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Detection of most commonly used pesticides in green leafy vegetables from sagar, india using direct injection hybrid micellar liquid chromatography

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ABSTRACT

Imidacloprid, chlorpyrifos, profenofos and cypermethrin are most commonly applied pesticides on green leafy vegetables. After a survey conducted to know the pesticide management practices in Sagar, India, a procedure based on hybrid micellar liquid chromatography coupled to a photodiode array detector has been developed and validated to monitor imidacloprid, chlorpyrifos, profenofos and cypermethrin content in green leafy vegetables. The method was validated following the guideline of SANTE/11,312/2021 in terms of: selectivity, linearity (r^2> 0.998), limit of quantification (0.09–0.25 mg/Kg, depending on the analyte under investigation), precision (<8.1%), and robustness (<5%). Chlorpyrifos was found to be the most commonly used pesticide among vegetable growers. It was found in seventy-six percent samples, profenofos in fifty-one percent, imidacloprid in eight percent and cypermethrin in four percent of the analyzed green leafy vegetable sample either individually or in combination. Sixteen percent of the collected samples were found to be negative for the selected pesticides. The developed procedure is rapid, easy to handle, green since it uses a low amount of toxic chemicals providing reliable results. The method was used to evaluate the eventual correlation between the analytical data and the information collected from the producers and users of these pesticides.

1. Introduction

Today green leafy vegetables are considered a good source of essential vitamins, minerals, and antioxidants, making them an integral component of a daily vegetarian diet [1,2]. Green leafy vegetables are more sensitive to changes in environmental conditions as well as are prone to frequent attacks by the pest. Greenhouses can be used to overcome the adverse effect on the environment, whereas pesticides are generally used to save vegetables from the attack of pests. The most common pesticides used on green leafy vegetables are monocrotophos (MONO), dichlorvos (DCV), chlorpyrifos (CPS), profenofos (PFF), cypermethrin (CP) etc.

Pesticides provide a vital benefit to agricultural production but at the same time, they may pose severe health issues for farmers and consumers of these agricultural products. In India, with changing agricultural practices, the consumption of pesticides has significantly increased. The excessive use of these pesticides is quite evident due to their presence in vegetables, animal feeds [3], food products [4], packed food [5] and even in human breast milk [6] and they can have serious health effects [7,8]. Pesticides show their toxic effects acutely and chronically. Common acute effects are vomiting, nausea, convulsions, rashes, blisters, blindness, dizziness, diarrhea, death, etc. In contrast, chronic effects include cancer, neuro-diseases (acetylcholinesterase inhibition, Parkinson's disorder), endocrinal disruption, diabetes, leukaemia, asthma and so on [9,10].

Traditional pesticides like CPS, PFF and CP, MONO, DCV have high efficiency in controlling insects for safety purposes and they fall in the 'Class I' type of pesticides. The EPA banned some of them like MONO or DCV in developing countries, including India. Nevertheless, in India, these pesticides are still being used on vegetables and fruits [10,11,12] because no legislation has been implemented to determine the maximum permissible concentration of pesticides in vegetables.

In recent years imidacloprid (ICP) an insecticide that belongs to the class of neonicotinoids (NN) is among the most commonly used in agriculture. The mode of action and chemical structure of ICP is similar to nicotine with a toxicity 700 folds lower than nicotine [13]. Therefore ICP can be considered a good alternative for those pesticides which cause toxicity.

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Several studies to detect ICP, CPS, PFF and CP in green leafy vegetables [14], fruit juices [15] and foods [16] were conducted using different chromatographic methods; high-performance liquid chromatography coupled to diode array detector (HPLC-DAD) [16], gas chromatography coupled to mss spectrometry (GC–MS) [17,18,19], liquid chromatography coupled to mass spectrometry (LC-MS/MS) [20,21]. Nevertheless, a hybrid micellar liquid chromatography (HMLC) can also be used. HMLC is a modified version of the high-performance liquid chromatographic (HPLC) technique, where the composition of the mobile phase is a modified aqueous micellar mobile phase with a major part of water, surfactant (above critical micellar concentration) and low concentration of short-chain alcohols (i.e., 1-propanol, 1-butanol, 1-pentanol) as an organic modifier. This change in the HMLC method facilitates the injection of extracts from the real samples after simple filtration onto the chromatographic column. This saves time and money consumed in the stepwise extraction process for sample pre-treatment and reduces environmental pollution caused by bulk organic solvents in conventional chromatographic methods [22,23]. For this reason, HMLC can be considered a green analytical method according to the indications given by National Environmental Method Index (NEMI), Green Analytical Procedure Index (GAPI) and Analytical Eco-Scale. Furthermore, this green technique has been successfully used to determine ICP in fruit juices.

In this study, a hybrid HMLC-PDA method was developed and validated for simultaneous separation and detection of ICP, CPS, PFF and CP in green leafy vegetables, which are the most common pesticides used in Sagar, underdeveloped, drought-prone area of Bundelkhand region of Madhya Pradesh in central India.

Therefore, the analytical method has made it possible to understand if there is a correlation between the obtained data and the information collected from those who produce and use the substance. This research article presents a method that belongs to the green analytical approach in chromatography. The methods used low toxicity solvents and waste in post-analysis is also reduced. These factors are very important for environmental conditions and the development of a low-cost and green method, which can be fundamental for those laboratories in underdeveloped and developing countries.

2. Materials and methods

2.1. Pesticide survey and data collection

2.1.1. The survey from vegetable growers

This study was carried out in Sagar (M.P.), India. Insecticide application-related information on leafy vegetables was collected from vegetable growers. Forty (40) vegetable growers were interviewed and considered representative of local vegetable growers who come in the periphery of 20 km from the Sagar city center. The distance was defined because leafy vegetables have a short lifetime and it was challenging to transport them from long distances. The survey of vegetable growers and pesticide dealers was conducted by direct interview method (questionnaire) in regional language. Information regarding types of leafy vegetables, the pesticide used, application rate per square meter (sqm), time of harvesting, frequency of harvesting etc. were collected.

2.1.2. The survey from pesticide dealers

The pesticide dealers of Sagar city were also interviewed. Ten local pesticide dealers who cover the major part of the city in pesticide distribution were interviewed. Information was collected about pesticides, which are currently in trend for application on green leafy vegetables, their daily selling prices, effectiveness on target insects, instructions and recommendations for their customers about pesticide management etc. The dealer survey was conducted to check whether vegetable growers followed the instructions given by the dealer or not.

2.2. Sample collection

Green leafy vegetable samples were collected during the winter season from four main vegetable markets of Sagar city i.e., Main mandi, Makronia bajariya, Bada bazar and Tilli road (**Fig. 1**). These four vegetable markets are the hub, where fresh vegetables arrive every day and from where retailers purchase the vegetables to be sold at the local level. Six types of leafy vegetable samples and two of each type were collected from the four main vegetable markets which are mentioned above. The vegetables included leaves of spinach (*Spinacia oleracea* L.), fenugreek *(Trigonella foenumgraecum* L.*)*, chickpea *(Cicer arietinum* L.*)*, onion *(Allium cepa* L.*)*, mustard *(Brassica juncea* L.*)* and coriander *(Coriandrum sativum* L.*)*. Therefore a total of 48 samples of the green leafy vegetables were collected. These vegetables were selected since they are the main leafy vegetables consumed in this region during the winter season.

The sample collection strategy included the collection of two samples for each of the selected leafy vegetables. Around one Kg sample from each category was purchased and collected in a sterile plastic self-locking bag, stored in an ice chest box and transported to the laboratory. The samples were then prepared for further analysis in the laboratory. The blank samples for all the examined green leafy vegetables were grown in the university horticulture garden without any pesticide treatment.

2.3. Chemicals and reagents

The standard ICP, CPS, PFF 99% pure and CP >98% pure were purchased from Sigma-Aldrich (Saint Louis, USA). The HPLC grade water was obtained from Indion Lab-Q Ultra water purification system, Ion Exchange (India) Ltd (Mumbai, India) for mobile phase and sample preparation. SDS (sodium dodecyl sulfate) to prepare micellar mobile phase and analytical grade sodium dihydrogen phosphate buffer (99%) to maintain the pH of micellar mobile phase were obtained from Himedia Laboratories Pvt. Ltd. (Mumbai, India). Solvents (1-propanol, 1-butanol, 1-pentanol, methanol) of HPLC grade were obtained from Rankem, RFCL Limited (New Delhi, India). 0.45 μm nylon membrane filters from Micron Separation Inc. (Westboro, MA, USA) were used for filtration of all the solutions.

2.4. Sample preparation

2.4.1. Standard samples

Standard stock solutions of 100 μg/mL were prepared in methanol and Ultrapure Type-I water in 2:1 ratio and stored in an amber glass volumetric flask and refrigerated at 4 °C. The stock solution was serially diluted for HMLC-PDA analysis. The standard ICP, CPS, PFF and CP solutions were prepared from the stock by successive dilutions in the mobile phase for the validation studies. The micellar mobile phase was prepared using 0.075 M SDS, buffered with 0.01 M sodium dihydrogen phosphate (NaH_2PO_4) at pH 7. At last four percent 1-propanol was added in the mobile phase as an organic modifier to enhance the chromatographic parameters.

2.4.2. Vegetable samples

Leafy vegetables were cut into small pieces and a five gram representative sample was crushed using mortar and pastel. Afterwards, the sample was transferred to a 25 mL centrifuge tube and 5 mL methanol and ultrapure Type-I water in 2:1 ratio were added to it. The tubes were centrifuged at 1500 rpm for 5 min., and the supernatant was filtered using a 0.45 μm nylon membrane filter for further chromatographic analysis. Blank samples were treated in the same way.

2.5. Chromatographic conditions instruments and software processing

The HMLC system used for the analysis was from Shimadzu Corporation (Shimadzu Prominence), Kyoto (Japan), having LC-20 AT iso-

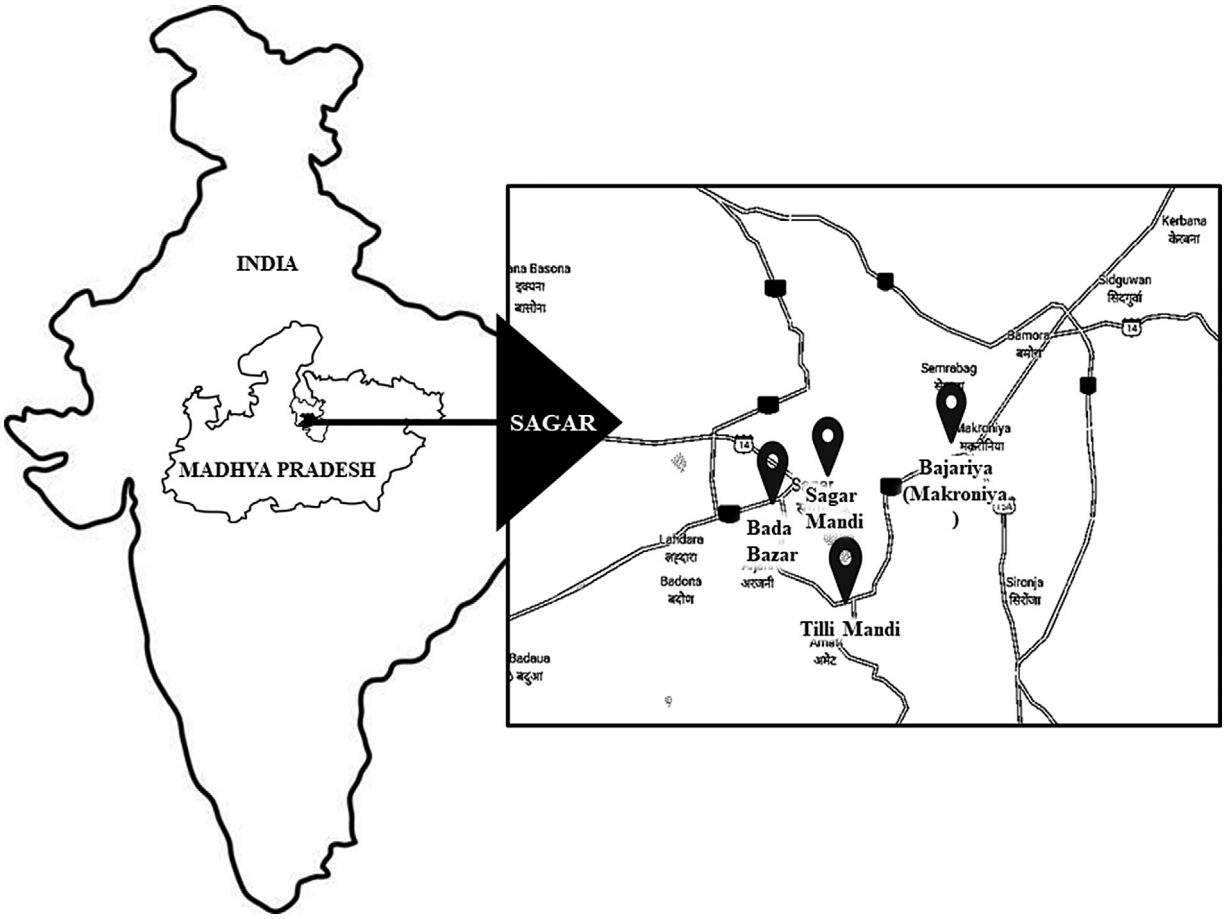

Fig. 1. Sample collection sites of Sagar city (India).

cratic pump, SIL-20AC auto-sampler, a photodiode array detector (SPD-M20A, 190–800 nm) and a Shimadzu C_{18} analytical column (250 mm length × 4.6 mm with 5 μm particle size), injection volume 20 μL. Isocratic elution using the aqueous micellar mobile at a flow of 1 mL/min., was used to separate the analytes. Data acquisition and elaboration were performed by the software Shimadzu LC Solution software version 1.22 SP1. The maximum absorbance for ICP was 270 nm, for CPS was 266 nm, PFF was 253 nm and CP was 244 nm.

Analytical balance Mettler-Toledo ME204 (Pocklington, United Kingdom) weighed the standards and incurred samples. Magnetic stirrer and the ultrasonic bath were purchased from PCI Analytics (Mumbai, India). Measurements of pH were performed using a Contech LAB pH meter, Model pH-103 (Mumbai, India).

All tables, charts, chromatograms and diagrams were made using the software MS Excel, MS Powerpoint, Origin Pro 2018 and Biorender.

3. Result and discussion

3.1. Pesticide dealer survey

The study started with a survey of local insecticide dealers, which clearly showed that conventional pesticides i.e., OPs (organophosphates) i.e. were available at lower prices (around ten times) in comparison to that of NN (ICP). In addition to the concentration of ICP (w/v), the percentage mentioned on the packing was lower than that of OPs and therefore, the required quantity of ICP was greater than OPs to kill the pest. For these reasons, ICP was not the preferred pesticide by vegetable growers. In the survey, it was found that the most commonly used pesticides by green leafy vegetable growers of sagar city were CP, CPS and PFF. Though vegetable growers of Sagar city rarely used ICP, but due to its advantages over traditional pesticides, it was also included in the study.

3.2. General pesticide management practice performed by vegetable growers

The leafy vegetables widely used in human alimentation may be attacked by various pests including flies, bugs, mites, worms and molluscs. Therefore to combat pests, pesticides liquids, granules or pellets are commonly applied on green leafy vegetables. Pesticides most commonly used by the vegetable growers are Calcron (PFF 50% EC), Dhanvan 20 (CPS 20% EC), Polytril P440 (PFF 40% + CP 4% EC), Nuvan (DCV 76% EC), Confidor 17.8 (ICP 17.80% SC). Apart from common pesticides, some of the other pesticides used by vegetable growers are indoxacarb, dimethoate, dichlorvos, and emamectin benzoate representing around 15% of the total pesticides used (**Fig. 2**).

The application time of pesticides is also different. It depends on environmental changes and the type of insects present. The most suitable application period is between 8–10 days instead of 15 days [24].

3.3. Chromatographic study for validation

3.3.1. Selection of chromatographic conditions

The micellar liquid chromatographic analysis started with the selection of suitable pH. ICP, CPS, PFF, and CP are ionizable compounds, the pKa of the protonated form are 1.6, 4.9, 1.3, 4.8 and the pKa of the neutral form is 11.1, 12.3, 12.6, 10.6 for ICP, CPS, PFF and CP, respectively [25]. Throughout the entire pH working range of C_{18} columns (2.5–7.5), the neutral form of selected compounds was predominant and no changes in the retention behavior in the selected pH range were then expected to occur. Experiments that were conducted using mobile phases

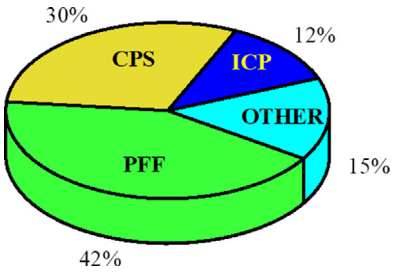

Fig. 2. The insecticide pattern for green leafy vegetables cultivated by local vegetable growers. The insecticides are labelled as follows: CPF= Chlorpyrifos, PFF= Profenofos, ICP= Imidacloprid.

containing 0.075 M SDS buffered at pH 3, 5, 7 showed minor variations in the retention time (Rt) of the analyte. Considering the fact that neutral pH 7 was good for column health, so pH 7 was finally selected as the optimum pH for further chromatographic analysis.

The octanol-water partition coefficient (log Po/w) of ICP; 0.57, CPS; 4.9, PFF; 4.6, and CP; 6.6 indicates that ICP is slightly hydrophilic while CPS, PFF and CP are hydrophobic in nature. The general concept in micellar liquid chromatography is that when surfactant (SDS) concentration increases, the Rt and efficiency (N) decrease [26]. A similar trend was observed in selected analytes using SDS in the range of 0.05–0.10 M. In the pure micellar mobile phase of 0.05 M SDS at pH 7 the Rt of the last eluted peak was 25 min., with a minimum efficiency (N) of 800 while using 0.1 M SDS at the same pH the values changed to Rt; 11 min., and N; 752 for selected compounds. The obtained chromatographic run time was adequate, but the efficiency was low. So it was decided to enhance the efficiency of the peak using a small amount of short-chain alcohol. Therefore, 1-propanol was selected as a modifier because it did not modify the elution strength of the mobile phase.

The hybrid mobile phases consisting of 0.05 M SDS- 4% 1-propanol, 0.075 M SDS-4% 1-butanol and 0.1 M SDS-4% 1-pentanol at pH 7 were tested. When 4% 1-propanol was added to 0.1 M SDS, the Rt decreased and the compound eluted near to dead time. Conversely higher concentration of 1-propanol was required to decrease the Rt in the case of 0.05 M SDS. Therefore 0.075 M SDS with 4% 1-propanol was found adequate. The experimental chromatographic parameters in the optimized mobile phase (Rt, N, B/A) were for ICP (4.0, 2078, 1.6), CPS (5.1, 2235, 1.7), PFF (6.3, 2165, 2) and CP (10.7, 2789, 2.5). The final mobile phase consisted of 0.075 M SDS-4% 1-propanol, 0.01 M NaH_2PO_4 buffered to pH 7, and carried out the chromatographic analysis of standard and real leafy vegetable samples.

The possibility to simultaneously analyze these four compounds using a mobile phase running under isocratic mode is very interesting. The optimized mobile phase uses low toxic organic solvent than typically employed in hydro-organic mobile phase.

3.3.2. Method validation

The method was validated following the guidelines of the SANTE/11,312/2021 including limits of detection and quantification, precision, and trueness [27], specifically devoted to the determination of pesticide residues in food and feed samples.

Specificity/selectivity was evaluated by analyzing blank samples of green leafy vegetables before and after spiking a mixture of 10 mg/Kg of ICP, CPS, PFF and CP. Peaks corresponding to the endogenous compounds of green leafy vegetables were eluted before 3.5 min., and no peak was detected at the window time of the analytes. In the fortified sample, no overlapping of the analytes with the front of the chromatogram or other matrix compounds was observed. The representative chromatograms corresponding to the analysis of blank (coriander leaves) and spiked samples of the same green leafy vegetable can be seen in **Fig. 3**.

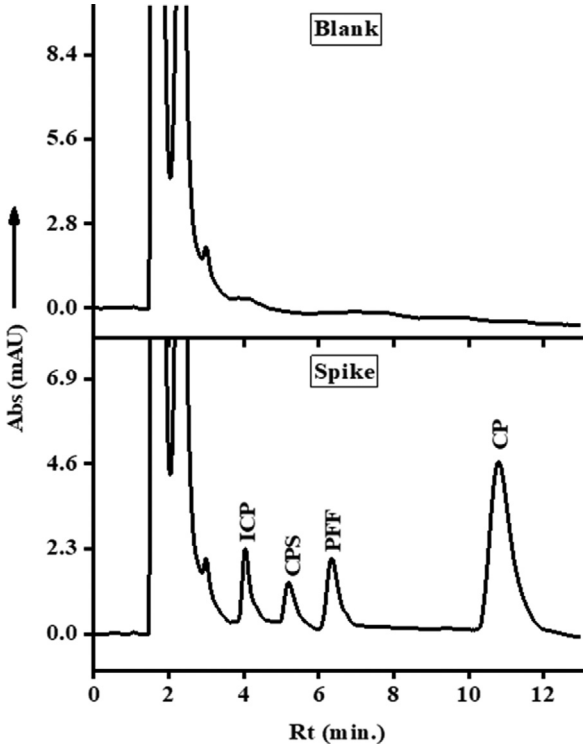

Fig. 3. Chromatograms obtained by the analysis of: (a) green leafy vegetables without any pesticide treatments (blank) (b) blank matrix spiked with 10 mg/Kg of ICP, CPS, PFF and CP in optimized mobile phase and detected at 244 nm.

In order to study the linearity of ICP, CPS, PFF and CP, nine dilutions ($n = 9$) were prepared from the stock solutions. Analysis was performed up to the range of 10 mg/L by $n = 5$ injections of each compound at different concentrations. The calibration curve was constructed using the average peak area vs concentration. The slope, y-intercept, coefficient of determination (r^2) and relative standard deviation (RSD%) were calculated by the least square linear regression method. The determination coefficient was in the range of 0.998–0.999 and the RSD% was 1.3 - 4.7% selected compounds, less than the maximal value indicated by the guideline. Limits of detection (LOD) and quantification (LOQ) for all the compounds were calculated following the 3.3 s criterion and 10 s criterion, respectively, taking the standard deviation of the y-intercept as that of the blank. The obtained results were based on the RSD of the response and slope of the calibration curve containing selected compounds in a concentration range close to LOQ. The compounds have LODs and LOQs in the range of 0.04 - 0.12 mg/Kg and 0.09 - 0.25 mg/Kg, respectively (Table 1). Therefore, the method detection limit was selected as the lowest detected concentration and the method quantification limit the lowest quantification concentration of the analytes.

The intra- and inter-day trueness and precision of the developed method were determined for green leafy vegetable matrix by spiking ICP, CPS, PFF and CP at lowest quantification level, middle quantification level and upper quantification level. The intra-day values were determined by analyzing six samples successively on the same day. Inter-day values were taken on five measurements of intra-day values taken over two months. Calculations of the closeness of agreement and dispersion were as previously detailed [26]. The obtained results are shown in **Table 2**. Results for relative recovery (93.6–107.5%) and dispersion (<8.1%) were inside the acceptance criteria from the guideline (70–120% and the value provided by the SANTE/11,312/2021 guideline [27]. The robustness of the method was examined by replicate injections ($n = 5$) of a standard solution at a concentration of 5 μg/mL under small changes in the SDS concentration (0.70–0.80 M), 1-propanol (4.8–5.2%) and pH (6.8–7.2) of the mobile phase. Insignificant differences in peak

Table 1
Rt, calibration data LODs and LOQs, RSD values obtained for ICP, CPS, PFF and CP using HMLC-PDA detector.

Analyte	Rt	Range (μg/mL)	r^2	Linear Regression	In green leafy vegetables (mg/Kg)		RSD% (n = 5)
					LODs	LOQs	
ICP	4.0	0.25–12	0.999	y = 0.778–0.086	0.12	0.25	2.3
CPS	5.1	0.18–10	0.998	y = 3.257+0.412	0.08	0.18	4.1
PFF	6.3	0.15–10	0.999	y = 2.325+0.254	0.07	0.15	3.2
CP	10.7	0.09–10	0.999	y = 5.118–0.082	0.04	0.09	4.7

Table 2
Intra- and inter-day trueness and precision for ICP, CPS, PFF and CP in green leafy vegetables.

Sample	Added concentration (mg/Kg)	Intraday[a]		Interday[b]	
		Trueness (%)	Precision (%)	Trueness (%)	Precision (%)
ICP	0.25	96.3	1.5	98.9	3.7
	2.5	98.2	2.2	96.8	1.3
	5	99	2.4	97.2	3.4
CPS	0.18	107.5	4.1	104.6	6.7
	2.5	105.2	2.2	100.5	3.3
	5	103.3	1.2	101.3	1.4
PFF	0.15	95.6	5.2	97.6	6.9
	2.5	97.5	3.6	96.2	5.0
	5	98.9	1.8	97.9	3.2
CP	0.09	93.6	7.3	94.3	8.1
	5	95.1	4.8	96.5	3.7
	10	96.8	2.9	97.6	3.4

[a] n=6.
[b] n=5.

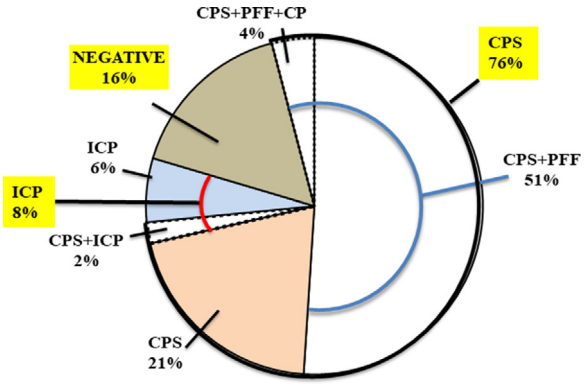

Fig. 4. Graph showing the percentage of green leafy vegetables positive and negative for all the analyzed pesticide samples.

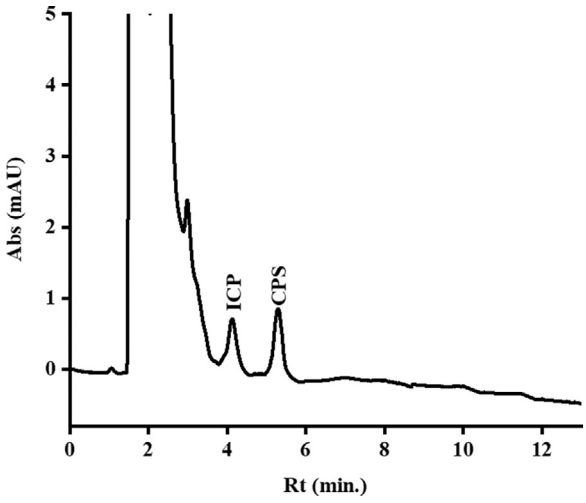

Fig. 5. Chromatograms obtained by analyzing coriander leaves show the presence of ICP (1.1 mg/Kg) and CPS (1.5 mg/Kg) in the optimized mobile phase and detected at 270 nm.

areas and lower variability in Rt were observed. The obtained results indicate that the selected factors remain unaffected by small variations in these parameters (RSD less than 5%).

3.4. Evaluation of pesticide residue in green leafy vegetable

All forty-eight green leafy vegetable samples collected from the selected sites were analyzed to detect the presence of ICP by the HMLC-PDA technique. The data obtained was used to crosscheck the vegetable growers statement and also to correlate it with the information collected from pesticide dealers.

In the chromatographic analysis CPS was found to be the most commonly used pesticide by vegetable growers of Sagar city and it was found in seventy-six percent of samples. Eight percent of samples were positive for ICP and sixteen percent of samples showed no pesticides (Fig. 4). For sixteen percent of sample where no pesticide was detected, the reason could be either no pesticides were used or the pesticides used were beyond the detection limit of the method. CPS was detected individually in twenty percent samples with PFF in fifty-one percent samples with CP+PFF and ICP in four percent and two percent samples respectively. In the case of ICP, it was individually detected in six percent of sample while with CPS in two percent of the analyzed samples (Fig. 4).

The concentration of ICP detected in onion leaves and mustard leaves was in the range of 0.20–2.34 mg/Kg. The residues of CP individually were not detected in any of the green leafy vegetable samples, however, it was detected along with CPS and PFF in a concentration of 0.16 - 2.4 mg/Kg. ICP with CPS was simultaneously detected in coriander leaves in the concentration of 1.1 and 1.5 mg/Kg (Fig. 5). PFF and CP were detected simultaneously in spinach samples with 3.9 and 2.4 mg/Kg concentrations, respectively, as reported in Fig. 6.

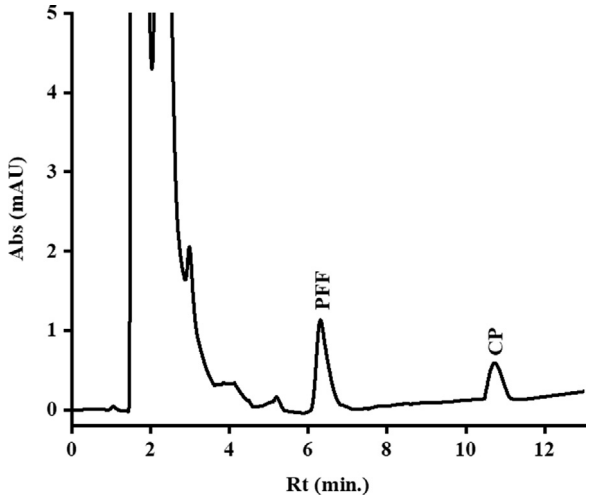

Fig. 6. Chromatograms obtained by analyzing spinach leaves show the presence of PFF (3.9 mg/Kg) and CP (2.4 mg/Kg) in the optimized mobile phase and detected at 256 nm.

The results indicated that while ICP was nontoxic and safer among well-known pesticides available in the market, it was still not very popular among vegetable cultivators. The analytical results confirmed the information obtained from insecticide suppliers and vegetable growers.

4. Conclusions

We here presented an HMLC-PDA method to determine ICP in leafy vegetables grown around Sagar city (India). This method belongs to the generation of green analytical approaches in chromatography. These green methods used low toxicity solvents and waste in post-analysis is reduced. These factors are very important for environmental conditions. Furthermore, the development of a low cost and green method can be fundamental for those laboratories present in underdeveloped and developing countries, still not equipped with the latest hyphenated mass spectrometric techniques and requiring analytical methodologies with low impact on the environment.

The developed method confirmed the use of the highly toxic CPS pesticide (seventy-six percent) compared to the ICP pesticide considered with very low toxicity (eight percent). According to the conducted survey, there is an urgent need to educate vegetable growers to follow safety measures by running awareness programs and campaigns organized by Universities in coordination with the respective governmental agency. The pesticide dealers should also be educated to suggest to vegetable growers on using less toxic pesticides than the routine ones.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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