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Extraction and Analysis of Organophosphorus Pesticides in Fruits and Vegetables: Review

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Abstract

Pesticides are used as an important factor to kill pests for agricultural purpose. These pesticides have contaminated all the things that are required for our daily life. There are different classes of pesticides; mostly used pesticide group for agricultural purpose is organophosphorus pesticides (OPPs). Most of the farmers use it regularly on vegetables and fruits. On the regular use of pesticides it causes harmful effects to the body. There are numerous methods have been developed for the extraction and quantification of multipesticide residues in vegetables and fruits. This review paper pertains to various extraction and quantification procedures used to analyse organophosphorus residues and among them the best extraction and analysis method is also given.

Keywords: Pesticides; Extraction; Quantification; Vegetables

Abbreviations: OPPs: Organophosphorus Pesticides; FAO: Food and Agriculture Organization; OCPs: Organochlorine Pesticides; EI: Electronic Impact; ESI: Electrospray Ionization.

Introduction

Fruits and vegetable are daily used by the human in their diet. Although fruits and vegetables are healthy but they are attacked by pest and disease so to overcome this issues framers use a large quantity of pesticides which enter through our body orally. Even though large percentages of pesticide are removed out through urine and fecal matter from the body, some pesticides are persistent, that they remain in body for a long time [1]. The food and agriculture organization (FAO) defines the pesticides as: "substances designed for interdicting, spoiling, enticing, repulsing or controlling any pest, including undesirable species of plants or animals, during the generation, storage, transport, distribution and processing of food, agricultural productions or animal feeds, for use as a plant growth corrector, defoliant, drying agent, fruit thinning agent or growing suppressor and substances applied to crops either before or after transport [2].

(i) Pesticides are classified in the following parts on the basis of its uses:
- Insecticide- for insects
- Herbicides- for plants
- Rodenticides- for rodent (rats and mice)
- Bactericides- for fungi
- Larvicides- for larvae

(ii) Pesticides are classified into the two parts on the basis of its biodegradability:

- Biodegradable: This can be broken down by microbes and other living beings into harmless compounds.
- Persistent: which take months or years to break down. They can be classified by considering their chemical forms or are derived from a common source or production method [3,4].

(iii) Pesticides are classified into the various parts on the basis of its chemical structure:

- Organophosphate: Organophosphate pesticides (OPPs) a remainly synthetic amides, ester or thiol derivatives of phosphonic or phosphinic acids, phosphoric acids. Most organophosphates are insecticides; they affect the nervous system by disrupting the enzyme that regulates a neurotransmitter [5].
- Carbamate: Same like organophosphorus pesticides, the carbamate pesticides affect the nervous system by disrupting an enzyme that regulates the neurotransmitters. Carbamates are esters derived from carbamic acid, which comprise one of the major classes of pesticides [6].
- Organochlorine pesticides (OCPs): It is a group of chlorinated organic substances representing one of the first synthetic insecticides used by humans [7].
- Pyrethroid: It is a naturally occurring pesticide, which is found in chrysanthemums (Flower). They have formed in such a way that they can increase their stability in environment, also a synthetic version of pyrethrin [8].

Toxicity of Each Pesticide

Toxicity means the capacity to cause injury or illness. There are two kinds of toxicity. First, Acute toxicity: Acute toxicity of a pesticide means the ability of the chemical to cause injury to a person within a short period of time. Second, Chronic toxicity: The chronic toxicity of a pesticide is determined by introducing it to the test animals and when a small doses repeated over a period of time it cause harmful effect are termed chronic effects [9].

Types of pesticides	Toxicity	Ref.
Organochlorine: Dieldrin – Endosulfan, DDT and lindane -	LD50: 1 to 50 mg/kg LD50: 51 to 500 mg/kg	[1]
Organophosphorous: Chlorpyriphos Phenthoate, Diazinon, Chlorfenvinphos, Dichlorvos, Dimethoate, Monocrotophos, Disulfoton, Demeton, TEPP Ediphenphos, Quinalphos, Ethion, Fenitrothion, Thiometon., Fenthion, Phorate,Phosphamidon,fonophos, Fensulfothion Formothion, Methyl Parathion, Mevinphos and Oxydemeton-Methyl Abate, Acephate, Ronnel, Coumaphos, Crufomate, Primiphos Famphur, Glyphosate, Malathion, Phenthoate, Triazophos, Methyl, Temephos, and Trichlorphon.	Extremely toxic (LD50: 1-50 mg/kg) to highly toxic (LD50: 51 to 500 mg/kg) Moderately toxic (LD50:501 to 5000 mg/kg) to Slightly toxic (LD50:>5000mg/kg)	[9]
Carbamates: Aminocarb, Dimetan Bendiocarb, Carbaryl, Carbofuran, Benfuracarb, Dioxacarb, Dimetilan, Formetanate, Methiocarb, Methomyl, Oxamyl, Propoxur. MPMC, MTMC, Aldicarb, Bufencarb, Isoprocarb, Pirimicarb.	Extremely toxic (LD50: 1 to 50 mg/kg) to highly toxic (LD50: 51 to 500 mg/kg) Moderately toxic (LD50: 501 to 5000 mg/kg) to slightly toxic (LD50: >5000 mg/kg)	[10]
Pyrethroids: Pyrethrum -	LD50 of over 1 gm/kg 10 to 100 grams.	[11]

Table 1: Depicts the pesticides and its toxicity.

Uses of Pesticides

The main use of pesticide is to increase profits of farmers by preventing the crops from disease and increase the food production. We are able to kill pest by pesticides. By producing more crops, produce more to sell, save money on labour costs, it also reduce the time for removing weeds manually. In addition to these, it has improved human's health. It was estimated that from 1947, by killing pests that carry or transmit diseases the pesticides have decreased the death rate due to diseases such as Malaria, bubonic plague, and typhus. It has been observed that a diet containing fresh fruit and vegetables and make sure that these are having only low pesticide residues. By eating fruits and vegetables, it helps us to reduce the risk of many cancers, high blood pressure, heart disease, and other chronic disease [12].

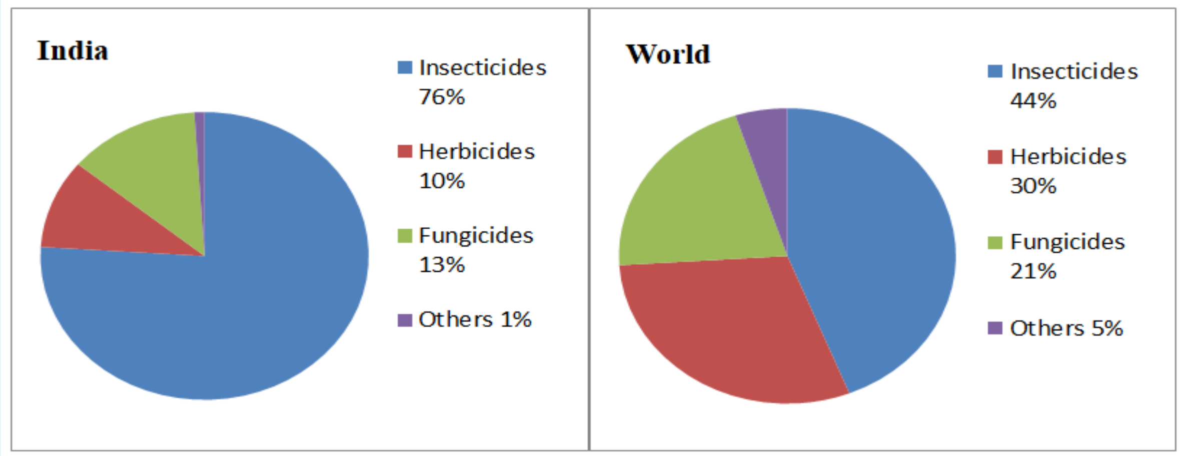

Figure 1: Depicts the use of pesticides.

Pesticides of Forensic Interest

Pesticide	Purpose	Ref.
Organochlorine: DDT, Benzene Hexachloride (BHC), Aldrin, Adieldrin, Endosulfan (thiodan), Endrin, Chlordane, Chlordecone (kepone), Heptachlor, Toxaphene etc.	It is used as insecticide and used for public and veterinary healthy signifance.	[13]
Organophosphorus: Chlorpyriphos, Diazinon, Dichlorvos, TEPP, Disulfoton, Ediphenphos, Ethion, Fenitrothion, Fenthion Dimethoate, Fonophos, Formothion, Methyl Parathion, Monocrotophos, Phenthoate, Quinalphos, and Thiometon etc.	It is most widely used insecticides. They are used in agriculture, the household, gardens, and veterinary areas.	[14]
Carbamates: Aminocarb, Carbaryl, Bendiocarb, Benfuracarb, Carbofuran, Dimetan, Dimetilan, Methiocarb, Methomyl, Dioxacarb, Formetanate, Oxamyl, Propoxur etc.	It is also mostly used in households, gardening and agriculture.	[2]
Pyrethroids: Allethrin, Permethrin, Cyfluthrin. Resmethrin etc.	They are sold in form of liquids, sprays, dusts, powders, mats, and coils. It used as household insect repellents and insecticides. It is used to prevent pest insects in granaries and in agriculture as pesticides.	[7]

Table 2: Depicts the list of pesticides of forensic interest.

Sl. No	Name of pesticide	Source	Extraction method	Instrumentation	Ref.
1	Diazinon, Parathion-Methy, Fenitrothion, Malathion, Chlorpyrifos, Phenthoate, Methidathion Profenofos, Ethion.	Apple, Peach, Orange, Pineapple and Grape.	solid-phase micro extraction (SPME) and supercritical fluid extraction (SFE), Matrix solid-phase dispersion (MSPD).	GC-NPD Analysis GC-MS Confirmation.	[15]

2	Simazine, Aldicarb, Alachlor, Malathion, Chlorpyrifos, Chlorfenvinphos, Phaslone, Diazinon, Acephate, Fenitrothion, Monocrotophos, Imidacloprid, triazophos, ethion, atrazine, propanil, quinalphos, and metribuzin.	Eggplant, Ladyfinger, Cabbage, Tomato,Chilli And Cauliflower	QuEChERS method.	An ultra-fast liquid chromatograph equipped with a triple–quadrupole ion trap hybrid mass detector operating in the MRM positive electrospray ion (ESI) mode was used for this study.	[16]
3	Phosalone and Chlorpyrifos	Red Grapes and Cherry	solvent-based ultrasound assisted liquid-liquid micro extraction.	analysis using HPLC-UV	[17]
4	Demeton-S-Methyl, Phorate, Diazinon, Tolclofos-Methyl, Malathion, Fenthion, Quinalphos, and Fenamiphos	Cabbage, Cauliflower Red Cabbage, Cucumber	dynamic microwave-assisted extraction (DMAE) combined with continuous flow microextraction (CFME)	GC–MS system	[18]
5	Dichlorvos, Phorate, Diazinon, Methyl Parathion, Fenitrothion, Malathion, Parathion, Ethion.	Apples, Tomatoes, Apple Juice	Solid-phase micro-extraction	GC-FPD	[19]
6	Methyl Parathion, Chlorpyriphos And Malathion	Spinach, Cucumber, Brinjal, Bottle Gourd, Ridge Gourd, Cauliflower And Cabbage.	Extraction n-hexane and dichloromethane	GC-ECD	[20]
7	Diazinon, parathion, methyl-parathion, malathion fenithrothion	Apple, pear peach and grapes	Headspace solid phase microextraction (HS-SPME)	Gas chromatography–nitrogen phosphorous detection (GC-NPD)	[21]
8	Acephate, Methamidophos, Monocrotophos, Omethoate, Oxydemeton-Methyl Vamidothion	Cabbage And Grapes.	ethyl acetate was the most favourable solvent for extraction,	liquid chromatography (LC)–mass spectrometry (MS)/MS	[22]
9	Ethoprophos, Sulfotep, Diazinon, Tolclofosmethyl, Fenitrothion, Chlorpyrifos Isofenphos, Methidathion, Ethion, Triazophos, Leptophos	Cabbage, Kale And Mustard	solid-phase microextraction (SPME)	Gas chromatography–flame photometric detection (GC–FPD)	[23]
10	Acepahte, Malathion, Quinalphos, Profenofos, Chlorpyrifos Triphenyl-Phosphate	Six Fruits And Twelve Vegetables	QuEChERS (quick, easy, cheap, effective, rugged and safe) extraction method	liquid chromatography coupled with tandem mass spectrometry	[24]

11	Dimethoate, Diazinon, Chloropyrifosmethyl, Parathion-Methyl, Malathion, Chloropyrifos Chlorfenvinphos	Strawberry	Magnetic dispersive micro solid-phase extraction	GC-FPD and GC-MS	[25]
12	Methidathion Malathion Azinphos-Methy Pirimiphos-Methyl Pyraclofos Phosalone	Tomato, Apple, Carrot, And Cabbage	dispersive solid-phase extraction (dispersive-SPE) with primary secondary amine (PSA) as the sorbent	A liquid chromatography–mass spectrometry (LC–MS)	[12]
13	Parathion, Diazinon, Chlorpyrifos, Ethion, Carbophenthion	Hot Pepper Lettuce Tomato	Modified QuEChERS-acetonitrile final step involved a dispersive solid phase extraction.	GC-ECD	[26]
14	Cypermethrin, Chlorpyrifos, Methyl Parathion, Ethion, Captan, Malathion, And Triazophos. Cypermethrin, Chlorpyrifos, Methyl Parathion, Ethion, Captan, Malathion, And Triazophos.	Apple, Grapes, Cauliflower, Cabbage, Peas, Potato	modified QuEChERS method	gas chromatograph quadrupole mass spectrometer (GC-MS/MS)	[27]
15	Ethoprophos, Parathion Methyl, Fenitrothion, Malathion, Chlorpyrifos, Profenofos.	Cucumber And Watermelon	dispersive liquid–liquid microextraction (DLLME)	gas chromatography–flame photometric detection (GC-FPD)	[28]

Table 3: Depicts the analytical techniques.

Conclusion

For the past 40 years, there is various sample preparation methodologies have been developed to extract these components from fruits and vegetables, although they generally consume a lot of time and laborious. In 2003, Anastassiades, Lehotay, Štajnbaher and Schenck introduced a methodology for pesticide extraction that is applicable to fruits and vegetables. This method, which has been described as quick, easy, cheap, effective, rugged and safe (QuEChERS) and is very easy to handle and less cost, it includes only few steps and it improves the qualitative without any loss to the analyte [29,30]. They help to concentrate and isolate the analyte of interest about appropriate levels and all the possible interferences are removed from the sample matrix, also helps to achieve a selective and sensitive chromatographic method of analysis [31]. For a qualitative/quantitative approach to analyse different pesticide groups different detectors can be coupled to chromatographic systems [32]. Some common detectors, such as electron capture detectors (ECD) and array diode (DAD), they are still used for the identification of pesticide due to their high sensitivity to certain group of compounds. However, for multiresidue analyses of foods the MS system has traditionally been applied more widely in due to it good resolution, sensitivity and the possibility of confirmation of the investigated component. Chromatographic techniques such as gas chromatography – GC and liquid chromatography – LC coupled with modern systems, such as triple quadrupole mass spectrometry, have shown that tandem mass spectrometry (MS/MS) is one of the most efficient techniques for the analysis multiresidue pesticide of different polarities in a different variety of foods materials [33]. A good analytical performance is presented by this technique (e.g., high selectivity, good resolution and efficiency) in control and determination of organic compounds in complex matrices, such as fruits. For the determination of several pesticides the main detection system MS/MS is currently used for organophosphate in fruit extracts. Gas chromatography tandem mass spectrometry (GC–MS/MS) with electronic impact (EI) ionization and Liquid chromatography tandem mass spectrometry (LC–MS/MS) with electrospray ionization (ESI) are considered the major modern techniques employed in multiresidue analysis [32].

Future Prospective in Forensic Science

Due to the increase in the importance of food safety, there has been a tremendous improvement in the pesticide residue analysis in fruits and vegetables. Various detection techniques and pre-treatment are being developed which has reduced the interference, time and sample size during analysis. Though, the choice of detection system and extraction remains the same which consists of the traditional detection system and extraction coupled with mass for quantification. However, these methods are expensive and time-consuming. Recently, the use of improved methods such as molecular imprinted polymer, biosensor and nanotechnology based method are used as better alternative for the detection of pesticides. However, in future, all these limitation will be resolved, to develop a eco-friendly and cost-effective method which can be used to detect a number of pesticide residues in a single run at lower limits below the maximum residual levels [34-36].

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