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RESEARCH ARTICLE

Multiresidue analysis of organophosphorus pesticides in fruits and vegetables by GC-NPD

Purushottam Trivedi[1, 2], V P Sharma[1], L P Srivastava[1] and Sarika Malik [2] *

1. CSIR - Indian Institute of Toxicology Research Lucknow, U.P.

2. Department of Chemistry, School of Sciences, Noida International University Gautam Budh Nagar, U.P.

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***Corresponding Author**

Sarika Malik

Abstract

This study reports the levels of 16 organophosphorus pesticide residues (OPP's) in fruits (papaya, mausami, banana, pomegranate and grapes) and vegetables (tomato, okra, cauliflower, brinjal and cabbage) of Lucknow city, India. The estimation of OPP's was done adopting a multiresidue analytical technique QuEChERS (quick, easy, cheap, effective, rugged and safe) employing GC-NPD system with capillary column. This method effectively remove pigment in fruits and vegetables samples using activated charcoal with primary secondary amine (PSA) followed cleanup through dispersive solid phase extraction(d-SPE) to further reduce matrix interference and contamination. Recoveries of the fortified pesticides in all samples ranged 73.4 - 86.9 % with relative standard deviations (% RSD) below 15% for most target analytes. In vegetables and fruits samples Σ OPP's ranged between 0.010-0.381 mg kg-1. Dichlorvos, phorate, chlopyrifos, chlorofenvinfos, malathion, profenofos and chloropyrifos methyl were detected in the present study which were well below maximum residue limit (MRL) (PFA-1954). Dimethoate , diazinon, methyl parathion, phorate sulfone, phorate sulfoxide, fenitrothion, ethion, edifenophos and phosalone were not detected in all the collected samples.

Introduction

Fruits and vegetables are an excellent source of nutrients that promote good health. Pesticides are widely applied in a variety of different ways during the production of foods to control the growth of weeds and fungi or to prevent crop damage by insects, mites, rodents, and other pests. Pesticides are also frequently used on crops post harvest to prolong storage life and improve quality. With the increasing volume of worldwide trade in agricultural products in recent years, analysts are paying increasing attention to the study of techniques for analysis of pesticide residues in agricultural products (Guo-Fang Pang *et. al.*, 2006). Currently organophosphorus pesticides (OPP's) enjoy wide use in the world as an alternative to pest control with organochlorine pesticides, (Lyton *et. al.*, 1996, Subhani *et. al.*, 2001, Toan *et. al.*, 2007) which leads to increased world food production. Regulatory and public concern over pesticide residues in fruits, vegetables has been increasing due to potential health hazards. The most commonly used multiresidue method for analysis of pesticides in fruits, vegetables uses 800 ml organic solvent (including 300 ml methylene chloride) per 100 g sample. Measuring trace levels of pesticide residues in the presence of sample matrix components that occur naturally is a challenging task. Many methods have been reported for the extraction of pesticides from fruits vegetables (Luke *et. al.*, 1981, Fillion *et. al.*, 2000, Cook *et. al.*, 1999, Sheridan *et. al., 1999,* Sojo *et. al.*, 1997, Valverde-Garcia et al. 1991, Taylor *et. al.*, 2002, Jansson *et. al.*, 2004). Recently, the "quick, easy, cheap, effective, rugged, and safe" (QuEChERS) approach has become the method of choice for the rapid extraction and cleanup of various sample types to determine pesticide residues (Koesukwiwat *et. al.*, 2010, Lehotay *et. al.*, 2005 & 2007, Anastassiades *et. al.*,2003, Mastovska *et. al.*, 2010, Cunha *et. al.*,2007, Paya *et. al.*,2007). Perhaps the two most widely employed organic solvents used for sample extraction are acetone, which is used in the Luke method (Guan *et. al.*, 2010) and acetonitrile, which is used in the QuEChERS method (Lehotay *et. al.*, 2005). QuEChERS is a new analytical method used to rapidly extract sample solutions. This method uses an ethyl acetate (EtOAc) extract that can be used in conjugation with various GC systems with element-selective and element-specific detectors for the determination of essentially all organophosphate classes. We have found this method to be ideal for analysis of EtOAc extracts for OPP's. To evaluate the suitability of QuEChERS extraction using EtOAc, the present study was performed to modify the QuEChERS method. This study emphasizes the analysis of the OPP's by QuEChERS using gas chromatography- nitrogen phosphorous detector (GC-NPD). The objective is to replace the time consuming portion of the Luke method for analysis of OPP's and to improve the efficiency of non polar pesticides by using a new modified QuEChERS. This approach has been shown in numerous laboratories to provide high-quality results, save time, labor and lower solvent consumption. Even though QuEChERS has been employed in several kinds of vegetables, fruits, grains and other foods. The most time-consuming part of the QuEChERS method is the use of column chromatography to prepare samples for GC-NPD, and this procedure can be scaled down to minimize the time and volume of solvents for analysis. In this study, standardized a more efficient method, adapting a cleanup with primary secondary amine (PSA) and charcoal for the analysis of OPP's residues in fruit and vegetable samples. The proposed method shows good sensitivity, recovery and allows for rapid analysis. The method requires only a small volume of solvent per sample and needs no special equipment. It covers a wide range of pesticides; applicable to various food commodities is ideally suited for use in a regulatory laboratory. The major advantage of the QuEChERS method is that it provides quantitative recovery of pesticides after PSA cleanup and the final extracts have greatly reduced matrix interference. This study describes the extension of QuEChERS methodology for the determination of OPP's in fruits and vegetables.

2 Materials and methods

2.1 Chemical

OPP's standards (Dichlorvos, Phorate, Dimethoate, Diazinon, Methyl Parathion, Chloropyrifos Methyl, Phorate Sulfone, Phorate Sulfoxide, Fenitrothion, Malathion, Chloropyrifos, Chlorofenvinfos, Profenophos, Ethion, Edifenfos and Phosalone) were procured from Supelco, Sigma-Aldrich USA, Fluka, Sigma-Aldrich Schweis and Rankem Pvt. Ltd. New Delhi, India. All solvents like n-hexane, acetone and ethyl acetate (HPLC grade) were purchased from Sigma-Aldrich Co. USA, Spectrochem Pvt. Ltd. India. They were glass distilled before use. Sodium chloride (NaCl) and anhydrous magnesium sulphate ($MgSO_4$) were procured from Himedia Pvt. Ltd. India. Primary secondary amine (PSA) bondasil 40 µm part 12213024 of Varian was used for sample preparation.

2.2 Sampling

Fruits (papaya, mausami, banana, pomegranate and apple) and vegetables (tomato, okra, cauliflower, brinjal and cabbage) obtained from supermarkets and farmers' market basket samples of Lucknow city, Uttar Pradesh, India for recovery analysis of various OPP's residues to detect pesticide residues that might be present. Fresh fruits and vegetables were collected and transported to the laboratory in clean polyethylene bags within 1 day. Each sample was identified clearly and indelibly by allocating a unique identification number. All analysis were undertaken within the shortest time possible (within 2 days) to minimize potential analyte losses. In this study QuEChERS method was applied.

2.3 Extraction and cleanup

The 100 g sample was washed, chopped and grind in warring blander and 10 g macerated sample of each food commodities was weighed into 50 mL polypropylene centrifuge tubes, the OPP's standard mixture were spiked into the samples, which were allowed to stand for 3-4 hr at room temperature and add 10mL EtOAc. Add 4 g of anhy. $MgSO_4$ and 1 g activated NaCl for removal of sediment and water which was performed simultaneously by mechanical rotospin and centrifugation. 1mL aliquots of the EtOAc extracts (upper layer) were transferred to 2mL micro centrifuge tubes containing 150 mg anhy. $MgSO_{4,}$ 100 mg. PSA and 10 mg. activated charcoal for cleanup and again micro centrifuge for 10 min at 8,000 rpm. The supernatant was collected into auto sampler vials and add 5.0 µL acidified EtOAc (with 5% formic acid). 1.0 µL clean extract was used for the OPP's analysis on gas chromatography

2.4 Gas Chromatography-Nitrogen Phosphorous Detector

An Shimadzu GC-2010/NPD (Shimadzu Technologies) equipped with fused silica capillary column, DB-1 (30 m × 0.25mm id) coated with 1% phenyl-methylpolysiloxane (0.25 µm film thickness) was employed for the separation and determination of OPP's using NPD. General operating conditions were as follows; Injector temperature: 250^0C; detector temperature 280^0C; ultra pure nitrogen was used as carrier gas at a constant flow rate of 1.46 mL/min, Hydrogen (H_2) 30 mL/min and zero air 60 mL/min, column temperature program: initially 95^0C for 4 min, increase at 2.5^{0}C/min to 170^{0}C hold for 7 min, then increase 225^{0}C/min hold for 10 min; injection volume: 1 µL split ratio 1:5.

2.5 Gas Chromatography - Mass Spectrometry

Positive pesticide residues were confirmed by GC-MS. A Perkin Elmer GC-MS consisting of Auto system XL Gas Chromatograph with a Turbo Mass Spectrometer was used for analysis. The column used is Elite-5MS fused-silica capillary column (30 m X 0.32 mm I.D., 0.25 mm film thickness). Carrier gas: helium (purity 99.999%) with a flow rate of 1.6 mL/min. One µL aliquot of the final extract was injected using the split-less mode. The oven temperature program is 100^{o}C for 1 min and then at 20^{o}C min^{-1} to 210^{o}C and hold for 1 min; then at 45^{o}C min^{-1} to 300^{o}C and hold for 1 min. The total runtime of the GC is 19.5 min. The injector temperature was set at 300^{o}C. The transfer line and source temperature was set at 280^{o}C and 230^{o}C respectively. Solvent delay for MS is 5 min.

3 Results and discussion

The recovery, limit of detection (LOD) and Retention time (RT) of OPP's in vegetables and fruits are shown in **Table 1**. Recoveries of 16 OPP's ranged 73.4 to 86.9% from the fortification level of 0.5 mg kg-1. The spiked samples as well as the unspiked control were analyzed in five replicates. Repeatability of the method was evaluated through the relative standard deviations (%RSD) associated to measurements of the pesticides taken during recovery. The LOD were calculated from the standard deviation of these determinations. LOD for 16 OPP's ranged from 0.001 to 0.010 mg kg-1. The level of pesticide residues in various vegetables were compared with their MRL fixed by Prevention of Food Adulteration Act. (PFA), Govt. of India 1954. The pesticides residue recorded below the detection limit were considered as non detectable (ND). Fruit and Vegetable samples analyzed in triplicate for the presence of pesticides residues are given in **Table 2**. Dichlorvos (0.016-0.120 mg kg-1), chlorpyriphos methyl (ND-0.128 mg kg-1) chlorofenvinfos (0.016-0.073 mg kg-1) and malathion (0.072-0.272 mg kg-1) in cabbage, dichlorvos (0.024-0.381 mg kg-1), phorate (ND-0.050 mg kg-1), malathion (0.016-0.322 mg kg-1) and chlorofenvinfos (ND-0.170 mg kg-1) in cauliflower were detected but none of these pesticides was > MRL. However in tomato three pesticide chlorpyriphos methyl (0.134-0.173 mg kg-1), chlorpyriphos (0.010-0.027 mg kg-1) and chlorofenvinfos (0.057-0.109 mg kg-1) were detected. In okra three samples contained profenophos (0.020-0.037 mg kg-1). It is interesting to note that vegetables samples have not shown the above MRL. In apple chlorpyriphos methyl (0.051-0.113 mg kg-1), chlorpyriphos (0.022-0.087 mg kg-1) chlorofenvinfos (0.071-0.111 mg kg-1) and profenophos (0.011-0.054 mg kg-1) were detected but none of these pesticides were >MRL. In pomegranate chlorpyriphos methyl (ND-0.219 mg kg-1) and chlorofenvinfos (ND-0.119 mg kg-1) was detected. In papaya, chlorpyriphos methyl (0.074-0.306 mg kg-1) and chlorofenvinfos (0.056-0.196 mg kg-1) were detected but none of these pesticide were > MRL. However in mausami chlorofenvinfos (ND-0.059 mg kg-1), were detected one sample.

The used chromatographic condition resulted to maximise the resolution among the peaks and minimize the total run time (about 37 min.) **Figure 1 (A & B).** Several gradient profiles are studied obtaining good response with the gradient describe in material and method section of instrument analysis. Other parameters such as column temp., flow rate and injection volume were studied in order to get a fast and reliable separation, obtaining the best results when 95°C was used as initial column temp., 1.46 mL/min as flow rate and 1µL injection volume for GC-NPD system. The sensitivity was better as split ratio 1:5 under these conditions retention time of OPP's were constant ranging from retention time from 3.99 (Dichlorvos) to 34.71 (Phosalone) (**Tabel-1**) Confirmation of detected pesticide residues were done by GC-MS.

Table 1 t_R, (min) retention time, Recovery (%), Limit of detection (LOD) of the organophosphate pesticides in fruit and vegetable samples

Pesticides	t_R, min	Masses, m/z	Elemental Compositions	Spiking Level (mg kg-1)	Recovery (%)	LOD (mg kg-1)
Dichlorvos	3.99	109*+127+185	$\underline{C_4H_7Cl_2O_4P}$	0.5	73.8	0.003
Phorate	11.82	75*+121+260	$C_7H_{17}O_2PS_3$	0.5	76.5	0.009
Dimethoate	12.05	87*+92+125	$C_5H_{12}NO_3PS_2$	0.5	81.4	0.003
Diazinon	14.95	137+179*+304	$C_{12}H_{21}N_2O_3PS$	0.5	78.8	0.002
Methyl Parathion	16.77	109+125+263*	C8 H10 NO5 P S	0.5	86.2	0.001
Chloropyrifos methyl	16.99	286+288*+125	$C_7H_7Cl_3NO_3PS$	0.5	84.4	0.003
Phorate Sulfone	18.20	109+183+277*	$C_7H_{17}O_4PS_3$	0.5	75.9	0.010
Phorate Sulfoxide	18.34	29+109+183*	$C_7H_{17}O_3PS_3$	0.5	80.0	0.003
Fenitrothion	18.66	277+260+125	$C_9H_{12}NO_5PS$	0.5	73.4	0.010
Malathion	18.92	125+127+173*	$C_{10}H_{19}O_6PS_2$	0.5	79.1	0.002
Chloropyrifos	19.49	314*+286+197	$C_9H_{11}Cl_3NO_3PS$	0.5	81.1	0.001
Chlorofenvinfos	21.27	323*+269+267	$C_{12}H_{14}Cl_3O_4P$	0.5	84.5	0.003
Profenofos	23.39	97+337+374*	$C_{11}H_{15}BrClO_3PS$	0.5	83.5	0.004
Ethion	25.96	97+153+231*	$C_9H_{22}O_4P_2S_4$	0.5	81.6	0.005
Edifenfos	26.95	310*+173+110	$C_{14}H_{15}O_2PS_2$	0.5	78.3	0.002
Phosalone	34.71	182*+184+367	$C_{12}H_{15}ClNO_4PS_2$	0.5	86.9	0.002

Table 2 Level of Organophosphate pesticide residues in fruit and vegetable samples

Pesticide	Commodity	Number of Sample		Mean (residues range) (mg kg-1)
		Analysed	Detected	
Dichlorvos	Cabbage	15	5	0.015 (0.016-0.120)
	Cauliflower	15	7	0.051 (0.024-0.381)
Phorate	Cauliflower	15	1	0.003 (ND*-0.050)
Chlorpyriphos methyl	Cabbage	15	1	0.008 (ND-0.128)
	Tomato	15	2	0.020 (0.134-0.173)
	Apple	15	2	0.010 (0.051-0.113)
	Pomegranate	15	1	0.014 (ND-0.219)
	Papaya	15	2	0.025 (0.074-0.306)
Malathion	Cabbage	15	5	0.051 (0.072-0.272)
	Cauliflower	15	3	0.044 (0.016-0.322)
Chlorpyriphos	Tomato	15	3	0.004 (0.010-0.027)
	Apple	15	3	0.010 (0.022-0.087)
Chlorofenvinfos	Cabbage	15	5	0.020(0.016-0.073)
	Cauliflower	15	1	0.011 (ND-0.170)
	Tomato	15	2	0.011 (0.057-0.109)
	Apple	15	2	0.012 (0.071-0.111)
	Pomegranate	15	1	0.007 (ND-0.119)
	Papaya	15	2	0.016 (0.056-0.196)
	Mausami	15	1	0.003 (ND-0.059)
Profenophos	Okra	15	3	0.006 (0.020-0.037)
	Apple	15	5	0.011 (0.011-0.054)

**ND-Not Detected*

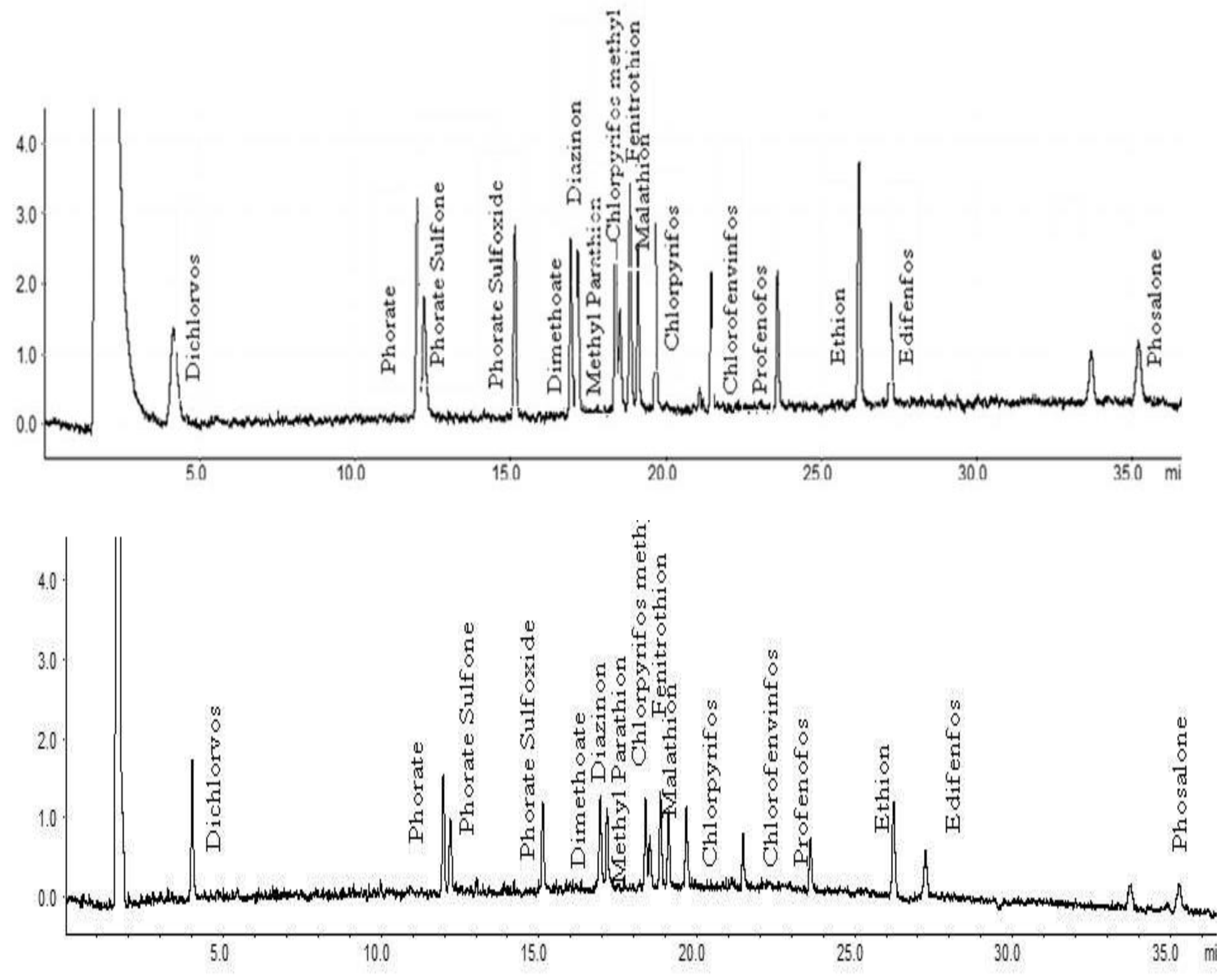

Fig 1. (A) GC-NPD chromatograms of 16 Organophosphate pesticides (B) Organophosphate pesticides spiked: Separation was performed using a DB-1 column. Peak identification

Sample extraction is important part of a multi-pesticide residues analysis method due to the different properties of the substances that have to be extracted simultaneously. Furthermore, traditional extraction of pesticide residues from food sample involves a first step of removing the moisture with anhy. $MgSO_4$, or in combination with strong extracting organic solvent EtOAc, followed by sample clean up with PSA. QuEChERS implies a dispersive-PSA as sorbent clean up material, but in this study 10 mg activated charcoal was added to gather with PSA for removing colors from the extract. This helps for the better response of consistent chromatographic peaks. On the other hand 5% formic acid was added in the extract for the stability of base liable pesticides. PSA was added to eliminate soluble pigments. It is obvious to observe that eigtht sample is extracted in less than 30 min. through this procedure. Hence it may use as fast and reliable screening method for pesticide residues analysis in food. Variation of pH and different fruits and vegetable samples affects recoveries of pH susceptible pesticides and their stability in the extract (Lehotay *et. al.*, 2005 & 2007 Aysal *et. al.*, 2007). EtOAc has been used for the extraction solvent to increase the recoveries of polar compound together with $MgSO_4$ (Mol *et. al.*, 2003). However, charcoal has property to absorb OPP's in fruits and vegetables resulting decrease recovery. Therefore, it is necessary to determine a proper charcoal dosage range in which colour/pigments could be substantially eliminated and an acceptable recovery owing to less pesticide adsorption would be ensured. Recovery in EtOAc as solvent where tested following addition of 10 mg charcoal in 1 mL extract samples has come suitable % recoveries in fruits and vegetables indicating charcoal as a higher absorptive ability to pigments.

4 Conclusion

It is clear that pesticides should be applied correctly according to their recommended dosage and usage frequency. However, in order to benefit from vegetable planting, OPP's were always applied in excessive dosage and frequency during the growing seasons of vegetables, fruits and resulted in food contamination. The results in this study provided important information on the current contamination status of vegetables and fruits in Lucknow city, India, and pointed to the need of taking further measures to control the misuse of some OPP's, such as chlorfenvinfos, chloropyrifos, dichlorvos, chloropyrifos- methyl, malathion and profenofos. This analytical methodology enables the determination of selected pesticide residues at trace levels with good analytical performance. This method was successfully applied to the analysis of fruit and vegetable samples, thus showing that it is suitable for the determination of the selected pesticides in real samples. The established method was successfully used to detect OPP's residues in fresh vegetables and fruits in which activated charcoal and dispersive-solid phase extraction were used to reduce contamination and interference from pigments and matrix.

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