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DETERMINATION OF MULTICLASS PESTICIDE RESIDUES IN MANGOES BY LIQUID CHROMATOGRAPHY –TANDEM MASS SPECTROMETRY

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ABSTRACT : The Development of an analytical method for the determination of 24 multiclass pesticides in mango at the ≤10 ng g^{-1} level. The method involves extraction of 10 g of homogenized mango samples (2 g of Sodium chloride- +8g of Magnesium sulfate) with 10 mL of Acetonitrile; Clean up by Dispersive solid phase extraction with a combination of primary secondary amine (PSA), graphitized carbon black (GCB) and anhydrous Magnesium sulfate and final estimation by LC-MS/MS with multiple reaction monitoring (MRM) mode. The mean recoveries were in the range 80-120%. The method quantifies over a linear dynamic range of 10-100 µg/kg. The methodology has been proven to be highly efficient and robust and thus the method is suitable for monitoring the Maximum Residue Limits (MRL) compliance of a wide range of pesticides combinations.

Keywords: Pesticide residues; Mangoes; D-SPE; LC-MS/MS

INTRODUCTION

Mango (*Mangifera indica*) is the leading fruit crop of India which is considered to be the king of fruits. Besides delicious taste, excellent flavour and attractive fragrance, it is rich in vitamin A&C. Mango occupies 22% of the total under fruit product comprising of 1.23 million hectares, (NABARD, 2003) with a total production of 11 million tonnes. To minimize the economic losses caused by the noxious insects, fungi and weeds over farmers rely on pesticides such as, acephate, atrazine, bitertanol, buprofezin, cartap, chlorfenvinphos, difenconazole, ethion, flusilazole, hexaconazole, iprobenfos, malathion, metalaxyl, methamidophos, methomyl, monocrotophos, penconazole, phosalone, phosphamidon, quinalphos, spinosad-a, spinosad-d, triadimefon, triazophos. When applied improperly residues of some of these pesticides can remain as such and can pose a significant hazard to human health. In India 54 pesticides are regularly monitored in exportable mangoes (APEDA, 2008). Today's market demands not only the quality of agricultural produce but also safety and environment-friendly production practices. Mango is rich in sugar and also contains variety of saturated, monosaturated and poly unsaturated fatty acids, which may interfere in LC-MS/MS analysis if coextracted and coeluted.

In this study, the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) methodology was employed as described in the literature (Anastassiades, et.al., 2003, Lehotay, et.al., 2005) in combination with gas and liquid chromatography and tandem mass spectrometric detection (LC-MS/MS) for the analysis of pesticide residues. The QuEChERS procedure involves in an initial extraction with acetonitrile followed by an extraction/partitioning step after the addition of a salt mixture. An aliquot of the raw extract is then cleaned up by dispersive solid-phase extraction (D-SPE). The final extract in acetonitrile is directly amenable to determinative analysis basing on LC and/or GC. LC and GC coupled to MS/MS detection provide good methods of identifying and quantifying numerous pesticides in food extracts. Due to the high selectivity provided by MS/MS detection.

This work aims, firstly, the develop a sensitive LC-MS-MS method for the determination of multiclass pesticide residues and secondly the method was applied for the monitoring the pesticide residues in mangoes collected from different market places in Andhra Pradesh (South India).

Experimental

Chemicals and materials

All the chemicals used were of analytical reagent grade. Pesticide standards were of >96% purity and purchased from Dr. Ehrenstorfer (Augsburg, Germany). The DSPE sorbents viz; primary secondary amine (PSA), graphitized carbon black (GCB), anhydrous Magnesium sulfate and octadecyl silane (C18), were received from United Chemical Technology (Bristol, PA).

Preparation of standard solutions

The stock standard solutions of single pesticides were prepared in methanol or suitable solvent at a concentration of 10 mg/mL. A working standard solution was prepared from standard mixture solutions of groups of pesticides stored at 2-8 ^{0}C.

Sample treatment

The procedure employed is similar to the so-called "QuEChERS" comprising the following steps: 500 g of the sample was taken from 1kg of the fresh mango sample then homogenized. 10 g of the sample was taken from homogenized sample then added 10ml of water, 10ml of acetonitrile, 2 g of NaCl and 8 g of anhydrous $MgSO_4$. It was shaken vigorously for1 min. The extract was then centrifuged (3700 rpm) for 4 min. For the clean-up step, 5 ml of the supernatant (acetonitrile phase) was withdrawn using a pipette and transferred to a 15-mL PTFE centrifuge tube containing 25 mg of primary secondary amine (PSA) sorbent, 75 mg of anhydrous MgSO4 and 25 mg of graphitized carbon black (GCB). It was then vigorously shaken for 20s. The extract was centrifuged again (3700 rpm) for 4 min. Finally a 1-mL aliquot of the extract was evaporated with a gentle stream of nitrogen until nearly dry and then reconstituted to a final volume of 1mL of the same organic solvent content as that of the initial mobile phase so that the extract contained the equivalent of 1g of sample per mL.

Table 1: Common name, activity and chemical class of the pesticides studied

Common name	Activity	chemical class
ACEPHATE	insecticide	Organophosphorus
ATRAZINE	herbicide	Triazine
BITERTANOL	fungicide	Azole
BUPROFEZIN	insecticide	–
CARTAP	insecticide	Carbamate
CHLORFENVINPHOS	insecticide	Organophosphorus
DIAFENTHIURON	insecticide	–
DIFENCONAZOLE	fungicide	Azole
ETHION	insecticide	Organophosphorus
FLUSILAZOLE	fungicide	Azole
HEXACONAZOLE	fungicide	Azole
IPROBENFOS	fungicide	Organophosphorus
MALATHION	insecticide	Organophosphorus
METALAXYL	fungicide	Xylylalanine
METHAMIDOPHOS	fungicide	Organophosphorus
METHOMYL	insecticide	Carbamate
MONOCROTOPHOS	insecticide	Organophosphorus
PENCONAZOLE	fungicide	Azole
PHOSALONE	insecticide	Organophosphorus
PHOSPHAMIDON	nsecticide	Organophosphorus
QUINALPHOS	insecticide	Organophosphorus
SPINOSAD-A	insecicide	–
SPINOSAD-D	insecicide	–
TRIADIMEFON	fungicide	Azole
TRIAZOPHOS	insecticide	Organophosphorus

Prior to LC/MS analysis the extract was filtered through a 0.25µm PTFE filter (Millex FG, Millipore). The recoveries obtained using this procedure were satisfactory. Common name, activity and chemical class of the pesticides studied
are presented in Table-1.

LC–MS analysis

An Agilent 1100 HPLC system equipped with binary pump was used for LC analyses. Different LC conditions were evaluated by making use of two chromatographic columns, different working flows and different injection volumes, in an approach intended to achieve optimum sensitivity. The columns selected for this study were C18 with different characteristics (100×2.1 mm i.d., 1.8 µm particle size and 150×4.6 mm, 5 µm particle size) from Agilent Technologies (Palo Alto, CA, USA). The mobile phases used in both columns were HPLC water, 0.1% formic acid (mobile phase A) and acetonitrile (mobile phase B). The LC gradient started with 20% of B and holed up to 1 min, and it was then gradually increased to 80% up to 2 min then put holed up to 13 min then decreased to 20% up to 15 min. Flow rates of 200 and 600 µL/min were explored in the C18 column. The flow rate assayed using a 100×2.1 mm i.d.column was the maximum recommendable for this column (200µL/min). Mass spectrometric analyses were carried out using API 4000 Q-Trap MS/MS system. Applied Biosystem/MDS SCIEX analyst software was used for data acquisition and processing. The collision cell (Q2) incorporates a system of linear acceleration (LINAC) of ions through the quadrupole, providing faster MS/MS scanning (reduced dwell times) without sensitivity losses and making the analysis of a large number of MRM transitions possible. Another advantage is that LINAC makes use of a field gradient to accelerate the fragment ions towards Q3 and so avoids "cross-talk" phenomena (Hemando, et.al., 2007). Optimization of the MS parameters was achieved by performing flow injection analysis (FIA) for each compound.
Table 2 shows the values of the instrumental settings optimized: declustering potential (DP); for precursor ions and collision energy (CE); and collision cell exit potential (CXP) for product ions. The analyses were performed using a turboionspray source in positive mode. The operation conditions were as follows: ionspray voltage, 5000 V; curtain gas, 20 (arbitrary units) nebulizer gas1and auxiliary gas 2 (GS1 and GS2) of 50 and 40, respectively; the probe temperature was 400 °C. Nitrogen served as the turbo gas and the collision gas. Mass calibration and resolution adjustments on the resolving quadrupoles were performed automatically using a 10–5 mol/L solution of polypropylene glycol (PPG) introduced via a syringe pump and connected to the interface. MRM experiments were carried out to obtain the maximum sensitivity for the detection of the selected pesticides. In these cases, the Q-Trap system operated in enhanced product ion (ESI) mode. The additional compound-dependent parameters optimized were: CES (collision energy spread) at 10 (arbitrary units) and AF2 (excitation energy) at values ranging from 10 to 20 V. *Table 2* also shows the MRM transitions used for the confirmation and quantification of pesticides. The confirmation of pesticides was performed by means of two MRM transitions and by monitoring the MRM ratio. The most intense MRM transition was selected for quantitation purposes.

Method Validation

Method accuracy and precision were evaluated by performing recovery studies using "blank" fruit samples (Mangoes) spiked at two concentrations 0.01 mg/kg (LOQ) and 0.05 mg/ kg (5×LOQ). "Blank" samples (10g) were spiked after homogenization. Mixed standard working solutions of 100 µL and 500 µL prepared in methanol containing all the pesticides at 1mg/L then left to stand for 1 hour before extraction(Garrido Frenich, et.al., 2004, Ferrer, et.al., 2005). All the experiments were performed in quintuplicate in each matrix on each day at both concentrations, in accordance with EU guidelines (European, 2006). Method quantification limit (MQL) was defined as the lowest concentration of the analyte in a sample that could be quantified with acceptable precision and accuracy (European, 2006).

The method detection limit (MDL) was defined as the lowest concentration of the analyte in a sample matrix resulting to a signal-to-noise ratio (S/N) of 3 for the less intense precursor/product transition (Pozo, et.al., 2006). Calibration plots were constructed by analysis of standard solutions prepared both in solvent and in each "blank" matrix solution at five concentrations in the range 10-100 µg/kg. Instrument detection limits (IDLs) were calculated on the basis of the standard deviation of results from replicate analysis (n=6) of a standard solution of concentration 10 µg/L.

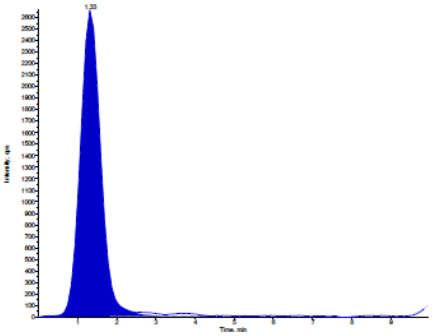
RESULTS AND DISCUSSION

LC analysis

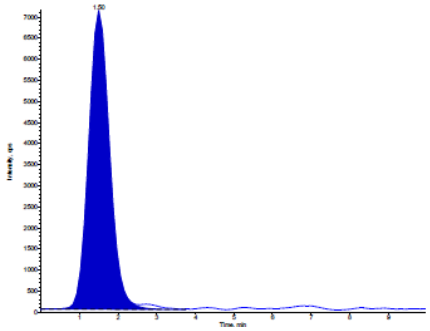
To achieve sufficient sensitivity for the detection of pesticides in mangoes, different LC conditions were assayed, as was discussed in the previous section. Multiresidue methods are always a compromise and given the variety of pesticides included for this method. The composition of the mobile phase chosen was water, 0.1% formic acid and ACN. One approach applied to improve sensitivity was the use of small particle size (e.g., 1.8µm) columns, which can provide an increased column efficiency with better baseline separation and narrower peaks than standard particle size columns (e.g., 3.5–5 µm). But, on the other hand, the sensitivity achieved in small particle size columns is limited by the volume of sample that can be injected. In high-demand conditions, small particle size columns, such as 2.1×100 mm, could even support then injection of higher volumes (e.g., 10 µL) than the maximum recommended (5 µL) without significant changes in the column pressure.

After comparing both columns, and using a mobile phase of water, 0.1% formic acid and ACN, the 2.1×100 mm column was chosen, at 1.8 µm, with an injection volume of 10 µL, in order to test a possible improvement in peak shape when a higher volume of sample is injected, exceeding the maximum recommended. Upon studying two flow rates—200 and 600 µL/min—in term of sensitivity, a superior response was observed at 200 µL, and so this was judged to be more suited to the trace determination of pesticides. The benefit of using higher flow rates is a reduction in analysis time, which is ideal for routine laboratory analysis. However, reduced sensitivity was observed at the higher flow rate explored, which could be associated with a dilution effect or a less stable spray.

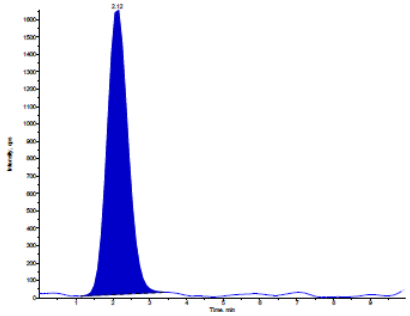
ACEPHATE: 184.0→143.0



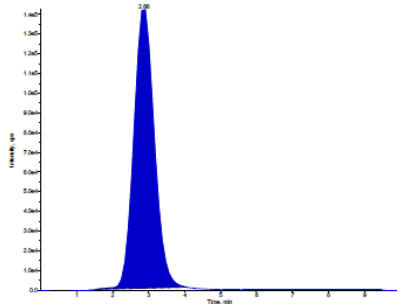
ATRAZINE: 216.0→174.0



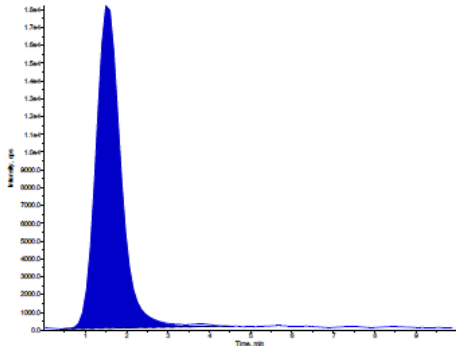
BITERTANOL: 338.0→269.4



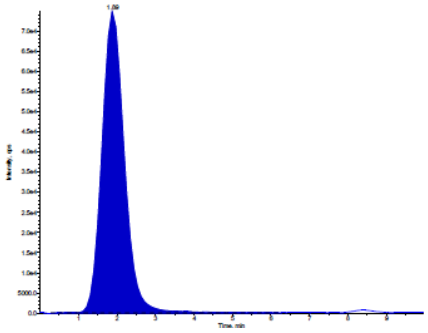
BUPROFEZIN: 306.1→201.0



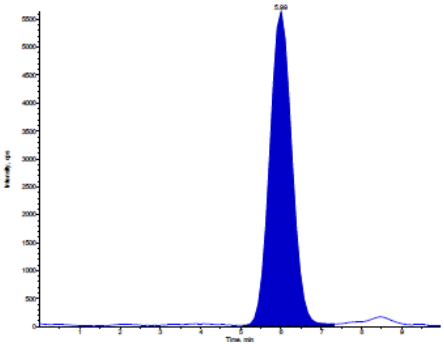
CARTAP: 149.9→105.0



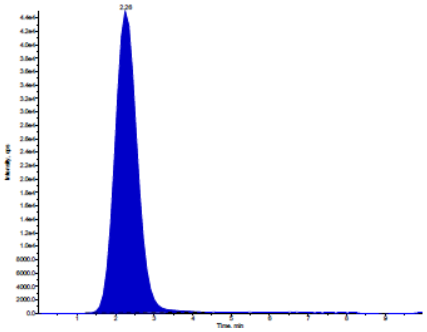
CHLORFENVINPHOS: 359.0→155.0



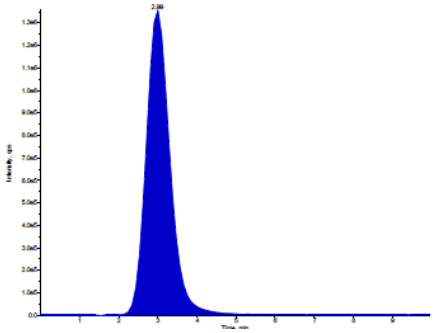
DIAFENTHIURON: 385.5→329.1



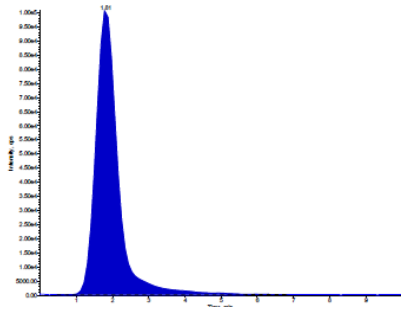
DIFENCONAZOLE: 406.0→337.0



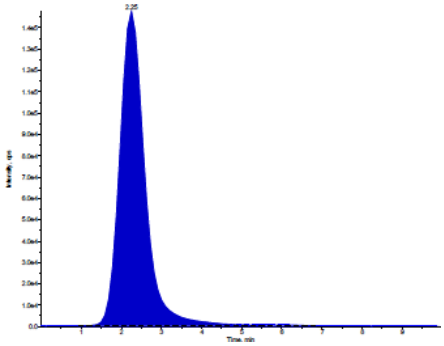
ETHION: 385.0→198.9



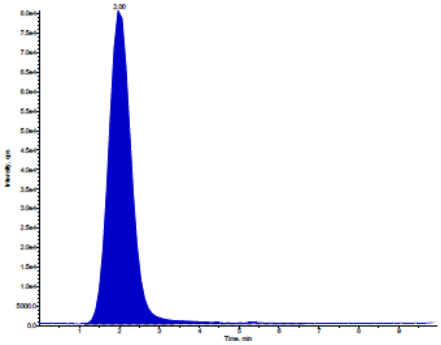
FLUSILAZOLE: 316.0→165.0



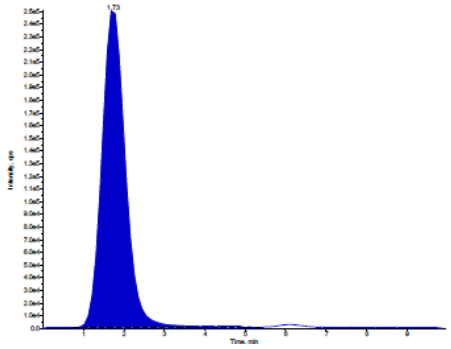
HEXACONAZOLE: 314.2→70.2



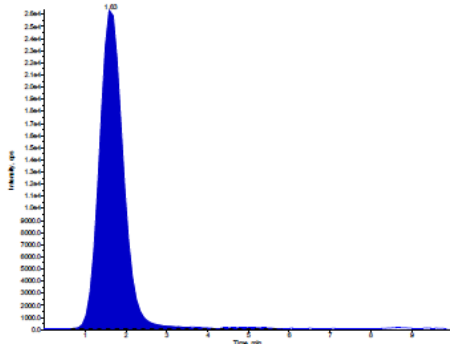
IPROBENPHOS: 289.0→91.0



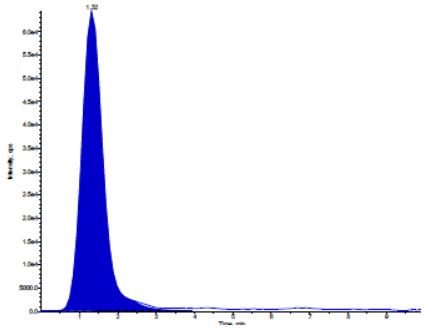
MALATHION: 331.0→127.0



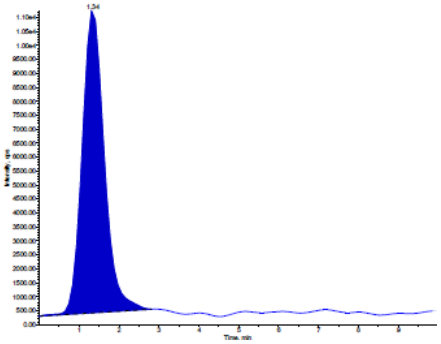
METALAXYL: 280.3→192.2



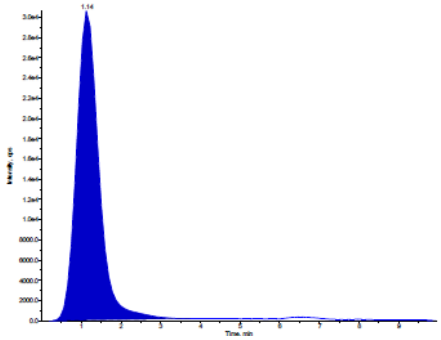
METHAMIDOPHOS: 142.0→94.0



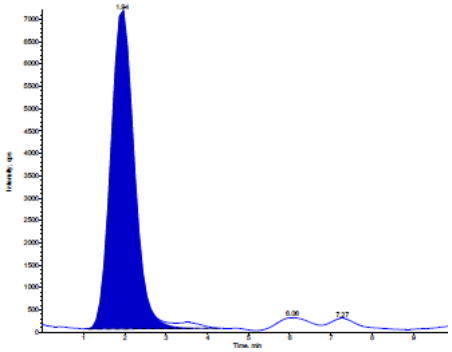
METHOMYL: 163.4→106.0



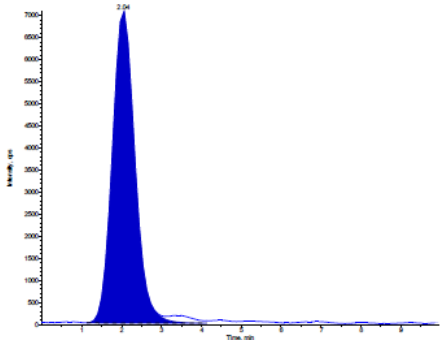
MONOCROTOPHOS : 224.0→127.0



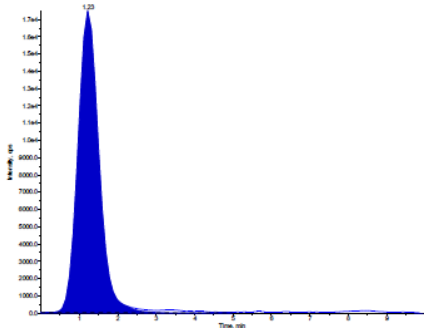
PENCONAZOLE: 284.2→70.0



PHOSALONE: 368.1→182.3



PHOSPHAMIDON: 300.2→174.2



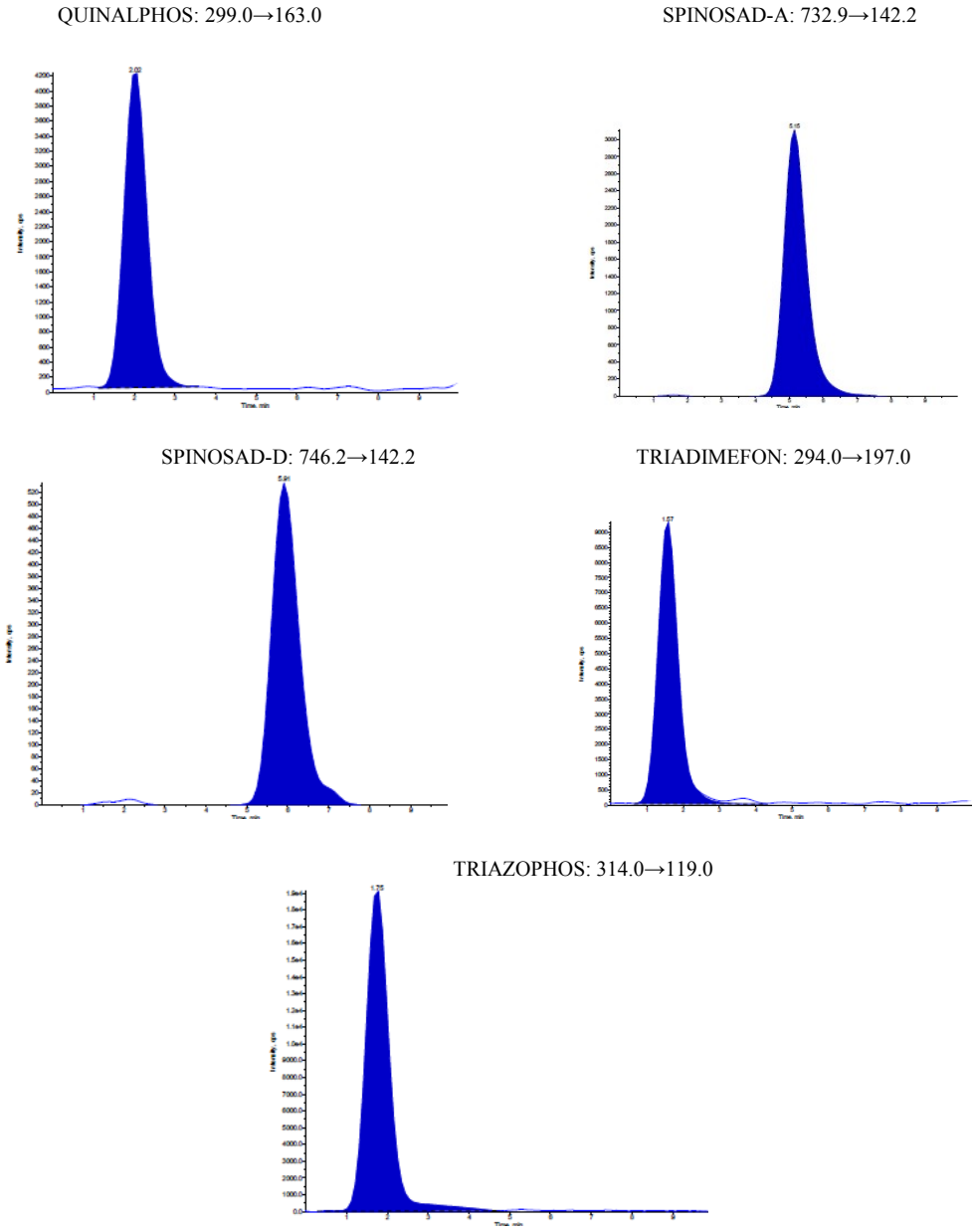


Fig. 1. Typical MRM profile of a fortified Mango sample at 10µg/kg, injection volume 10 µL.

LC conditions assayed, increase in term of sensitivity were observed. Table 2 presents the results obtained from the LC conditions assayed using the 2.1×100 mm column with a 1.8 µm particle size.

Qualitative evaluation of MS data

The Q-Trap systems working in MRM operation mode yield a high selectivity, which is well-suited to multiresidue methods. However, when the multiresidue method includes a wide range of analytes and the matrix sample is complex, additional analyzer features can be vital to the success of the analytical method. The presence of matrix or analyte interference can prove problematic when interpreting the analytical results. Among the pesticides included during the development of the multiresidue method.

Table 2 : Analyte MS-MS transitions, retention time and instrument conditions

Peak number	pesticide	Retention time (Minimum)	M[a]	MS/MS m/z .amu	DP(V)[b]	CE(V)[c]	CXP(V)[d]
1	ACEPHATE	1.33	183.01	184.0/143.0	44.34	27.22	11.12
2	ATRAZINE	1.50	215.09	216.0/174.0	52.43	24.67	14.78
3	BITERTANOL	2.12	337.18	338.0/269.4	48.76	19.85	9.18
4	BUPROFEZIN	2.86	305.16	306.1/201.0	38.79	28.27	8.57
5	CARTAP	1.53	237.06	149.9/105.0	46.94	37.46	12.39
6	CHLORFENVINPHOS	1.89	357.97	359.0/155.0	61.58	33.87	14.37
7	DIAFENTHIURON	5.99	384.22	385.5/329.1	47.32	20.93	10.73
8	DIFENCONAZOLE	2.26	405.06	406.0/337.0	59.21	27.56	16.21
9	ETHION	2.99	383.99	385.0/198.9	53.35	23.93	13.46
10	FLUSILAZOLE	1.81	315.10	316.0/165.0	64.86	32.46	9.63
11	HEXACONAZOLE	2.25	313.07	314.2/70.2	49.37	24.71	15.93
12	IPROBENPHOS	2.00	288.09	289.0/91.0	56.88	26.95	16.49
13	MALATHION	1.73	330.04	331.0/127.0	40.83	18.73	11.63
14	METALAXYL	1.63	279.15	280.3/192.2	54.56	30.86	6.07
15	METHAMIDOPHOS	1.32	141.00	142.0/94.0	39.15	22.93	12.42
16	METHOMYL	1.34	162.05	163.4/106.0	65.25	38.47	7.85
17	MONOCROTOPHOS	1.14	223.06	224.0/127.0	52.94	25.86	9.48
18	PENCONAZOLE	1.94	283.06	284.2/70.0	57.19	27.63	18.41
19	PHOSALONE	2.04	366.99	368.1/182.3	58.83	32.16	8.80
20	PHOSPHAMIDON	1.23	299.07	300.2/174.2	62.49	36.59	17.62
21	QUINOLPHOS	2.02	298.05	299.0/163.0	49.34	23.76	6.00
22	SPINOSAD-A	5.15	731.46	732.9/142.2	53.88	30.41	9.72
23	SPINOSAD-D	5.91	745.48	746.2/142.2	43.80	16.63	7.21
24	TRIADIMEFON	1.57	293.09	294.0/197.0	63.96	37.43	15.31
25	TRIAZOPHOS	1.75	313.06	314.0/119.0	56.84	31.39	12.61

[a] M is molecular mass.
[b] Declustering potential.
[c] Collision energy.
[d] Cell exit potential.

Matrix effect

Evaluation of matrix effects, which usually result in significant deterioration of the accuracy and precision of an analytical method, was conducted during method development (Alder, et.al., 2006, Soler, et.al., 2007, Niessen, et.al., 2006). The matrix-induced suppression in target signals was prominent for a large number of pesticides, which possibly occurred as a result of suppressions in the ionization process at the ESI probe due to coeluted matrix compounds. The slopes of the matrix-matched calibration equations were significantly different to pure solvent-based calibrations at a 95% level of statistical confidence. An overall signal suppression by 25-80% was observed for most of the compounds. The use of D-SPE sorbents improved the peak shape, as a result removal of the coeluting interfering compound. An increase in the quantities of D-SPE sorbents or changing their proportion did not improve the extent of cleanup and instead resulted in adsorption loss of residues. The use of 25mg of GCB was optimum to remove the color of the matrix, but an excess quantity affected the recovery of Phosalone, Spinosad, due to surface adsorption on GCB. For, some Azole derivatives like Triadimefon, and Organophosphorus pesticides like Acephate, Ethion, the recoveries increased by nearly 20% when D-SPE cleanup was performed with 25 mg of PSA + 25 mg of GCB. In general, the recoveries of all of the test pesticides were within the range of 80-120% at all four levels of fortifications.

The cleanup effect could be attributed to the removal of fatty acids and sugars by PSA, whereas GCB was effective in removing Chlorophyll, Carotenoids and any other plant pigments. Because β-carotene is the chief Carotenoid compound in mango, its concentration in uncleaned and cleaned extracts was compared by HPLC to assess the cleanup effect. PSA alone could not remove any β-carotene as observed by HPLC analysis. However, D-SPE with 25mg of GCB could remove more than 90% β-carotene from the acetonitrile extract. An increase in GCB to 50 mg could completely remove the Carotenoids, but it affected the recovery of several compounds. The addition of C18 sorbent did not result in any significant improvement in recoveries and hence was not considered.

Recovery study

The recovery rate of each pesticide at two different fortification levels was evaluated in order to assess the extraction efficiency of the proposed method. For this 50g of blank sample (mangoes grown without application of any pesticide) were spiked with 0.010 mg/kg and 0.050 mg/kg of pesticides. Resulting samples were mixed and allowed to stand for 15 min before extractions. Six replicates at each fortification level were prepared. Concentrations of pesticides were calculated by measuring peak areas from extracted-ion current profile and by comparing them with those obtained from matrix-matched standards of a concentration similar to that of sample. Sample data were processed by external standard technique and five-point calibration. The recovery values are presented in Table-3.

Table 3*:* Recoveries of pesticides from fortified mango samples

Pesticide	Added (mg/kg)	Recovery(%)[a]	RSD(%)[a]	LOQ (mg/kg)
ATRAZINE	0.010	79	13	0.01
	0.050	85	11	
BITERTANOL	0.010	90	10	0.01
	0.050	96	13	
BUPROFEZIN	0.010	88	14	0.01
	0.050	84	9	
CARTAP	0.010	86	15	0.01
	0.050	94	11	
CHLORFENVINPHOS	0.010	88	14	0.01
	0.050	92	10	
DIAFENTHIURON	0.010	94	8	0.01
	0.050	99	10	
DIFENCONAZOLE	0.010	78	15	0.01
	0.050	84	10	
ETHION	0.010	91	9	0.01
	0.050	96	11	
FLUSILAZOLE	0.010	89	14	0.01
	0.050	92	10	
HEXACONAZOLE	0.010	93	12	0.01
	0.050	99	10	
IPROBENFOS	0.010	86	13	0.01
	0.050	94	11	
MALATHION	0.010	92	14	0.01
	0.050	102	12	
METALAXYL	0.010	88	10	0.01
	0.050	96	8	
METHAMIDOPHOS	0.010	79	15	0.01
	0.050	86	11	
METHOMYL	0.010	84	12	0.01
	0.050	88	10	
MONOCROTOPHOS	0.010	92	9	0.01
	0.050	96	7	
PENCONAZOLE	0.010	94	13	0.01
	0.050	99	10	
PHOSALONE	0.010	96	11	0.01
	0.050	88	9	
PHOSPHAMIDON	0.010	85	14	0.01
	0.050	92	12	
QUINALPHOS	0.010	98	13	0.01
	0.050	94	10	
SPINOSAD-A	0.010	82	8	0.01
	0.050	86	6	
SPINOSAD-D	0.010	95	11	0.01
	0.050	90	9	
TRIADIMEFON	0.010	92	10	0.01
	0.050	96	8	
TRIAZOPHOS	0.010	88	12	0.01
	0.050	96	10	

RSD(%): relative standard deviation; LOQ: limit of quantification.

[a] Each value in the mean of six determinations.

Application of the method to real samples

The proposed method has been applied for the routine analysis real mango samples collected from different market places in Andhra Pradesh (South India). The results (Table 4) showed the concentration of pesticide residues in all the samples analyzed was below the EU Maximum Residue Limits (MRL).

Table 4 : Concentration of pesticide residues in mangoes (mg/kg) collected different places in Andhra Pradesh, India

Pesticide	MS-1	MS-2	MS-3	MS-4	MS-5	MS-6	MS-7	MS-8	MS-9	MS-10	MRLs EU
ACEPHATE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
ATRAZINE	ND	0.013	0.043	0.016	0.013	0.026	ND	0.009	0.015	ND	0.05
BITERTANOL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	#
BUPROFEZIN	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
CARTAP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	#
CHLORFENVINPHOS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
DIAFENTHIURON	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	#
DIFENCONAZOLE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01
ETHION	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01
FLUSILAZOLE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
HEXACONAZOLE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
IPROBENPHOS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	#
MALATHION	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
METALAXYL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
METHAMIDOPHOS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01
METHOMYL	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
MONOCROTOPHOS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	#
PENCONAZOLE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
PHOSALONE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
PHOSPHAMIDON	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01
QUINALPHOS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05
SPINOSAD-(A+D)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
TRIADIMEFON	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01
TRIAZOPHOS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01

ND: not detected.
(Mean±SD) (n=3).

Conclusions

The proposed multi-residue LC–-MS–MS method fulfils established criteria for sensitivity, selectivity, and confident identification imposed by legislation for detection of pesticide residues at low concentrations in mangoes, that operated at fast scan acquisition times in MRM mode. The MRM ratio can provide a key parameter during quantitative evaluations, especially when coeluting analytes or matrix interferences are present during multiresidue analysis. The MRM ratio of the selected pesticides, evaluated within the concentration range from 10 µg kg^{-1} (LOQ) to 100 µg kg^{-1}. The procedure, based on the "QuEChERS" method and before the sample analysis. The method was validated on the basis of SANCO European guidelines. Recovery and within-laboratory reproducibility for the pesticide, matrix combinations studied were satisfactory. The proposed method proved to be a valuable tool for assessment of the occurrence of pesticide residues of different chemical classes in food commodities.

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