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Scientific Methods for Evaluation of Organophosphorus and Carbamate Pesticide Residues in Fruits and Vegetables: A Review

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Abstract: At present time uses of pesticides and insecticides are increased day by day and leads to contamination in food web and food chain. Excessive use of pesticides causes severe health problems in animals including microorganisms to human being. As a result of the use of too many pesticides, all the basic necessities of life such as air, water and food had become contaminated. Among various insecticides, organophosphorus and carbamate insecticides are derivatives of phosphoric acid and amino carboxylic acid, respectively. These are most commonly used in various fruits and vegetables. The ceaseless utilization of pesticides has made the malicious impacts on environment. Accordingly, various methods have been created by various administrative organizations and research centers and are applied regularly for the measurement and checking of pesticides residues in fruits and vegetables. The current study relates to different extraction and quantification methods used around the world to evaluate organophosphorus and carbamate residues in different fruit and vegetables.

Keywords: Pesticides, Agriculture, Contamination, Fruit, Vegetables, Organophosphorus, Carbamate

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Introduction

Pesticides that gather in the biological system enter the food chain and influence non-target organism or species. They reach to the ocean or lake through ground water or surface water and influence life structures likes phytoplankton, zooplankton, shrimps, clams and fishes (Mahmood *et al.,* 2016; Weber, 2018). It is assessed that there are around 1000000 ongoing disease and passings because of pesticides harming over all every year (Vander Werf, 1996). Food is the principal route of exposure through which pesticide pollution can be caused. Exposure to pesticides through utilization of food is correlated as multiple times higher in size when contrasted with different exposure such as air and water (Claeys *et al.,* 2011). Pesticides are of greater concern due to their persistent,

bioaccumulation, lipophilicity and adverse effects on human health. These pesticides can enter the human body by consuming contaminated fruits and vegetables. Major health effects associated with pesticides include cancer, birth defects, neurological disorders, endocrine disruption and reproductive effects. The effects that can occur are either acute or chronic. Acute exposure can result in rashes, diarrhea and dizziness. Serious health includes cancer, reproductive effects, thyroid and endocrine disruption (Gan *et al.,* 2005). Pesticide residues are a main issue for consumers and make most problems worldwide. Hence, there is an extraordinary interest in the decrease of residues on agricultural products and diminishing human exposure of these synthetics (Ghani *et al.,* 2010; Gongaleg-Rodriguez *et al.,* 2011).

Washing is the first cycle used to reduce pesticides residues over the outer layer of product (Hassan *et al.,* 2019). Viability of washing process relies upon compound attributes, mode of activity, pesticide harvest, water solvency and times. Contact pesticides do not enter into the wares (Gongalez-Rodriguez *et al.,* 2011; Heshmati *et al.,* 2020; Polat *et al.,* 2021). The presence of pesticides residues in food items has forever involved serious concern. The issue is particularly serious when these items are taken fresh (Solecki *et al.,* 2005).

The utilization of pesticides in agribusiness has expanded after world war-II to expand the world food creation. There had been marked advancement of various types of pesticides having a place with different groups. The utilization of pesticides and extra-natural contamination, because of modern emanation during the creation of pesticides, have brought about event of residues of these chemicals and their metabolites in each part of climate for example air, water and soil alongside in the vegetables and organic products (Bai *et al.,* 2006).

(A) *Methods for analysis of organophosphorus pesticide residues*:

Gas chromatography, liquid chromatography and chemiluminescence have been the most broadly involved methods for analysis of organophosphorus pesticides (OPP).

Gas chromatography (*GC*):

Patel *et al.* (2004) used a technique for resistive heating gas chromatography (RH-GC) with FPD for the screening of OPPs (Dichlorvos, methamidophors, acephate, fonofos, dimethoate, chlorpyrifos methyl, chlorpyrifos, diazinon, pyragophos and etrimfos) in products of the soil (peach, grapes, lettuce and sweet pepper). Naturally created fruits and vegetables were separated in ethyl acetic acid and derivation arrangement and dissected on RH-GC-FPD. 30 g of homogenized sample was mixed with 60 ml ethyl acetic acid derivation, 30-40 g anhydrous sodium sulfate and 5-6 g sodium hydrogen carbonate. The sample was set in a water shower at 30 ℃ for no less than 20 min and afterward was homogenized for 30 second. The separated natural layer was evaporated to dryness under a stream of oxygen free nitrogen.

The resulted concentrate was reconstituted with ethyl acetic acid derivation and afterward infused into RH-GC-FPD for investigation. It took just 4.3 min for the partition of 20 pesticides. Normal recuperations acquired were 70% and 116% for pesticides spiked at 0.01 mg/kg and 0.1 mg/kg, respectively with associated relative standard derivation (RSD) values to be less than 20%. Pesticides residues of OPPs, OCPs, carbamates and pyrethroids categories (acephate captan, chloropyrifos, diazinon, dieldrin, endosulfan, HCH, ethion, iprodione and quintogene) in fruits and vegetables (beet, carrot, cucumber, tomato, summer squash, papaya, strawberry and perrimmon) were observed in Sao-Paulo city of Brazil by (Gebara *et al.,* 2005).

Lopez-perg *et al.* (2006) reported on the dynamics of business definitions of two insecticides, nematicides, a herbicides and mix of two fungicides. The centralizations of the dynamic fixings were checked all through the developing times of the potatoes and in the 0-1 cm and 1-15 cm soil layers. The strategy utilized for pesticide

assurance was gas chromatography with mass specific discovery. The main pesticide recognized in potato tubers was metalaxyl and the fixation of it was not exactly around 50% of the most extreme remaining residual point.

Gas Chromatography- Mass spectrometry (*GC-MS*):

Hajslova *et al.* (1998) assessed 37 normal pesticides (OPPs, OCPs, pyrethroid and carbamates) like parathion, ethion, diazinon, dichlorvos, parathion methyl, metha-midophos, metalaxyl, femitrothion, endosulfan sulfate, I, II endosulfan, chlofenvinphos, chlorpyrifos, iprodione, lindane and permethrin in wheat, orange, cabbage and different fruits and vegetables obtained from near retail market of Czech Republic by utilizing GC-MS-ECD. 50 g of each test was mixed for 5 min with 250 ml ethyl acetic acid derivation and 100 g anhydrous sodium sulphate. The suspension was separated through a layer of sodium sulphate and concentrate was concentrated by utilizing rotating evaporator to 50 ml. The sample volume was changed in accordance with 100 ml by adding cyclohexance. For extract remove up, 2 ml aliquot of unrefined was stacked on elite execution gel penetration chromatography (HPGPC) section. The stream pace of versatile stage (Cyclohexance/ethyl acetic acid derivation 1.1 v/v) was 1 ml/min with dump time of 16 min and assortment time of 14 min. The elute was further dissipated under tuning evaporation and delicate stream of nitrogen. The residue was then reconstituted in 1 ml of toluence and infused into GC-MS-ECD/NPD for examination of different pesticides residues. The recuperation rates for pyrethroid, cypermethrin, fevalerate and others were viewed as 62%, 91%, 95% and 92-103%, respectively. Salvador *et al.* (2006) checked 24 OPPs (Chlorpyriphos, disulfoton, parathion methyl, malathion) in 20 samples of various vegetables (Green beans, cucumber, pepper, tomato and eggplant) from Spain. 15 g of finely cleaved and homogenized sample was blended in with 50 ml dichloromethane for 2 min at 19000 rpm and 50 g anhydrous sodium sulfate was added to blend and was saved for 2 min and separated through 9 cm Buchner channel. Dissolvable was dissipated to dryness on rotating evaporation. The last solution was diluted with cyclohexane and infused into GC-PF-PD indicator. Rates were somewhere in the range of 73% and every available ounce of effort and accuracy was better compared to 15%. Its LOD was under 0.01 mg/kg much lower than the MRL values specified by EU.

Low pressure gas chromatography-mass spectroscopy (*LP-GC-MS*):

Moreno *et al.* (2006) recorded a multi residue technique for assessment of various sample treatments to decide 65 pesticide residues (OPPs, OCPs and Pyrethroids) in greasy vegetable grids like Avocado by LP-GC-MS. They analyzed customary natural dissolved extraction helped by a high velocity homogenizer to composed fluid extraction (PLE). For extraction helped by rapid homonizer, the new vegetable sample was cleaved and homogenized with 50 ml of acetic acid deviation cyclo-hexane combination (1:1 v/v) and 10 g anhydrous Na_2SO_4 were added and completely blended utilizing high speed homogener for 2 min. The Concentrate was separated through a permeable plate channel. For PLE extraction process 5 g of new sample was blended and homogenized. The sample was moved to the cell and the extraction interaction was performed consequently with similar solvents utilized for extraction helped by fast homogenizer. Prior to infusing the last answer for GC-MS/MS, these samples were cleaned up by gel penetration chromatography (GPC). This strategy has shown the relevance of LP-GC-MS/MS for fatty vegetables networks. This study showed that the recuperation ounce of effort with RSD Values lower than 19% at 12-50g/kg spiking levels. The LOQ (0.04-8.33 g/kg) were within a reach underneath the MRL values set by EU.

Liquid chromatography (*LC*):

Rial-otero *et al.* (2003) used a new multipesticide residues assurance technique for fourteen

fungicides. The proposed strategy depends on LLE and SPE followed by liquid chromatography and diode exhibit identification (HPLC-DAD). Dichloromethane acetone (75:25, v/v) was viewed as the most fitting dissolvable blend for extricating fungicides in white graphs. Also silica cartridges were viewed as generally suitable for separate purging purpose. Quality parameters for sample recuperation rates (Ca. 85% for practically all target mixtures) and accuracy (somewhere in the range of 15% and 16%) were reported lower than maxima residual limit set by the 76/895/ECC and 90/642/ECC mandate. Five different white graph tests utilized for vinification, created in Rias Baixas region in Galicia (NW Spain) were dissected and it was traced down that the fixations for those recognized fungicides in grape tests were lower than those carried out by European regulations.

Liquid chromatography- Mass spectrometry (*LP-MS*):

The resultant residue was disintegrated in methanol and infused into LC-MS/MS. The technique was substantial for 57 unique pesticides (Imagalil imidacloprid, linuron, methiocarb, methonyl, oxamyl, oxamyl-oxime disulfoton, disulfoton sulphate, phosphate etc.) and their metabolites. The recuperation rates were 70-100 per cent. The proposed technique was fast for examination of pesticides in single assurance step at any additional clean up step (Jansson *et al.,* 2004).

Gas Liquid chromatography (*GLC*):

Kumari *et al.* (2004) utilized Hewlett Packard 5890A gas liquid chromatograph (GLC) combined with capillary sections utilizing ECD and NPD for examination of different pesticides. 26 samples contained pesticides residues more than MRL values. Among all pesticides, mono-crotophos residue was higher than MRL in 3 samples of brinjal, 1 samples of okra, cauliflower and smooth gourd. Chlorpyrifos was present in 3 samples of cauliflower and 8 samples of cabbage. The LOD of the technique was viewed as 10-50 ng for OCPs, 5-20pg for manufactured pyrethroid, 50-10 pg for OPPs and 25-50 ng for carbamates. In spiked sample, the recuperations for various classes of pesticides were 83-125% for OPPs, 80-111% for OCPs, 73-95% for SP and 82-104% for carbamates.

Chemiluminescence method (*CL*):

Many researchers decided the pesticides residues by utilizing GC, thin layer chromatography (TCZ) and HPLC etc. Since the pesticides particularly OPPs are known to be cholinesterase inhibitors, hardly any researchers used the inhibitory impact of these mixtures on acetycholinsterase or different catalysts to develop numerous biosensors for the assurance of their pesticides (Vakurov *et al*., 2004). The Chemiluminescence technique has turned into an alluring scientific device in pesticide residue assurance as of late as the GC and LC are relatively costly (Xiao-Zhou *et al.,* 2006).

(B) *Ordinary and advance methods for detection of carbamate pesticides*:

In pesticides analysis advanced technologies are introduced as an option to the regular chromatographic techniques joined with specific sensors. The chromatographic methodology yielded delicate, explicit and dependable scientific discoveries not withstanding they are time consuming complicated and expensive with a high natural dissolvable utilization, which is unsatisfactory for analyzing large samples (Van Dyk *et al.,* 2011).

Capillary electrophoresis (*CE*):

Atting *et al.* (2021) used a micro extraction method for particular pre concentration of N-Methyl carbamate in water before CE examination utilizing temperatures controlled IL-DLPME in an alkaline buffer. Micro extraction with ionic fluid and elution with a trace amount of dichloromethane was utilized to get the samples. MMWCNTs upgraded ionic fluid-analytic restricting and recuperation analyzed to utilizing basic nanomaterial's as sorbent. Cheng *et al.* (2007) described a CE with amperometeric discovery in view a polyamide-changed carbon

paste electrode to decide carbamate in alkaline water solutions.

Enzyme linked immunosorbent assay (*ELISA*):

Immunochemical methods for example, enzyme-linked immunosorbent assay (ELISA), have as of late earned revenue and respect as quick and minimal expense extraction and recognition methodology for pesticide compounds. In light of the antigen-antibody interaction, this scientific methods can give high awareness and particularly (selectivity) for specific sorts of pesticides. Furthermore, since it can stack quite a large number samples simultaneously, it empowers quick and exact evaluation of pesticide residues in agricultural things before transportation. For sure, the essential benefit of ELISA for distinguishing pesticides residue in the accommodation of sample preparation techniques (Watanabe, 2011).

Molecular imprinted polymer (*MIP*) *biosensor*:

As of late Li *et al.* (2018) distributed a work that exhibited the development of a MIPs, biosensor to identify pesticides using a carbon paste electrode modified with surface MIP microspheres and assessed utilizing cyclic voltammetry.The methodology utilized on vegetable samples showed high responsiveness with significant recoveries ranging from 97.2 to 101%. Li *et al.* (2017) utilized differential pulse voltammetry to fabricate a MIP-based sensor to examine paraoxon and displayed magnificent dependability later.

Optical biosensor:

Xavier *et al.* (2000) used an optical fiber biosensor for evaluating propoxur and carbaryl in vegetable harvests inhibitory effect on the AChE enzyme. The straight unique scopes of carbaryl and propoxur are 0.8-3.0 mgL^{-1} separately. Nonetheless, propoxur has lower discovery limit (0.4 ng) than carbaryl in the biosensor (25 ng). Ultrasonic extraction was used to recognizing propoxur in spiked onion and lettuce with recuperation rates going from 93 to 95% for onion samples at the different fixation levels studied.

Electrochemical biosensor:

Electrochemical are building up forwarded momentum as an original identification on guideline expanding responsiveness, particularly and repeatability (Vale and Lotti, 2015). Biosensors in principle are comprised of a few cathode fram works, containing helper, reference and working cathodes that make electrical signs when an objective biomolecule communicates with an acknowledgment component (Krieger, 2001; Koshlukova, 2014).

Conclusion

For many years, pesticides have been used extensively in agriculture to protect against insects, pests, weeds and moulds. Due to which crop productivity increases. Therefore pesticide residues should be monitored in fruits, vegetables, pulses and cereals as well as in components of the environments. The present review attempts to describe the use of various quantification techniques for the extraction of pesticides residues in fruits and vegetables.

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