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RESEARCH ARTICLE

DETERMINATION OF PESTICIDES IN VEGETABLES AND FRUIT FROM SUPERMARKETS OF LUCKNOW CITY USING GAS CHROMATOGRAPHY-MASS SPECTROSCOPY.

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Abstract

Pesticide use becomes an integral part of modern agricultural practices and may cause the threat of its presence in different food commodities. In this context 31 pesticides were analyzed in different vegetables and fruit samples collected from different malls in Lucknow city, India. Extraction and cleanup of pesticide residues was done by QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method using ethyl acetate as a extraction solvent and different sorbents like primary and secondary amine, charcoal for dispersive solid phase cleanup of matrix component. Analysis of pesticide residues was done by using gas chromatography equipped with electron capture detector (GC-ECD) and detected pesticide was further confirmed by gas chromatography and mass spectrometry (GC-MS). Validated method was found accurate (% recovery 79-104%) and precise with relative standard deviation (%RSD) of less than 15. Limit of detection ranged from 1.49-5.25 mg kg^{-1} and limit of quantification ranged were 4.46-15.74 mg kg^{-1}. In overall 270 analyzed samples of vegetable and fruits only 35 samples were detected with pesticide residues in which only 9 pesticides are found above MRL value according to CODEX/FSSAI MRL values. Pesticide residues were detected in cauliflower, cabbage, brinjal, green pea, broccoli, apple, grapes and banana.

Introduction:-

Fruits and vegetables are important part of balanced diet requirement of every human, for improved health. Vegetables and fruits are major source of fibers, minerals and vitamins.[1-3]. Fruit and vegetables are traded worldwide to persuade the growing demand. Farmers utilize pesticides to preventing pests, boost production, and for plant diseases which create great problems in vegetable and fruit production. Pesticides are special class of chemical compounds that have toxicity and they are widespread use in agricultural practice for field and post-harvest protection of crops. Currently pesticides like organochlorine, organophosphates, synthetic pyrethroids, herbicides enjoy wide use in the world. Among these classes organophosphate and synthetic pyrethroids gain a considerable popularity due to their broad-spectrum activity, low bioaccumulation potential, and relative immobility in soil.

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Farmers regularly use these groups of pesticides on various vegetables, fruits, cereals and pulses [4-8]. It is also reported that high level of pesticides uses are common with applications being carried out on periodic basis throughout the growing season.[9] Recently there has been a significant increase in the importance of pesticide residues analysis to evaluate the residual load of pesticide on different food commodities and to make a transparent system of use for better implementation of good agricultural practices [10-12]. Human are directly and indirectly exposed to pesticides. Monitoring of pesticide residues in fruits and vegetables help to assess the potential risk of these products to consumers' health and provide information on the pesticides that have been used in the field crops [13-15]. Furthermore, the usage of pesticide has been accompanied by risks to human health and the environment because of their high persistence and bioconcentration in food [16]. According to some health experts, if we exposed for a prolonged period, these pesticides can prove fatal. "Pesticides may produce neurological toxicity, neurodevelopment impairment, disturbances in the immune system and reproductive system and can affect vital organs like the kidney and liver as well as the endocrine system. Someone also cause food poisoning or allergic reactions [17].

Pesticide production and use in the country shows a different pattern from global trends insecticide use is around 75% in the country, compared to 32% in the world. Herbicide use is only 12% in the country while worldwide, consumption is 47%, while carbamate and synthetic pyrethroids compounds are used the most globally [45% together], in India, organophosphates constitute 50% of the consumption [18].

The main aim of this study was to investigate the presence of pesticide residues in different supermarket foods (fruit and vegetables) in Lucknow Uttar Pradesh, India. Samples were collected from three different malls. The study includes the application of QuEChERS (Quick, Easy, Cheap, Effective Rugged, and Safe) methods [19-23]. for the estimation of 31 pesticides comprising 13 organochlorines (OCs), 8 Organophosphates (OPs), 7 Synthetic Pyrethroids (SPs), and 3 Herbicides (H) in 14 vegetable and fruit samples.

Material and Methods:-

Reagents and Solutions:-

All solvents and chemicals used in this study were analytical grade ethyl acetate-hexane, acetone were purchased from Sisco Research Laboratories Pvt. Ltd. (Mumbai, India). Sodium chloride (NaCl) and magnesium sulfate (MgSO4) were procured from Sigma-Aldrich Pvt. Ltd (Bangalore India). PSA and bondasil (40 μm) from Agilent Technologies (Santa Clara, CA, USA) were used. Pesticide standards such as Organochlorines (α-HCH, β- HCH, λ-HCH, δ- HCH, Endosulphan Sulphate, α-Endosulphan, β-Endosulphan, p,p'-DDE, p,p'-DDD, , o,p'-DDE, o,p'-DDT, p,p'-DDT, Aldrin) Organophosphates (Dichlorvos, Phorate, Phosphamidon, Chloropyrifos-Methyl, Parathion-Methyl, Malathion, Chlorpyrifos, Ethion,) Synthetic pyrethroids (α-Cypermethrin, Fenvalerate, Fenpropathrin, λ-Cyhalothrin, Bifenthrin, Cyfluthrin, δ-Methrin) Herbicides (Butachlor , Pendimethylene, , Alachlor) were procured from Supelco (Belfonte, PA, USA). A stock solution of individual pesticides were prepared in n-hexane at an approximate concentration and diluted to intermediate solution of 100 mgl−1. Working standard of mixture of pesticides was prepared at concentrations of 0.01, 0.05, 0.1, 0.25, 0.5, 1.0 and 5.0 mg L^{-1} from individual intermediate solution of pesticides by serial dilution.

Sample collection:-

Fresh samples were purchased from three different mall of Lucknow. Eleven different vegetables including cabbage, cucumber, cauliflower, capsicum, green chilli, brinjal, green pea, tomato, okra, bitter gourd, broccoli and three different fruits apple, banana, grapes were collected from different supermarkets from Lucknow. Five samples from each different variety were collected. The samples were properly packed and labeled with unique sample identity and transported to laboratory and refrigerated at 4 $^{o}C \pm 2$. Then samples were properly extracted and analyzed within 24 h from the time of their collection from the markets.

Extraction and cleanup:-

Vegetable and fruit samples were washed, cleaned, chopped, and grind in warring blander. 10g macerated sample of each vegetables in triplicate was taken for multi-pesticide residue analysis by QuEChERS method. Ten grams of macerated sample was taken in 50 ml centrifuge tube and mixed with 10 ml Ethyl acetate, 4 g of anhy. $MgSO_4$, 1 g NaCl. Centrifuge tube was vigorously shaken and rotospined for 10 minutes at 50 rpm. Then extract was centrifuged for 10 min at 8,000 rpm. 1 ml aliquot of vegetable and fruit extract was cleaned with 150mg $MgSO_4$, 100mg primary and secondary amine PSA and 10mg activated charcoal. The extract was again shaken for 10 min at 50 rpm on

rotospin and centrifuged for 10 min at 8,000 rpm. The supernatant was collected in GC vial and one 1 µL of clean extract was used for GC-ECD analysis

Analysis:-

GC-ECD:-

Pesticide residues were analyzed on (Shimadzu GC-2010) GC equipped with fused silica capillary column DB-5 (30 mt × 0.25 mm id) coated with 5%phenyl-methylpolysiloxane (0.25 µm film thickness) using Ni-63electron-capture detector (ECD). General operating condition were as follows: Column temperature program: initially 165^0C for 1.50 min, increase at 3^0C min^{-1} to 225^0C hold for 2 min, then increase at 3.50^0C min^{-1} to 260^0C hold for 2.50 min then increase 3.50^0C min^{-1} to 280^0C hold for 5 min. Injection volume 1 µl nitrogen flow rate 0.50 ml min^{-1} and makeup 30 ml min^{-1} with split ratio 1:10; using carrier gas (N_2) 99.5%; Injector port temperature 180^0C; detector temperature 300^0C

GC-MS Conditions:-

GC-MS analysis was performed by using Trace GC ultra gas chromatograph connected to a Quantum XLS mass spectrometer (Thermo Scientific, FL, USA). GC was equipped with MS-5 capillary column (30 m×0.25 mm i.d. ×0.25 µm film thickness) containing a stationary phase of 5 % phenyl and 95 % methyl polysiloxane. The injection was carried out in split less mode at an injector temperature of 280 °C. Helium gas (purity 99.999 %) was used as a carrier gas at a flow rate of 1.0 ml min^{-1}. The oven temperature program was as follows: the initial oven temperature was held at 55 °C for 3 min, and then increased to 150 °C at the rate of 10 °C min^{-1} and further increased to 230 °C at the rate 3 °C min^{-1} and hold for 5 min. Finally, the oven temperature was increased to 300 °C at the rate 10 °C min^{-1} and hold for 10 min (total run time 60 min). The ion source and transfer line temperature were set at 220 °C and 290 °C, respectively. All the samples were analyzed in full scan mode.

Results and discussion:-

Extraction procedure is the crucial step in the multipesticide residue determination due to the presence of variety of macromolecule like pigments, steroids, sugar content in fruit commodities etc. Therefore, the selectivity of the extraction procedure has to be increased to obtain good recoveries for a broad range (polar as well as non polar) of pesticides. In this study, ethyl acetate was selected to obtained high recoveries of pesticide and to minimize the use of chlorinated solvents, which are associated with toxicity issues to humans. Salts like magnesium sulphate are used to remove moisture content and sodium chloride was used to break the emulsion and to enhance the phase separation for good recovery of pesticides. Cleanup of extract is required to reduce the co-extractive and matrix interference. In cleanup process magnesium sulphate was further used to remove residual moisture and PSA was used to remove colour content like pigments or sugar contents.

Result of method validation parameter showing the suitability of method for pesticide residue analysis. Recovery of pesticide varies from 79 to 104 % and limit of detection ranged from 1.49-5.25 mg kg^{-1} and limit of quantification ranged were 4.46-15.74 mg kg^{-1}. The accuracy and precision were also validated in accordance with the European Commission (EC) guidelines (SANCO/2007/3131) [24]. Response of pesticides were found to be linear, with a square of correlation coefficient of (r^2) higher than 0.98 for all pesticides Table-1.Inter and Intraday precision of the method is evaluated by % relative standard deviation associated with recovery estimation and % RSD was found less than 9% and 15% respectively.

Validated method is used for pesticide residues analysis in different vegetables and fruits. All the samples of vegetables and fruits were analyzed in triplicate. The summary of number of samples detected with pesticide residues and their levels in vegetable and fruit samples were collected from supermarkets are shown in table-2. In overall 270 analyzed samples of vegetable and fruit only 35 samples were detected with pesticide residues in which only 9 pesticides are found above MRL value according to CODEX/FSSAI MRL values.

Pesticide residues were detected in cauliflower, cabbage, brinjal, green pea, broccoli, apple, grapes and banana remaining varieties of vegetable and fruits were not detected with pesticide.

In cauliflower, chlorpyrifos and bifenthrin were found in three and one samples respectively. Residues of chlorpyrifos and bifenthrin were ranged from 0.023-0.120 mg kg^{-1} and ND-0.110 mg kg^{-1} respectively in which chlorpyrifos was found above MRL in only one samples of cauliflower. In cabbage parathion methyl and chlorpyrifos were found and their residues were ranged from 0.040-0.090 mg kg^{-1} and 0.068-0.134 mg kg^{-1}

respectively. Residue of parathion methyl was found above MRL in only two samples. In brinjal three pesticides form three different collection points were detected with γ-HCH, Chlorpyrifos and α-endosulphan and their residues were ranged from 0.051-0.210 mg kg^{-1}, 0.145-0.720 mg kg^{-1} and ND-0.032 mg kg^{-1} respectively and residues of chlorpyrifos was found above MRL in only one sample. In green pea two pesticides α-endosulphan and cypermethrin were detected and residual levels were ranged from 0.035-0.187 mg kg^{-1} and 0.320-0.823 mg kg^{-1} respectively. Residues of cypermethrin ware found above MRL value in only one sample. In broccoli two pesticides δ-methrin and chlorpyrifos were detected, their residues ranged from 0.027-0.176 mg kg^{-1} and ND-0.253 mg kg^{-1} respectively and in only one sample residues of δ-methrin was found above MRL value. Fruit samples are also detected with pesticides. In apple β-HCH and malathion was detected, residual levels were ranged from 0.067-0.206 mg kg^{-1} and 0.218-0.631 mg kg^{-1} respectively and residual level of malathion was found above MRL value in only one sample. In grapes parathion methyl and chlorpyrifos were detected and residual levels were ranged from 0.162-0.341 mg kg^{-1} and 0.075-0.614 mg kg^{-1} respectively and residual level of both pesticides were above MRL in one sample. Banana samples were detected with bifenthrin and residual levels was ranged from 0.028-0.135 mg kg^{-1} and in only one sample residual level was found above MRL.

The presence of pesticide residues in vegetables and fruits is a global phenomenon. In present study authors have reported the residues of different class of pesticides in fruits and vegetables collected from supermarkets of Lucknow city. Out of total analyzed samples only 9 samples are detected with pesticide residues above CODEX/FSSAI MRL values. The present study shows a detection of different class (OCs, SPs and OPs) pesticides in both fruits and vegetables. Study observed that more OP (chlorpyrifos, parathion methyl and malathion) and SP (bifenthrine cypermethrin, δ-methrin) residues in fruits and vegetables of supermarket samples are frequently found. The consumption of raw vegetables and fruits containing these pesticide residues exceeding MRLs is a major concern for consumers, especially for children and adults. Vegetable and fruit samples are important part of our food diet so proper care should be taken to use safe level of pesticide for avoiding risk to human life. The result also depicts the need for regular monitoring of a large number of samples for pesticide residues from local as well as supermarkets. Suggestions extracted from the study that awareness at farmer's level to administer proper use of pesticides concentration on crop, safety education, and strict regulation on use of pesticides.

Conclusion:-

Present shows the potential of QuEChERS method in pesticide residue analysis in different vegetables and fruits with excellent method validation result. Out of total 270 analyzed sample 35 sample were detected with pesticides in which only 9 samples was detected with residual level above CODEX/FSSAI MRL values(25-26). Pesticide residues analysis in food commodities should be carried out on regular basis to avoid the harmful exposure of consumer population. Data generated in the study helps the regulatory agencies in pertaining the rules and regulation of food safety. Pesticides applications should be done as per the good agricultural practices to avoid the detection of pesticide above MRL values in final harvest food products.

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Conflict of Interest:-

All authors declare that they have no conflict of interest.

Table-1:-Result of method validation parameter; retention time (RT), R^2, limit of detection (LOD), limit of quantification (LOQ), accuracy and precision.

S.No	Pesticides	RT	R^2	LOD (µg kg^{-1})	LOQ (µg kg^{-1})	Mean % Recovery in different vegetables and fruits Spiking Level (µg kg^{-1})			Precision %RSD at Spiking Level 100 (µg kg^{-1})	
						20 (µg kg^{-1})	100 (µg kg^{-1})	200 (µg kg^{-1})	Inter day	Intra day
1	Dichlorovas	3.76	0.993	4.54	13.63	85	89	92	3	6
2	Phorate	9.18	0.998	3.09	9.27	83	91	86	4	7
3	α-HCH	9.40	0.987	2.63	7.90	90	93	103	6	10
4	β- HCH	9.90	0.990	2.60	7.79	91	86	105	4	5
5	γ- HCH	10.59	0.988	3.98	11.95	86	88	86	3	9
6	δ- HCH	10.81	0.991	3.22	9.65	86	79	92	5	10
7	Phosphamidon	13.20	0.996	2.72	8.16	79	80	82	8	11
8	Chlorpyrifos-methyl	13.42	0.995	3.04	9.13	80	84	95	7	7
9	Butachlor	13.92	0.992	3.10	9.30	84	93	102	6	11
10	Parathion-Methyl	14.31	0.993	3.42	10.26	93	90	89	6	7
11	Malathion	14.57	0.991	2.75	8.26	90	91	92	4	8
12	Chlorpyrifos	15.13	0.996	2.84	8.53	91	87	91	3	9
13	Aldrin	15.88	0.987	4.51	13.52	87	93	89	5	11
14	Endosulphan Sulphate	16.88	0.989	3.60	10.79	93	92	86	9	10
15	Pendimethylene	17.54	0.989	4.05	12.16	92	91	90	7	13
16	α-Endosulphan	19.79	0.992	5.15	15.44	91	94	92	3	14
17	Alachlor	19.96	0.995	2.31	6.92	80	92	91	5	8
18	p,p'-DDE	20.55	0.996	3.60	10.79	96	91	97	6	10
19	p,p'-DDD	21.02	0.986	5.04	15.12	92	97	93	4	11
20	β-Endosulphan	21.30	0.993	3.84	11.53	92	93	89	7	7
21	o,p'-DDE	22.38	0.995	4.96	14.87	84	89	85	2	8
22	Ethion	23.13	0.990	3.61	10.84	83	85	92	3	6
23	o,p'-DDT	23.43	0.987	3.19	9.56	80	82	104	1	5
24	p,p'-DDT	23.70	0.995	4.36	13.08	89	95	91	3	7
25	Fenpropathrin	24.69	0.989	2.80	8.39	96	102	94	6	10
26	Bifenthrin	24.89	0.993	5.25	15.74	102	96	92	3	7
27	λ-Cyhalothrin	27.54	0.992	3.86	11.57	92	96	91	4	8
28	Cyfluthrin	32.34	0.991	1.49	4.46	90	91	97	8	12
29	Cypermethrin	36.92	0.996	2.68	8.05	91	89	93	7	9
30	Fenvalerate	38.30	0.990	2.94	8.81	89	86	92	2	6
31	D-Methrin	43.25	0.987	3.90	11.70	86	83	91	6	11

Table- 2:-Results of pesticide residues analysis in different vegetables and fruits and comparison of detected residual level with respective maximum residue level (MRL)

Commodities	Pesticide Detected	Residue range (mg Kg^{-1})	Mean±SD (mg Kg^{-1})	Number of Sample analyzed	Number of Sample Detected with pesticide	Number of Sample above CODEX /FSSAI MRL Values	FSSAI MRL Value (mg Kg^{-1})	CODEX MRL Valu(mg Kg^{-1})
Cauliflower (Brassica oleracea)	Chlorpyrifos	0.023-0.120	0.012±0.031	15	3	1	0.05	0.05
	Bifenthrine	ND-0.11	0.007±0.028	15	1	0	4	NA
Cabbage (Brassica oleracea)	parathion methyl	0.040-0.090	0.009±0.025	15	2	1	0.2	0.05
	Chlorpyrifos	0.068-0.134	0.013±0.038	15	2	0	0.5	1

Brinjal (Solanum melongena)	γ-HCH	0.051-0.210	0.017±0.055	15	2	0	1	NA
	Chlorpyrifos	0.145-0.720	0.058±0.187	15	2	1	0.5	NA
	Endosulfan- α	ND-0.0321	0.021±0.083	15	1	0	2	NA
Green pea (Pisum ativum)	Endosulfan- α	0.035-0.187	0.020±0.049	15	3	0	2	NA
	Cypermethrin	0.320-0.823	0.076±0.222	15	2	1	NA	0.7
Broccoli (Brassica oleracea)	δ-Deltamethrin	0.027-0.176	0.014±0.045	15	2	1	NA	0.1
	Chlorpyrifos	ND-0.253	0.017±0.065	15	1	0	0.5	2
Apple (Malus pumila)	HCH- β	0.067-0.206	0.030±0.068	15	3	0	1	NA
	Malathion	0.218-0.631	0.057±0.169	15	2	1	4	0.5
Grapes (Vitis vinifera))	Parathion methyl	0.162-0.341	0.034±0.095	15	2	1	0.2	0.5
	Chloropyrifos	0.075-0.614	0.065±0161	15	4	1	0.5	0.5
Banana (Musa acuminata)	Bifenthrine	0.028-0.135	0.014±0.037	15	3	1	NA	0.1

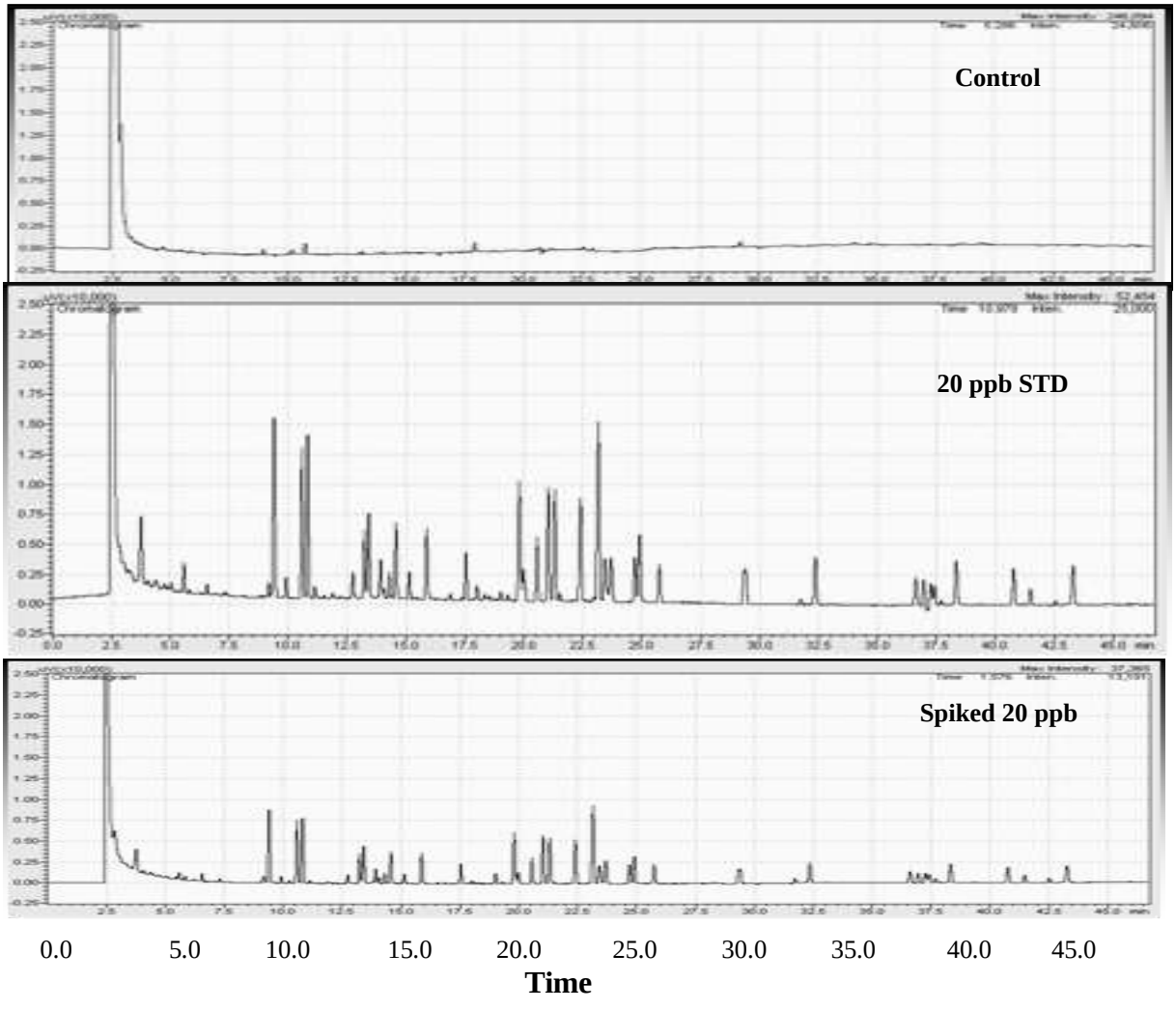

Fig 1:- Recovery of pesticides in cauliflower at 20 ppb concentration

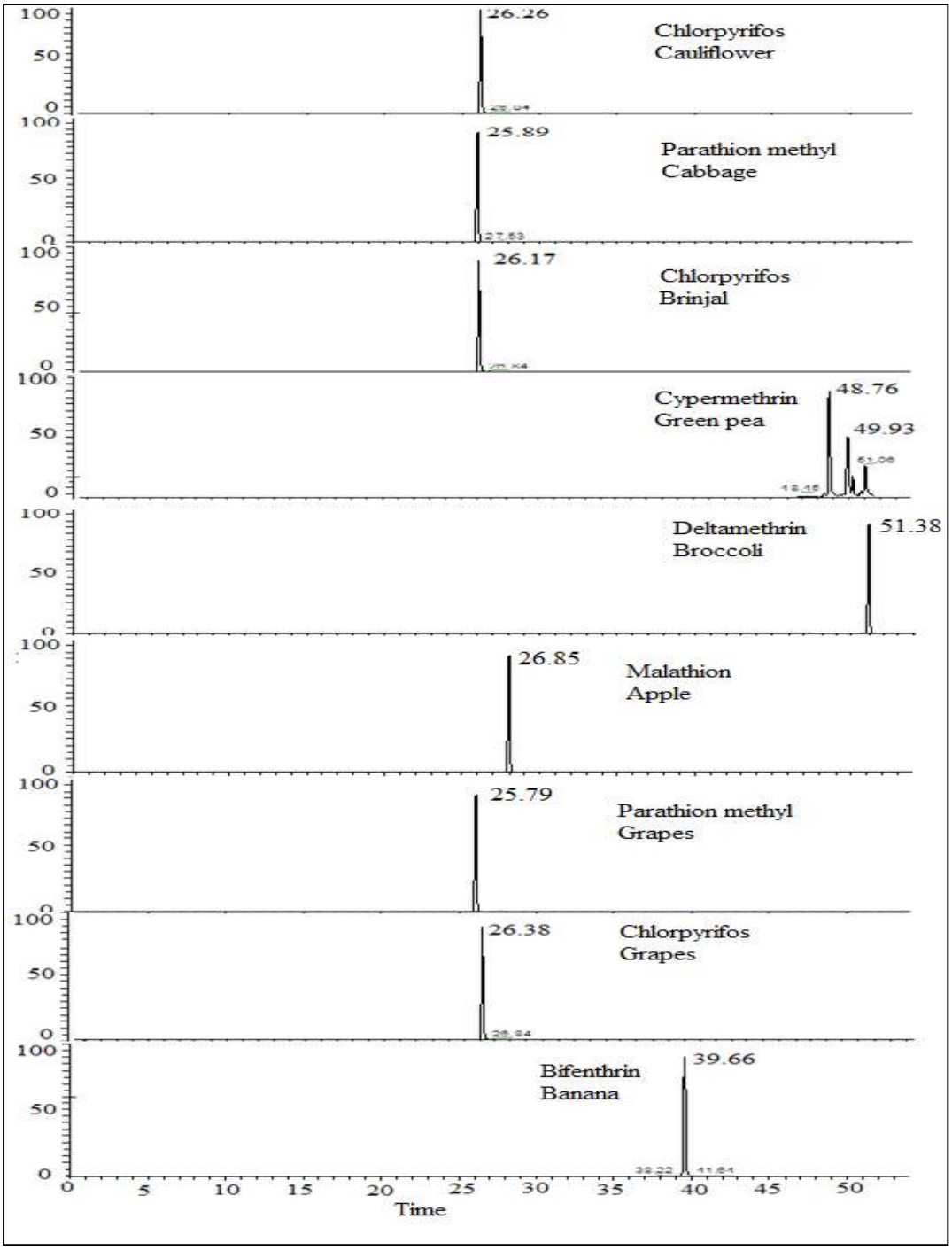

Fig-2:- GCMS confirmation of all samples above MRL value

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