek® was diluted using ethyl acetate to prepare stock solution of about 1ppm standard mixture for more than 60 analytes. From this, concentration levels of 10 ppb, 50 ppb, 100 ppb, 200 ppb, 300 ppb, 400 ppb and 500 ppb were prepared.

• Preparation of matrix matched standard linearity levels

Locally purchased Turmeric powder was used as a sample. It was extracted as per the sample extraction method (2-1) to prepare matrix blank. Further it was spiked with above calibration levels to prepare matrix match linearity of 1 ppb, 5 ppb, 10 ppb, 20 ppb, 30 ppb, 40 ppb and 50 ppb.

• Preparation of pre-extraction spike samples (Recovery samples)

In order to determine the extraction efficiency of the method, recovery study was conducted. For this, 2 g sample was spiked with pesticide standard mixture to prepare recovery samples of 10 ppb and 20 ppb. The spiked pesticides were then extracted, analyzed and quantified against matrix matched linearity to study their recoveries.

2-2. MRM method development

For MRM method creation, Shimadzu's Smart Pesticide Database Ver.2 was used and the retention times of all analytes were predicted with the help of n-Alkane standard mixture. Pre-optimized MRM transitions present in the Smart Pesticide Database and accurately predicted retention times enabled creation of MRM method with overlapping segments resulting in optimum dwell time required for high sensitivity. For each component, minimum two MRM transitions were analyzed.

2-3. GCMS/MS Analytical Conditions

The analysis was carried out on Shimadzu GCMS-TQ8040 NX as per the parameters in Table 1.

Table 1. Analytical conditions

Chromatographic parameters			
• Column	: SH-Rxi™-5Sil MS (30 m L x 0.25 mm I.D. x 0.25 µm)		
• Injection Mode	: Splitless		
• Injector Temp.	: 250.0 °C		
• Sampling Time	: 2.00 min		
• 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	: 1.0 µL		
• Injection Type	: High Pressure Injection		
• Total Program Time	: 50 min		
• Column Temp. Program	: Rate (°C/min) Temperature (°C) Hold time (min)		
	- 70.0 2.00		
	25.00 150.0 0.00		
	3.00 200.0 0.00		
	8.00 280.0 18.13		
Mass Spectrometry parameters			
• Ion Source Temp.	: 230.0 °C		
• Interface Temp.	: 280.0 °C		
• Ionization Mode	: EI (Electron Ionization)		
• Acquisition Mode	: MRM		

3. Results

Extracted matrix blank sample was screened and none of the pesticides involved in this study were detected. Calibration curve was plotted for matrix matched standards in the range of 5 ppb to 50 ppb. Linear response with r^2 more than 0.985 was obtained. Recovery samples of 10 ppb and 20 ppb were extracted in triplicates and their % RSD at LOQ level was found to be less than 20%. Recoveries of the same were in the range of 70% to 120%. Based on linearity, precision and recovery, the LOQ for each analyte was determined. The statistical results for all analytes are shown in Table 2.



Figure 2 GCMS-TQ8040 NX Triple quadrupole system by Shimadzu

Key Features of GCMS-TQ8040 NX

1. Smart Productivity : Achieving superior productivity through dedication to efficiency.

2. Smart Operation : Supporting easy creation of methods and data analysis.

3. Smart Performance : Enabling highly sensitive simultaneous analysis of multiple components.

The fusion of these three Smart features makes this universal triple quadrupole GC-MS applicable in any field, where it is sure to deliver the utmost performance.

Table 2. Quantitation results

Sr. No.	Group/Category	Name	Ret. Time (min)	EU-MRLs (ppb)	LOQ (ppb)	% Recovery at LOQ (n=3)	% RSD (n=3)
1		Chloroneb	9.36	10	10	75	19.5
2		4,4'-Dichlorobenzophenone	21.00	100	10	70	11.7
3		Fenson	21.29	10	10	72	17.3
4		Isodrin	21.70	10	10	112	15.4
5		Chlorbenside	23.41	100	20	69	4.7
6	Organo-chlorine	trans-Nonachlor	24.11	10	20	83	19.9
7		Chlorfenson	24.52	100	10	73	11.5
8		o,p'-DDD	25.20	1000	10	74	7.1
9		Endrin	25.76	100	20	80	19.9
10		Ethylan (Perthane)	25.95	20	10	78	6.4
11		cis-Nonachlor	26.38	10	10	73	17.5
12		Tefluthrin	16.39	700	10	76	10.8
13		Tetramethrin-2	29.22	10	20	77	12.2
14	Synthetic pyrethroids	Cyhalothrin-1	30.33	50	10	77	17.4
15		Cyhalothrin-2	30.58	50	10	74	19.1
16		Fluvalinate-1	34.78	10	20	86	5.2
17		Fluvalinate-2	34.93	10	20	75	18.0
18		Metalaxyl (Mefenoxam)	18.81	50	10	94	14.8
19		Chlorthal-dimethyl	20.55	50	20	82	13.3
20	Herbicide methyl esters	Chlozolinate	22.57	50	10	88	15.7
21		Fluazifop-P-butyl	26.06	4000	20	71	8.9
22		Chlorobenzilate	26.21	100	10	75	4.7

Table 2 (Continued). Quantitation results

Sr. No.	Group/Category	Name	Ret. Time (min)	EU-MRLs (ppb)	LOQ (ppb)	% Recovery at LOQ (n=3)	% RSD (n=3)
23		Dichlobenil	7.20	50	10	73	6.0
24		Trifluralin	13.39	50	10	105	17.7
25		Benfluralin	13.43	100	20	69	15.8
26		Di-allate-2	13.62	50	10	78	1.6
27		Dicloran	14.24	50	20	73	10.0
28		Fluchloralin	15.84	10	10	78	7.3
29		Tri-allate	16.45	100	10	91	19.8
30		Pentachloroaniline	17.10	2000	20	70	9.3
31		Dimethachlor	17.60	50	10	73	13.9
32		Metolachlor (S-Metolachlor)	20.23	50	10	71	7.7
33	Organo-nitrogen	Triadimefon	21.05	50	10	78	5.2
34		MGK 264-1	21.61	10	10	82	17.1
35		Diphenamid	21.63	10	10	72	13.3
36		Isopropalin	21.83	10	10	73	11.9
37		Tolyfluanid	22.51	100	10	72	15.8
38		Pretilachlor	24.86	10	10	69	19.7
39		Oxadiazon	25.16	50	10	80	16.5
40		Oxyfluorfen	25.39	50	10	80	15.9
41		Flusilazole	25.39	50	10	83	14.1
42		Fenpropathrin	29.40	20	20	69	6.7
43		Tebufenpyrad	29.54	50	10	81	12.9
44		Pyridaben	31.84	50	10	72	14.8
45		Mevinphos-2	8.14	20	10	70	15.7
46		Mevinphos-1	8.15	20	10	70	15.7
47		Methacrifos	9.18	50	10	76	17.0
48		Fonofos	15.55	10	10	72	5.6
49		Parathion-methyl	17.66	3000	10	78	18.5
50		Chlorpyrifos-methyl	17.78	5000	20	70	20.1
51		Tolclofos-methyl	18.13	50	10	79	7.3
52		Fenchlorphos	18.68	100	20	70	9.0
53		Pirimiphos-methyl	19.42	50	20	69	9.7
54		Fenitrothion	19.51	50	20	69	14.3
55		Malathion	20.10	20	10	81	19.7
56	Organo-phosphorous	Chlorpyrifos	20.30	1000	10	75	6.3
57		Bromophos	21.38	10	10	74	20.5
58		Pirimiphos ethyl	21.63	50	20	75	15.4
59		Bromfenfos-methyl	22.70	10	10	93	19.3
60		Quinalphos	22.88	50	10	83	3.5
61		Iodofenphos	24.48	10	10	78	11.4
62		Bromfenphos	24.51	10	10	71	10.3
63		Chlorthiophos-2	26.62	10	10	76	9.4
64		Chlorthiophos-3	26.62	10	10	82	19.2
65		Triazophos	27.01	100	20	77	14.4
66		Carbophenothion	27.32	10	10	94	10.5
67		Coumaphos	31.79	10	20	73	18.9

4. Conclusion

➤ Smart Pesticide Database feature enabled automatic creation of MRM method with overlapping segments and optimum dwell times for achieving high sensitivity at trace level even in complex matrices like turmeric powder.

➤ All the analytes showed LOQ less than or equal to EU-MRLs set for turmeric.

➤ The MRM method developed for these pesticides can be used for analyzing various commercially available turmeric powder samples.