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Multiresidue analysis of 13 pesticides in spice usingQuEChERS-based method and gas chromatography-triplequadrupole mass spectrometry.

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Abstract*:A reliable and rapid method for the determination of pesticides was established using a QuEChERS (quick, easy, cheap, effective, rugged and safe) based extraction procedure in highly pigmented and complex spice matrices, namely red chilli (Capsicum annum Linn.). Gas Chromatography with tandem mass spectrometry (GC–MS/MS) was used for the confirmation and quantification 13 expected pesticide residues in different red chilli samples under invesigation. In this study, QuEChERS extraction procedure was followed and optmised. In the optimization step, dry ice was used to improve the separation of the acetonitrile layer and aqueous layers instead common salts. In dispersive step, three sorbents such as 60 mg Primary Secondry Amine(PSA), 60 mg Octa-decyl(C_{18})Silica and 15 mg of Graphitized Carbon Black(GCB);and 375 mg $MgSO_4$ were used for better extraction of pesticide residues in various red chilli samples. Electron ionization (EI)at positive mode was applied to simultaneously detect all the 13 pesticides in samples. Multiple reaction monitoring mode(MRM) choosed for quantification of expected pesticides, at least two abundant fragment ions per analyte was applied. Matrixmatched calibration was performed well with an linear correlation coefficient (r^2) >0.98638, calibration linearity range of 5–200 ng .mL^{-1}. Recoveries ranging from 75% to 117% and relative standar deviation of <20% were observed for the present investigation in accordance with the performance criteria required by the European Commission. The limit of detection (LOD) and Limit of Qquantification(LOQ) were found to be 0.04 to 0.5 ng.mL^{-1} and 0.1 to1.8 ng.mL^{-1}respectively. The validated and established procedure was finally applied to screen pesticide residues and its quantitative estimation in ten real red chilli samples. In the present investigation, dimethoate was detected in one spice sample out of ten samples*

Keywords: *QuEChERS, GC–MS/MS,Redchilli, Pesticide residues,Multiple Reaction Modes (MRM).*

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I. Introduction

Chilli(Capsicum Annum Linn) Is An Important Spice And Vegetable Crop, Which Is Extensively Grown Chilli (Capsicum annum Linn) is an important spice and vegetable crop, which is extensively grown both under rain, fed and irrigated conditions in about 8.01 lakh hectares in India [1]. Andhra Pradesh and Karnataka are two major states in producing and exporting red chilli compared with other states in the country and world. The red chilli being majourly produced from Guntur in Andhra Pradesh is the main region. Dry chilli powder is used as coloring agent in pharmaceutical for flavor and pungent [2]. The European Union (E.U) represents the largest markets for spices in the World. Germany, UK, Romania and Hungary responsible for 19%,16%,14%, and 12% respectively of the total consumption of the EU in the World[3]. Chilli crop is vulnerable to multitude of several microbes such as chillithrips, scirtothriops, dorsalis hood and yellow mite,polyphagotarsonamuslatus(Banks). Therefore varoous kinds of pesticides are widely applying for crop management and effective crop yeild. Few pesticides have been registered for using in chilli by central insecticide board and registration committee (CIB&RC), Government of India. Current agriculture practices rely on various pesticides that are harmful substances human health and environment. Their residues may appear in agricultural products due to improper use of agrochemicals to given crops (e.g. application of pesticides at dosages above the level authorized for the given crop) or improper conditions of harvesting and storage (e.g. application of pesticides during storage, insufficient withdrawal period applied between the date of the last pesticide treatment and harvesting). These sources have been causing the contaminated food products as well as surrounding environment.

The European countries (U.K, Italy, Greece, Germany, Spain ,Netherlands etc..) frequently monitoring the imported agricultural products time to time. Some chilli products were rejected due to presence of pesticide residues such as ethion, triazophos, chlorpyriphos,phosphamidon, cypermethrin, fenvalverate and dicofol, E.Coli and aflatoxin [4].The EU established Rapid Alert System for Food and Feed (RASFF) in 1979 for monitoring the food samples [5] with an objective of safety measures. The RASFF reported that, pesticide residues in chilli and spice paprika since 1998[7]. Few insecticides such as chlorpyriphos (2001, 2004),ehion(2000, 2001, 2008, 2010, 2011, 2013), triazophos(2001), cypermethrin(2001,2004), carbendazin(2008), hexaconazole (2008), and one fungicide i.ecarbendazin (2009) were found in Chilli and Spice paprika [6]. Codex Alimentarius Commission (CAC)Food and agricultural organization(FAO) of the united states, European Union(EU) and other food safety regulatory bodies have Maximum residue limits(MRL) for various commodities along with spices[8,9]. The Codex MRL has been used as global reference but some countries followed their own MRL values (Australia, Canada, China, EU,Japan, Republic of Korea etc) [10,11]. The MRL values variation influence the exported and imported the agriculture products. In 2009 Republic of Korea exported paprika to Japan, the MRL values of paprika is 2.0 mg/Kg which was deviated with Republic of Korea. Japan Monitoring Agency was tested imported paprika samples, they were detected levels of 0.7 mg/kg which is exceeded their MRL value (0.4 mg/kg) [12,13,14]. Therefore, at that time Japan tightened its monitoring inspection on Korean paprika samples [14].

Analysis of paprika is challenging as they are often present atlow concentrations of pesticides in complex matrices. To achive the low quantification of pesticidal residues, the sample preparation method should be effective. For the rapid analysis of pesticide residues, traditional methods such as Soxhelt extraction, solvent extraction, Liquid-Liquid extraction etc less commonly used due to laborious, more time and solvent consumption and tediousexperimental procedure.Therefore, modern sample preparation methods and clean-up steps have been introducing in food analysis. These includes solid-phase extraction (SPE),gel permeationchromatography (GPC),supercritical-fluid extraction (SFE), microwave-assisted extraction (MAE), pressurized-liquidextraction (PLE), ultrasound-assisted extraction (UAE),molecularly imprinted polymers (MIPs), matrix solid-phase dispersion (MSPD), solid-phase micro-extraction(SPME), QuEChERS, and liquid phase micro-extraction (LPME)[15]. Among these sample preparations, the QuEChERS approachtakes advantage of the wide analytical scope and high degree ofselectivity and sensitivity followed by gas and liquid chromatography(GC and LC) coupled to mass spectrometry (MS) for quantitative detection of pesticide residues. The application ofQuEChERS procedure showed highly promising results for montering the samples, when comparedto other methods(16,17).Anastassiades et.al developed QuEChERS method, which is become a very popular technique for a different types of food and other samples such as cereals[18], honey[19], tobacco[20], fruit andvegetables[21], tea[22]. One hundred plausible pesticides were determined in spices(red chilli ,black and white paper) by used QuEChERS method[23]. The original QuEChERS methods by use of acetate [24] citrate [25] buffering versions not found satisfactory recoveries. The red chilli powder was belonging to dry food commodities, therefore necessary addition of water to sample thus promoting extraction efficiency[26]. The spices contain fatty components and pigments, which are not easily removed in sample preparation so that modified QuEChERSmethod provides to eliminate the strong matrix effects .

The opted analytical tool should be high sensitive and selective to detect the rapid analysis of pesticides in food samples. The gas chromatography (GC) and liquid chromatography (LC) allows the simple ,rapid and automated determined the pesticides in various food samples. In addition that, GC (or) LC Coupled with specific detector which has been plays key role in selective analysis. The detectors have been using widely in analysis such as Electorn capture detector (ECD), Nitrogen phosphorus detector (NPD),Flame photometric detector (FPD), Mass spectrometer etc. The MS/MS detector was selectively employed, as it removes more matrix interferences than single quadruple in selected ion monitoring (SIM) mode.In recent years the MRL values are very low concentrations, so that lowLODs and simultaneous quantification and confirmationcan be achieved due to the high selectivityof triple quadrupole (QqQ) analysers in selectedreaction monitoring (SRM) mode.The multiple reaction montering mode also highly selective for quantification of pesticide in samples with combination of GC or LC.

The present study aimed to develop a simple, reliable and rapid method for determination of multiresidue analysis of pesticides in paprika (chilli powder) by using GC-MS/MS coupled with EI source under MRM mode for applying to real samples. This method could advantage as a model procedure for other multiresidue pesticide analysis of Chilli powder or products.

II. Materials And Methods

1.Chemical Reagents:

All pesticide reference standards (purity>97.0%) were obtained from sigma Aldrich (Bangalore, India). HPLC grade solvents such as acetonitrile(MeCN), acetic acid(HOAc),ethyal acetate, analytical-grade anhydrous magnesium sulfate ($MgSO_4$), dry ice and disposable syringe filters (PVDF,0.2 µm)were procured from by Indian scientific company (Tirupati, A.P, India). The primary secondary amine (PSA) and graphite carbon black (GCB) were procured from phenomenex company (Hyderabad, T.S, India). were purchased from Indian scientific company.A.P

2.Apparatus:

GC-MS/MS analysis was performed using a Agilent 7890A was equipped auto sampler and coupled to a triple quadrupole mass analyzer (Agilent 7000B) for sensitive and reliable analysis of pesticide residues. The GC was connected with an Agilent 19091s-431UILTM HP-5 MS capillary column (30 m × 0.25 µm ID × 0.25 mm film thickness). Sample injection was carried out using programmable temperature vaporization inlet in splitless mode at a temperature of 70 °C, which was increased to 90°C at 17° C/s in the evaporation phase. Further, the temperature was increased to 280°C at 10°C/s in the transfer phase and to 280°C at 14.5°C/s in the cleaning phase. Helium (purity 99.999%) was used as a carrier gas at a flow rate of 1.2 mL/min. The oven temperature was programmed as follows : initial oven temperature was held at 70°C for 1 min, increased to 150°C at 10°C/min, and further increased to 200°C at 3°C/min, with a hold time of 4 min. Final temperature of 280°C was attained at 10°C/min and held for 10 min (resulting in a total run time of 15 min). The ion source and transfer line temperatures were set at 200 and 280°C, respectively. All samples were analyzed with multi-reaction monitoring (MRM) mode in Quantification .

4.Sample preparation

Ten grams of paprika was weighed, transferred into a 100 mL polypropylene centrifuge tube and added 30mL acetonitrile and 10 ml ultra-pure water. The centrifuge was shaken vigorously by vortex shaker for 4 min and then set for 45 min .The centrifuge was subjected to 2 minutes of ultrasonic assisted extraction. Then, 10 grams of ice granules were discharged into tube and continued until layer separation formed. Then 5 mL of the upper layer was transferred to the dispersive tube which contains 60 mg PSA , 60mgOcta-decyl (C_{18}), 15 mg of GCB and 375 mg $MgSO_4$.The mixture was then vortex –mixed for 2 minutes. Finally the residue was reconstituted in 1 mL ethyl acetate and filtered with a 0.22 µm organic filter, which is ready for injection into GC MS/MS.

5.Stock solutions Preparation:

Stock solutions of 1µg.mL^{-1}standard mixtures of2-phenyl phenol ,Anthraquine,Atrazine,Benthiocarb,Bifenthrin,Chlorpyrifos,Dimethoate,Etrifoms,Kresoxim-methyl, Metolachlor,Metribuzin,Oxadiazon,Paclobutrazol were prepared by diluting 1mL of each standard from stock solutions 1 into 10 mL ethyl acetate in a 10 mL volumetric flask. The stock solution were stored at -25^{0}C.

6.Working solutions:

Thirteenworking standard sets were prepared using the serialdilution method (5, 15, 30, 50, 100,and 200ng.mL^{-1}) . The standard sets were dividedinto aliquots, sealed in ampoules and stored at -30^{0}C untilneeded. These standards were then used as standards for thedetermination of limits of quantification(LOQ),limits of detection (LOD), the linearity and recovery experiment.

7.**Preparation of blank samples:**

The Chilli powder commodities were used for the spiking experiments. Chilli powder samples were produced organically and were purchased from a general store. To avoid contamination with pesticides, the chilli powder samples were extracted twice with acetonitrile to remove any pesticideresidue and were then used as blank samples for the spiking experiments. The extracted samples were tested by GC–MS/MS.

8.Method Performance:

Chilli powder blank samples was used for method evaluated sensitivity and precision. The relative standard deviation and recoveries were determined for four replicates at five concentration levels (5,10,20,50,100,200 ng/mL) all the target compounds such are 2-phenyl phenol ,Anthraquine,Atrazine,Benthiocarb,Bifenthrin, Chlorpyrifos,Dimethoate,Etrifoms,Kresoxim-methyl, Metolachlor,Metribuzin,Oxadiazon,Paclobutrazol showed good recovery (>70) values obtained were satisfactory.

III. RESULTS AND DISCUSSION

1.Extraction procedureefficency:

In recent days the QuEChERS extraction procedure suitable for modified approach established on nature of analyte property, matrix composition and instrument. This method serve a usefulpurpose to improve results or practical efficiency for the given analyte(s)/matrix(es) applications, but some others have differencesonly due to personal preferences.The choice of normal extraction procedures, solvents such as ethyl acetate [27] acetone [28] and acetonitrile [29] were used. Among these solvents acetonitrile solvent has more advantages such as less interference from proteins and lipids therefore achieves high recovery values.Sung woo Lee et.al reported that, the dry ice- partitioning QuEChERS method used for the determination of 168 pesticides in paprika, creatively using dry ice to promote the separation of the upper MeCN layer without the salting-out effect and to avoid the possible degradation of thermal effect produced by the addition of salts such as $MgSO_4$ and NaCl[30]. The current study MeCN was used at initial extraction and conditioning in d-SPE step but finely reconstituted with ethyl acetate for the convenient to GC-MS/MS.Chilli powder contained pigments and fatty acids which are not contribute to any peaks on chromatogram of GC MS/MS but increasing the maintenance the columns and instrument. PSA has a capable to remove the fatty acids and other organic acids from sample matrix [31,32],which is not completely remove the lipophilic co-extracts of the acetonitrile extracts from three low fat baby food extracts.The C_{18} is a another option for eliminate the lipophilic and low fatty compounds, lipids and non-polar interferences from food matrices [33,34].Georgakopoulous et.al reported that ,the GCB was used to reduces the pigments from oil matrices and vegetables [35]. In Current study, d-SPE step 60 mg PSA, 60 mg C_{18}, 15 mg of GCB and 375 mg $MgSO_4$were used. The extraction was colorless and transparent by using of GCB (15 mg) which reveals that GCB useful to remove the pigments in chilli sample. Therefore, PSA,C_{18} and GCBoptimized condition provided good recovery and having an excellent clean-up for removing a variety of matrix compounds. Further, it was observed that dry ice effectively separated the layers in tube with short time and without temperature influence on the extraction.

2.Optimization Conditions :

Optimization of MS/MS conditions such as Qualifier, Quantifier ions, and collision energies was studied. At the beginning, three to four transitions were chosen for every pesticideto determine the most suitable quantification and qualificationtransitions. In most of the cases, the predominant intense product was selected as the quantifier ion without interference. However, for some cases, the qualifier with less intense was chosen as the quantifier ion since therewas fewer interference. In general, the higher mass range (m/z) for the quantifier and product ions is selected and the bettersignal-to-noise ratio will be obtained. The optimized MRMtransition and other chromatographic experimental data are shown in Table.1. The corresponding chromatograms were shon in supplementary data.

Table .1 Retention time, MRM transitions for Qualifier and quantifier ions of selective pesticides

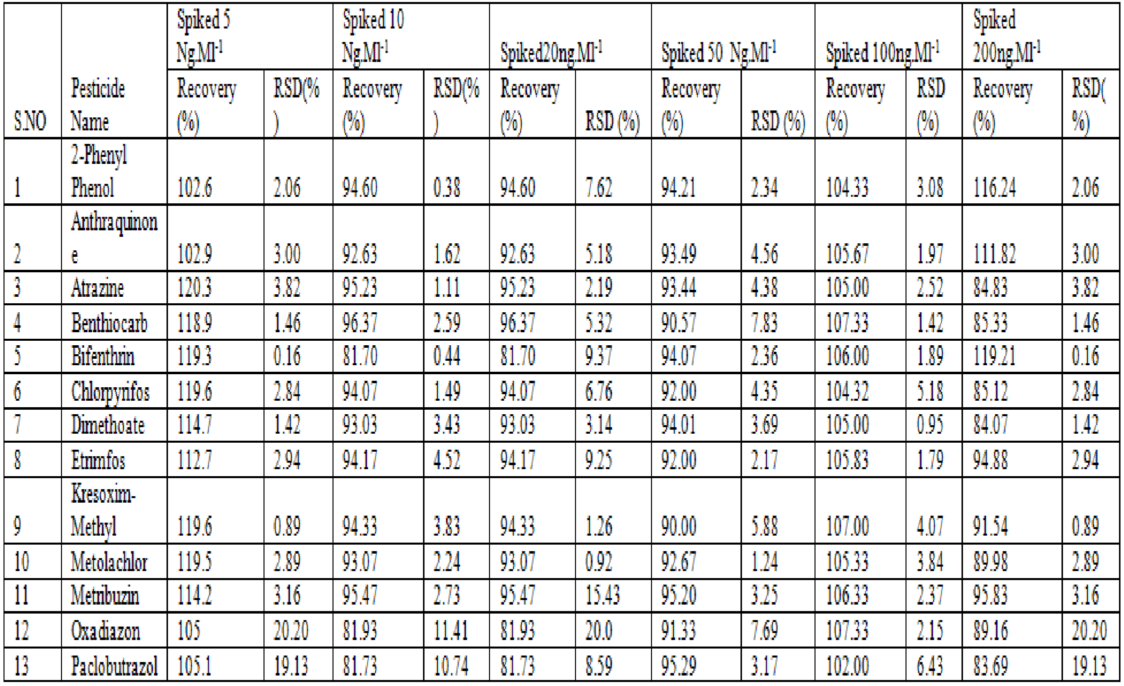
S.NO	Pesticide Name	Retention Time t_R^a (Min)	Regrassion Coefficient (R^2)	Quantification MRM 1	Quantification MRM 2	LOD ng.mL^{-1}	LOQ ng.mL^{-1}
1	2-Phenyl Phenol	6.27	0.99235	169.7→115.0	169.7→141.2	0.4	1.6
2	Anthraquinone	9.91	0.99189	207.8→180.1	207.8→152.2	0.2	0.7
3	Atrazine	7.86	0.99222	200.2→202.8	214.9→58.1	0.5	1.8
4	Benthiocarb	9.72	0.98638	256.9→100.1	100.0→72.0	0.4	1.2
5	Bifenthrin	13.83	0.98932	181.2→166.2	181.2→165.2	0.2	0.6
6	Chlorpyrifos	9.88	0.99045	198.9→171.0	196.9→169.0	0.5	1.7
7	Dimethoate	7.63	0.99426	124.9→79.0	124.9→47.0	0.2	0.6
8	Etrimfos	8.48	0.99049	291.9→181.1	181.1→153.1	0.2	0.7
9	Kresoxim-Methyl	11.73	0.98465	116.0→63.0	116.0→89.0	0.5	1.7
10	Metolachlor	9.82	0.99062	162.2→133.2	238.0→162.0	0.1	0.4
11	Metribuzin	9.36	0.99142	198.0→55.0	198.0→82.0	0.04	0.1
12	Oxadiazon	11.55	0.98799	174.9→76.0	174.9→112.0	0.1	0.5
13	Paclobutrazol	10.87	0.99662	236→167.1	125.1→89.0	0.1	0.4

3.Methodof validation:

The method was validated by assessing linearity (expressed as r^2), precision (expressed RSD), and accuracy (expressed as recovery). In this study 5,10,20,50,100 and 200 ng.mL^{-1}concentrations were using each analyte for constructed the calibration curves .Good linearity obtained by pure reference standards as well as matrix matched solvents. Correlation coefficient values were>0.98 in almost all cases ,which is depicted in table 1.

The recovery studies and precision of the proposed method was carried out by spiking of 13 pesticide samples at five concentration levels (5,10, 20,50,100 ng.mL^{-1}). Each spiked chilli sample was evaluated for five replicates (n=5). On the basis of resultant data obtained, the quantified and qualifier ions are to be evaluated using MRM values and its related information is shown in supplementary data.Recoveries of 13 spiked pesticidesin chilli samples were found to be in the range of 81.93-119.6% and their graphical representation shown in fig.1.According to European Commission SANTE/11945/2015 the recoveries should be in the range of 70-120%, than that method would be acceptable [36]. Therefore obtained recoveries values and established method is acceptable and found to be fit for analysis of pesticides in paparika.The established method was found to be good precision, which is confirmed interms of relative standard deviations (RSDs) and values are incorpoted in table.2. The evaluated RSD values were found to in good agreement which are lower than 20%.

Table.2 Standard addition Recovery Experiment Results at 5,10,20,50,100 And 200 ng.mL^{-1} Fortification Levels (n = 5).



S.NO	Pesticide Name	Spiked 5 Ng.Ml^{-1}		Spiked 10 Ng.Ml^{-1}		Spiked20ng.Ml^{-1}		Spiked 50 Ng.Ml^{-1}		Spiked 100ng.Ml^{-1}		Spiked 200ng.Ml^{-1}	
		Recovery (%)	RSD(%)	Recovery (%)	RSD(%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD(%)
1	2-Phenyl Phenol	102.6	2.06	94.60	0.38	94.60	7.62	94.21	2.34	104.33	3.08	116.24	2.06
2	Anthraquinone	102.9	3.00	92.63	1.62	92.63	5.18	93.49	4.56	105.67	1.97	111.82	3.00
3	Atrazine	120.3	3.82	95.23	1.11	95.23	2.19	93.44	4.38	105.00	2.52	84.83	3.82
4	Benthiocarb	118.9	1.46	96.37	2.59	96.37	5.32	90.57	7.83	107.33	1.42	85.33	1.46
5	Bifenthrin	119.3	0.16	81.70	0.44	81.70	9.37	94.07	2.36	106.00	1.89	119.21	0.16
6	Chlorpyrifos	119.6	2.84	94.07	1.49	94.07	6.76	92.00	4.35	104.32	5.18	85.12	2.84
7	Dimethoate	114.7	1.42	93.03	3.43	93.03	3.14	94.01	3.69	105.00	0.95	84.07	1.42
8	Etrimfos	112.7	2.94	94.17	4.52	94.17	9.25	92.00	2.17	105.83	1.79	94.88	2.94
9	Kresoxim-Methyl	119.6	0.89	94.33	3.83	94.33	1.26	90.00	5.88	107.00	4.07	91.54	0.89
10	Metolachlor	119.5	2.89	93.07	2.24	93.07	0.92	92.67	1.24	105.33	3.84	89.98	2.89
11	Metribuzin	114.2	3.16	95.47	2.73	95.47	15.43	95.20	3.25	106.33	2.37	95.83	3.16
12	Oxadiazon	105	20.20	81.93	11.41	81.93	20.0	91.33	7.69	107.33	2.15	89.16	20.20
13	Paclobutrazol	105.1	19.13	81.73	10.74	81.73	8.59	95.29	3.17	102.00	6.43	83.69	19.13

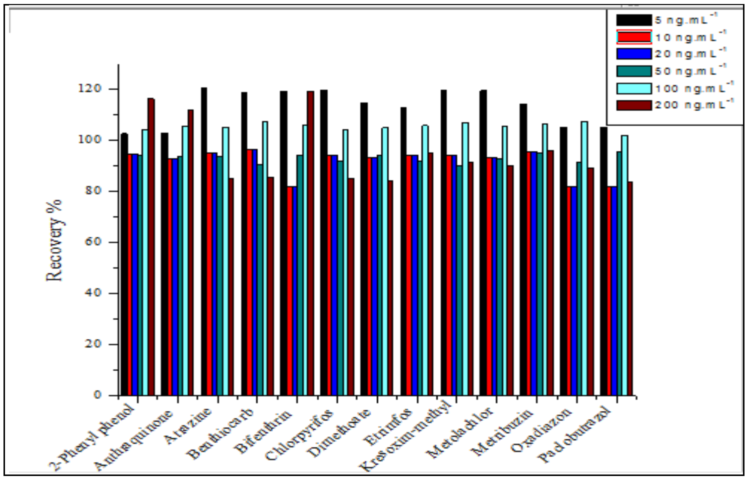


Fig.1 Recovery percentages at 5,10,20,50,100,200 ng.mL^{-1} of 13 spiked concentrations.

The limit of detection (LOD) and limit of quantification (LOQ) values were calculated by using signal to noise ratio (S/N) multiplication with 3 and 10 in the range 0.04 to 0.5 ng.mL^{-1} and 0.1 to1.8 ng.mL^{-1}respectively [37].The established LOQ allow for the identification and quantification of target analyteswhich is below the MRLs as per the EU legislation by European union .

4.Matrix Effect:

In the present work, Matrix effect (M.E) is either signal suppression or enhancementof the analyte due to the co-elution of matrix components .Matrix effect calculated by comparing the slopes of calibration curves prepared in pure solvent and in matrix extract. It is reported that signal enhancement is always observedin GC-MS/MS analysis. The matrix effectsalso depend heavily on the chemical property of the analyteand sample preparation procedure. Therefore, study of matrix effect is also essential in quantification of selective pesticide samples. The matrix effect is calculatedusing the equation:

$$\%\mathrm{ME} = \frac{Slope\ of\ matrix\ matched\ curve}{slope\ of\ solvent\ curve} \times 100$$

The matrix effects can be classified into three types based on percentages such as No matrix effect occurred when thevalues were between _20% and 20%, a medium matrix effect wasbetween _50% and _20% or 20% and 50%, and a strong matrixeffect was below _50% or above 50% [38]. Cervera et.al reported that, approximately 80% of 130 pesticides obtained positive % of MEin paprika samples, hence showed signal enhancement with GC-triple quadruple tandem mass spectrometry[39]. In this study all the 13 pesticides were found soft ME in paprika samples and correspondingly shown singnal enhancement. So, it was observed that very less matrix effect found during the analysis.Table .3 Matrix effect calculated by slope of matrix slope and solvent slope.

S.NO	Pesticide Name	Matrix slope	Solvent slope	M.E(%)
1	2-phenyl phenol	43909.04353	41854.77197	4.90809
2	Anthraquinone	95286.61553	90689.77757	5.06875
3	Atrazine	30257.73188	28831.63296	4.94630
4	Benthiocarb	196120.1558	183907.5963	6.64059
5	Bifenthrin	199727.8447	177247.9149	12.68276
6	Chlorpyrifos	66336.61796	62981.41149	5.32729
7	Dimethoate	101320.3471	97164.52708	4.27709
8	Etrimfos	55971.12832	53044.05386	5.51819
9	Kresoxim-methyl	166259.8259	155323.5699	7.04095
10	Metolachlor	529231.3542	501852.9493	5.45546
11	Metribuzin	69120.60809	65723.5123	5.16876
12	Oxadiazon	112731.943	106149.2904	6.20131
13	Paclobutrazol	154576.4479	149690.3399	3.26414

The proposed modified QuEChERS method was successfully applied to 10 paprika samples ,which were collect from from local market in pulivendula , kadapa, A.P, India. Out of ten, one sample shows positive rspondse of dimethoate residue, their residue range about 4.0 ng/mL.

IV.CONCLUSION

A very quick, easy effective, rugged, reliable and accurate multi-resuide method was developed for determination &estimtation of pesticide residue in chilli powder by GC –MS/MS .The optimized method was satisfactory and got good results which are found to met validation criteria in respect of chilli powder samples . Out of ten, one sample shown positive response pertaining to dimethoate residue with a concentration of 4.0 ng/mL. The observed concentration of dimethoate found to be within the MRL value. The established and optimisedQuEChERS method is useful to monitoring of pesticide resudes in real food samples during routine checkto minimize healthrisks.

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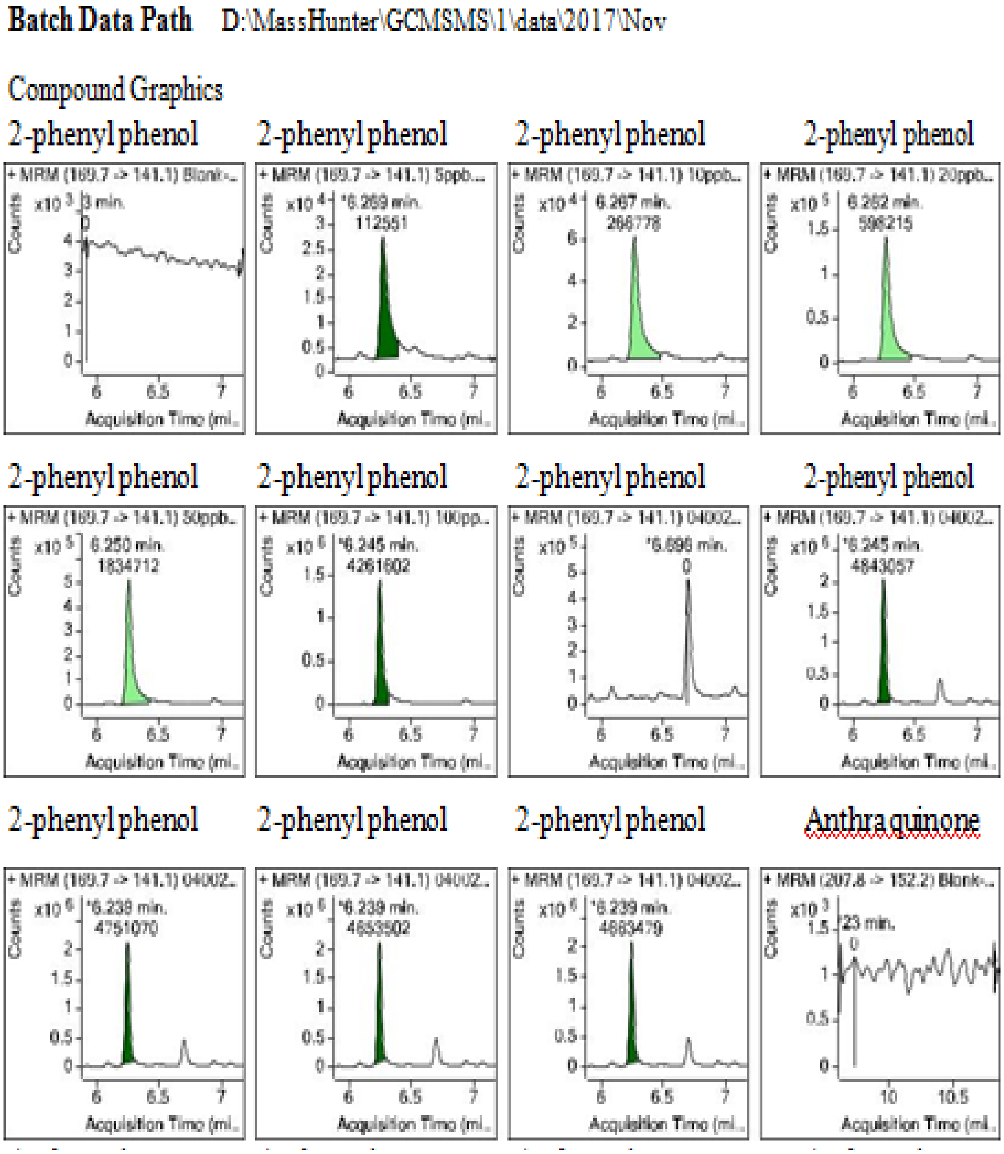
Supplementary data



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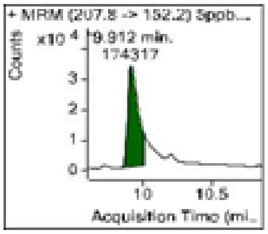

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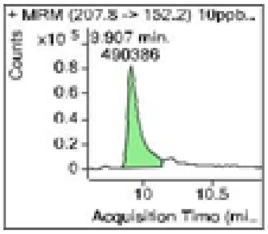

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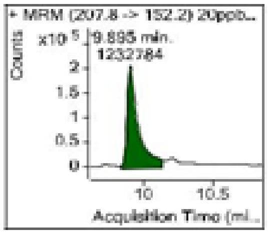

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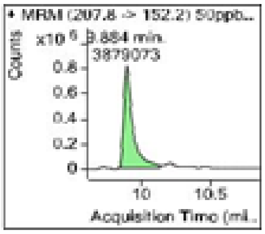

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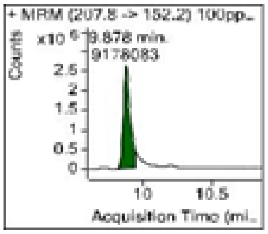

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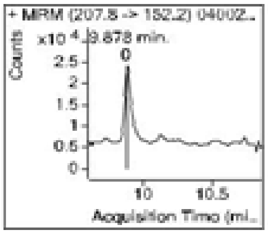

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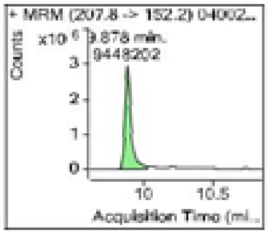

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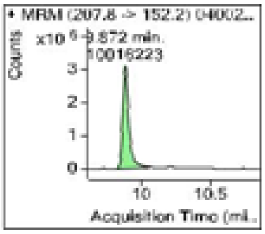

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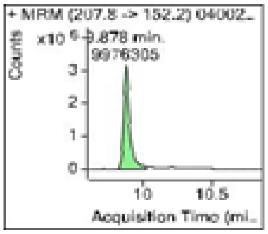

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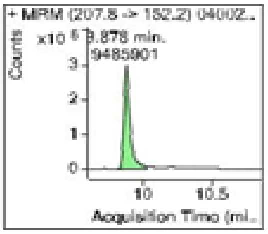

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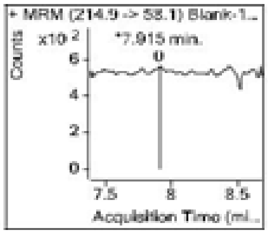

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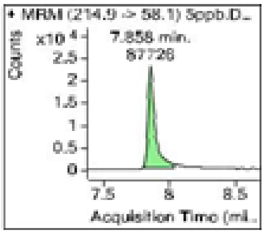

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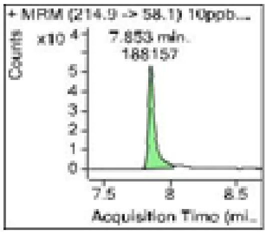

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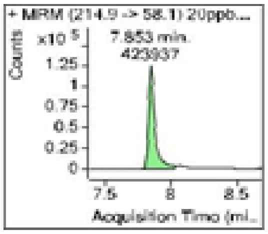

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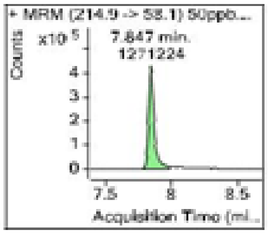

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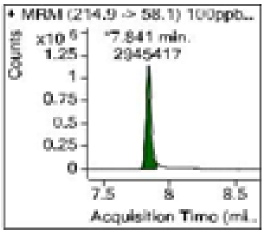

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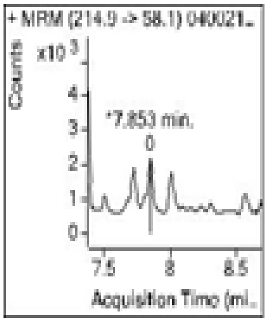

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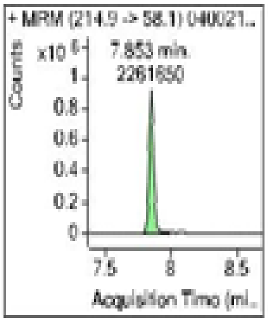

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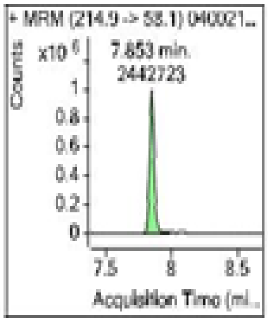

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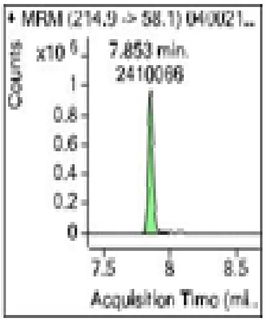

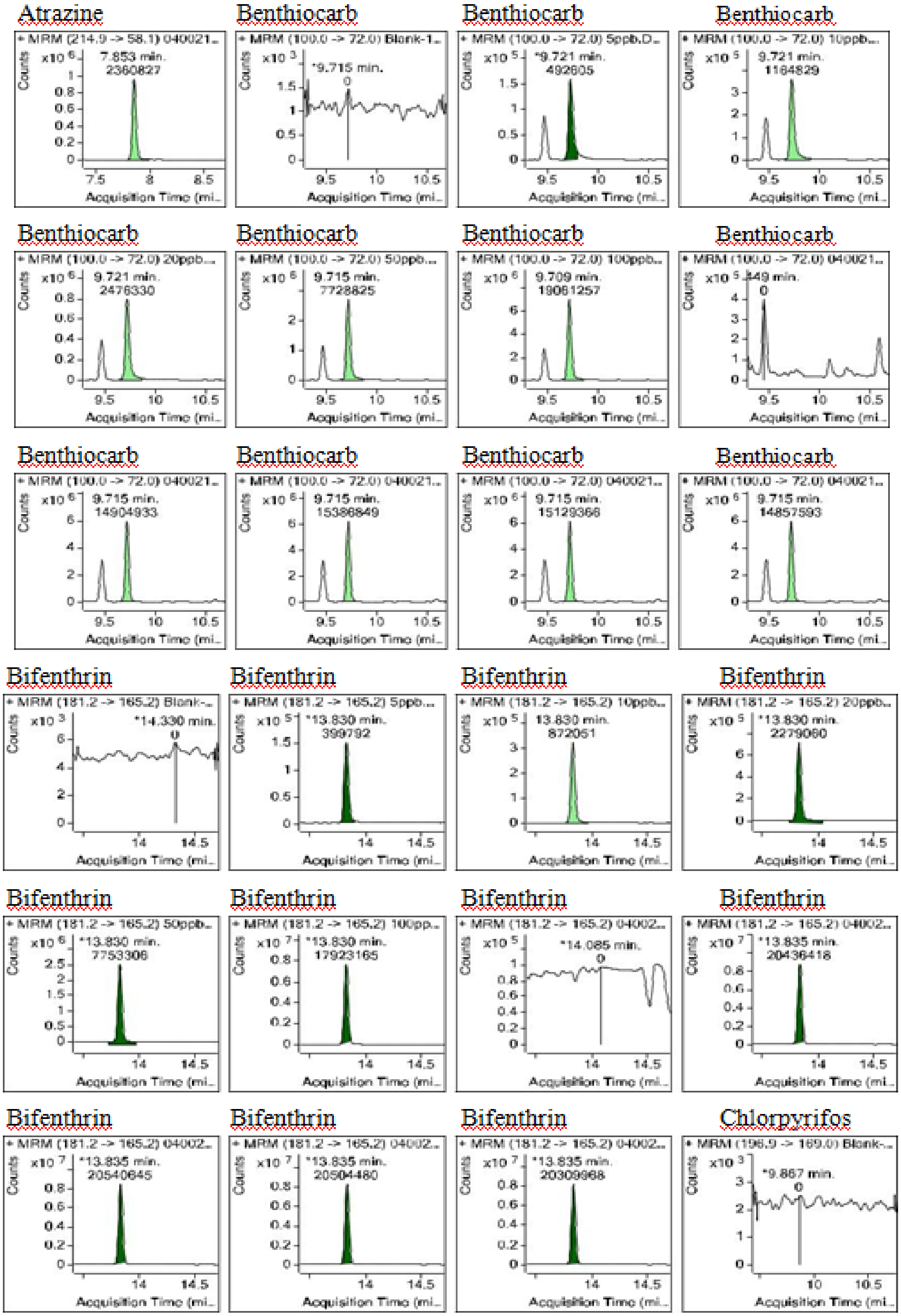
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Bifenthrin
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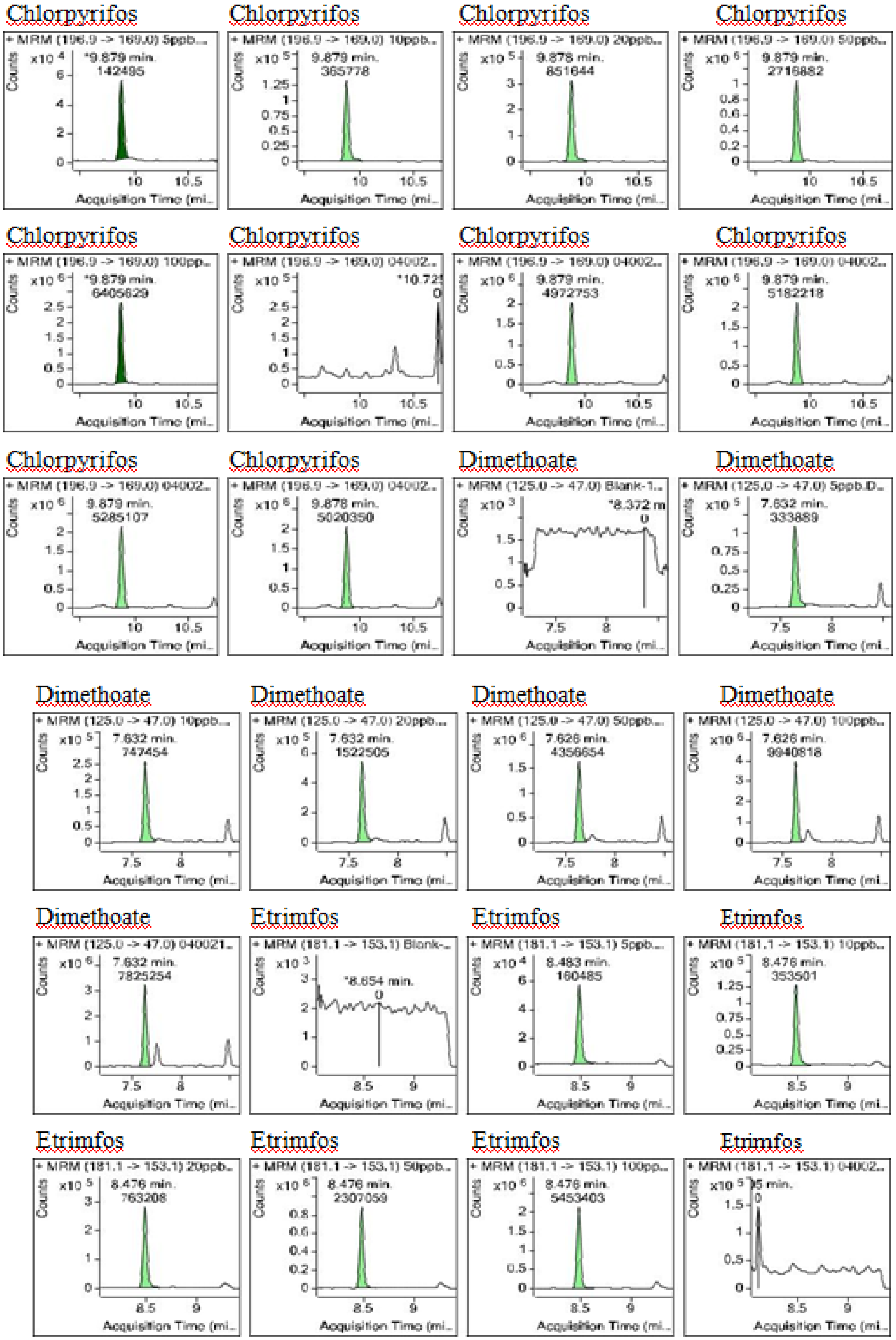
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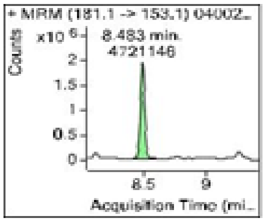

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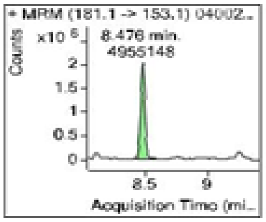

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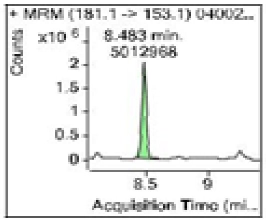

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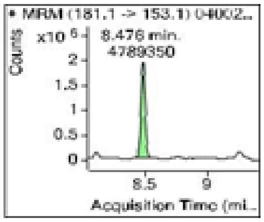

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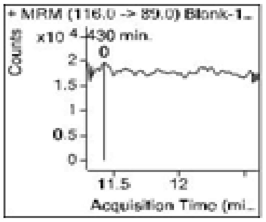

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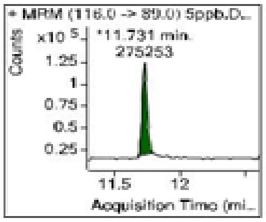

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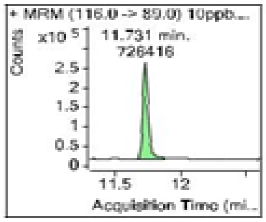

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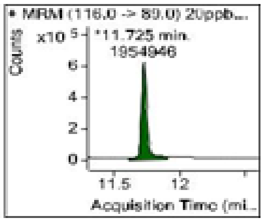

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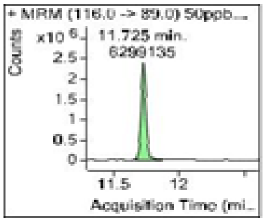

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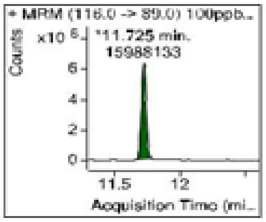

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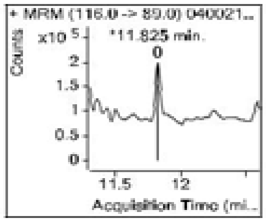

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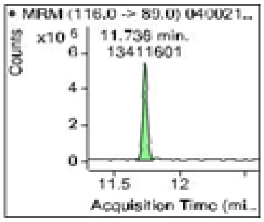

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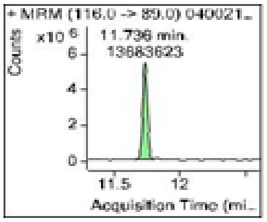

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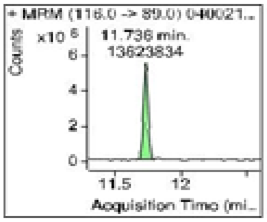

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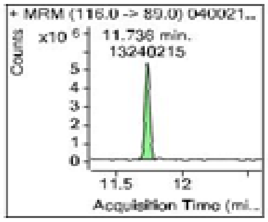

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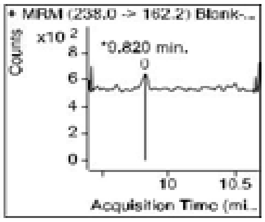

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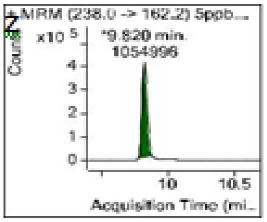

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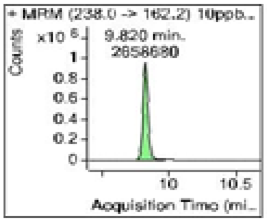

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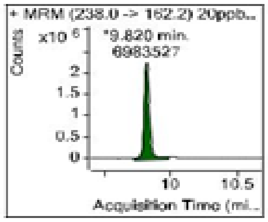

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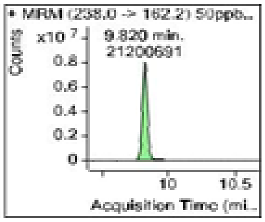

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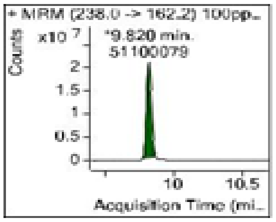

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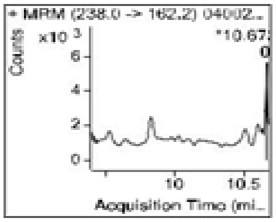

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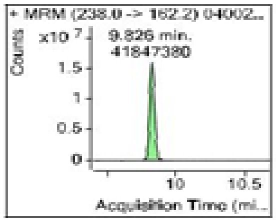

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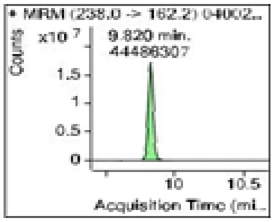

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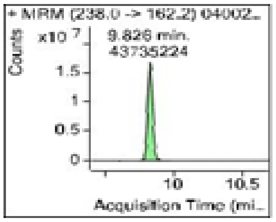

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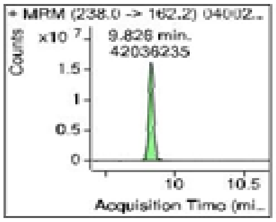

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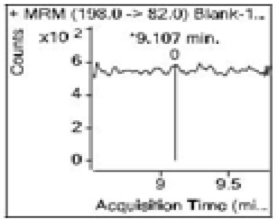

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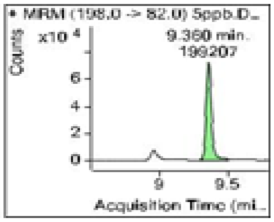

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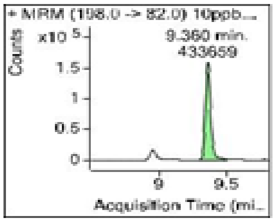

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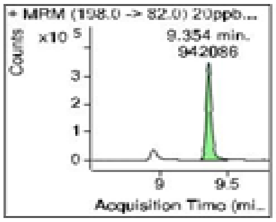

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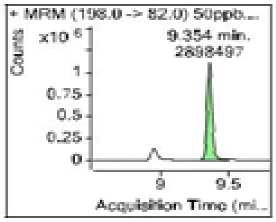

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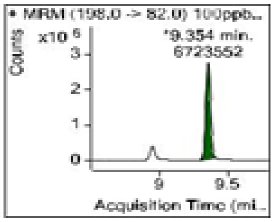

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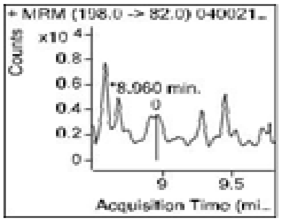

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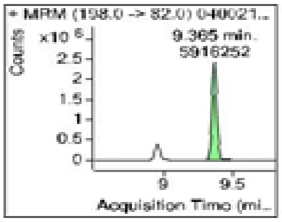

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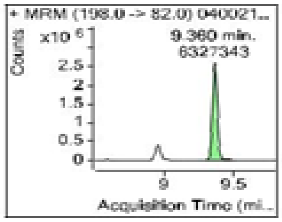

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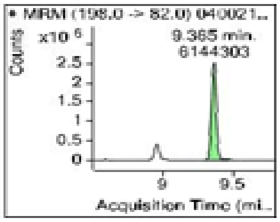

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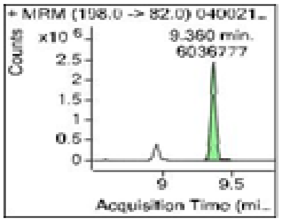

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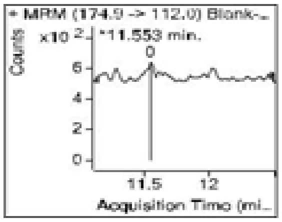

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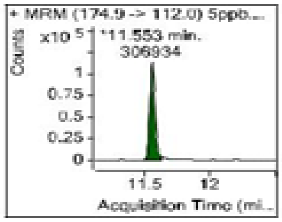

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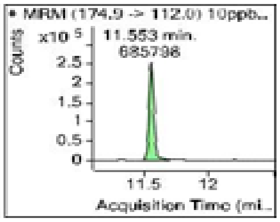

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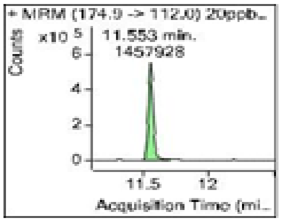

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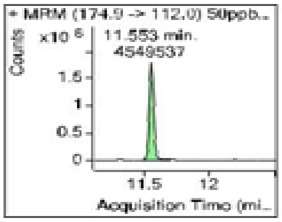

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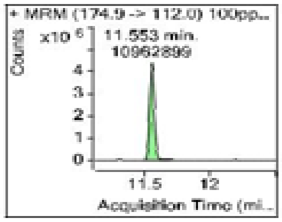

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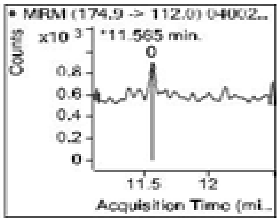

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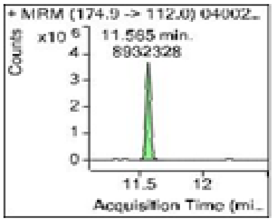

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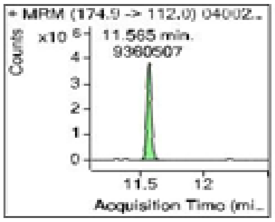

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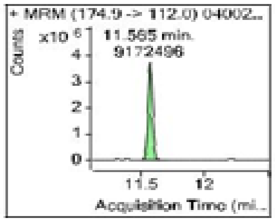

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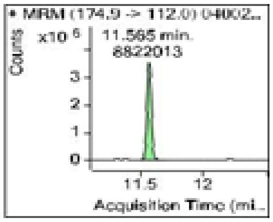

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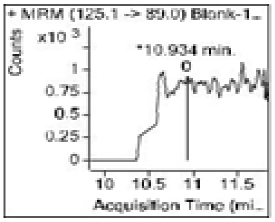

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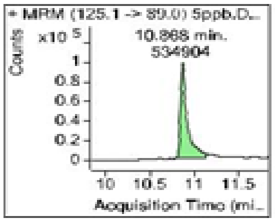

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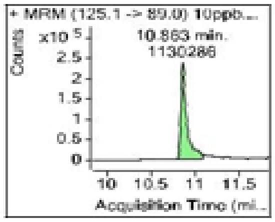

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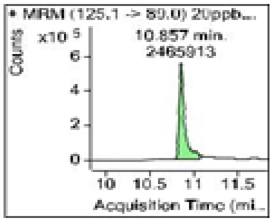

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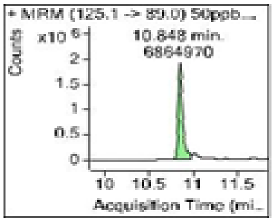

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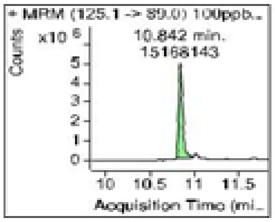

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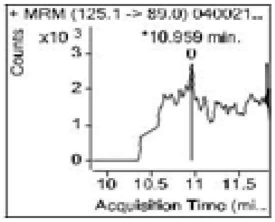

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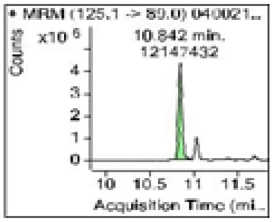

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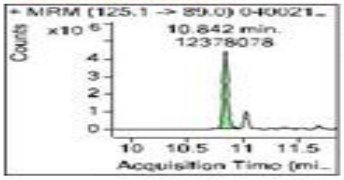

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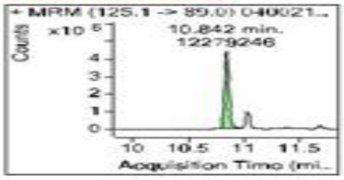

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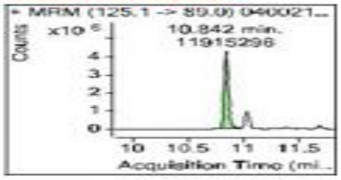

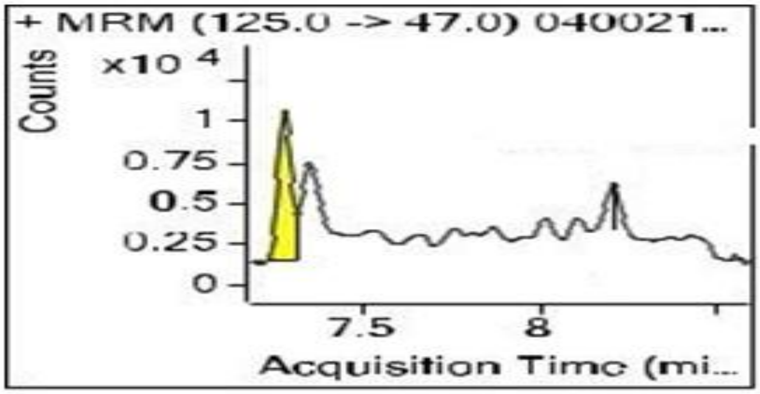

Dimethoate found one sample.

C. SivanandhaReddy"Multiresidue Analysis Of 13 Pesticides In Spice Usingquechers-BasedMethod And Gas Chromatography-TriplequadrupoleMassSpectrometry."International Journal of Engineering Science Invention (IJESI), vol. 07, no. 04, 2018, pp 01-15