



## Analysis of Fruits and Vegetables for Pesticide Residues Using Gas Chromatography-A Review

### KEYWORDS

Pesticide, Gas chromatography, Fruits and vegetables

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**ABSTRACT** *The application of pesticide is severe in both developed and developing countries to their efforts to eradicate insect-borne, endemic diseases and to protect forests, plantation and fiber crops. The application of pesticides in agriculture has greatly improved the food production worldwide. Samples of fruits and vegetables subjected to residue analysis across the world exhibited the presence of pesticides in varying proportion. Average recoveries and RSD% of different insecticides for different fruit and vegetable and observed percent recoveries for OC, SP,OP and Carbamate respectively varied from 80-111%, 83-123%, 73-90% and 82-104% at different spiking levels. The major pesticides detected include acephate, chlorpyrifos, cyfluthrin- $\beta$ , Cyfluthrin- $\lambda$ , cypermethrin, deltamethrin, dichlorvos, fenvalerate, monocrotophos and carbufuran.*

### Introduction

Increased population exerted tremendous pressure on the need and demand of agricultural productivity. Farmers using pesticide to increase the quantum yield of crops and thwart away the diseases and pests. Pesticides are more selectively used during growth phase of the plants and post harvest treatment of agricultural commodities (Levitt and Wehr, 2001). Pesticide application has considerable impact on the food production worldwide and recent years showed the development of the export market is hindered by concerns about pesticide residues and inadequate monitoring. Control programmes in various countries is constrained due to weak legislations and inept handling of the officials. Pest infestation in fruits and vegetables is a common phenomenon and pesticide application is the need of the hour to achieve the desired yield in the crops. Pesticides like organochlorines, organophosphates, synthetic pyrethroids and carbamates are commonly used by the agriculturists across the globe.

### Pesticide detection in fruits and vegetables: Global scenario

An attempt has been made to review the work undertaken by various researchers elsewhere in the world using gas chromatography for the detection of pesticides. Pesticides are one among the chemicals that were added to an agro-ecosystem and referred as agro-chemicals. With the advent of high yielding varieties of plants, damage by pest and predators also has taken driver's seat causing considerable economic loss to the farmers.

Dogheim et al., (2001) monitored and analysed the vegetable and fruit samples and 76.1% of the total samples showed minimum detectable pesticide residue compared to 2.59% contained residues exceeding the MRL and 23.9% of samples with detectable residues. Fernandez et al., (2001) recorded pesticides viz., Chlorpyrifos, chlorpyrifos methyl imazalil,  $\beta$ -endosulfan, dicofol and endosulfan sulphate with relative deviation from 7 to 17% and mean recoveries ranged from 82% for endosulfan to 96% for imazalil. Martinez et al., (2002) evaluated 30 multiclass residues in fresh vegetables with relative standard deviation < 16.9% for all compounds and recovery efficiencies ranged from 70-119% at two fortification level. Residues of OPPs and OCPs noticed in vegetables and fruits with

range of values from mg/kg to  $\mu$ g/mg level (Sandra et al., 2003). Mol et al., (2003) observed that cabbage and grape samples showed average recoveries of 80 to 101% for OPPs pesticide residues like acephate, methamediphos, monocrotophos, Omethoate, Oxydemeton methyl and vamidathion. Cucumber samples contained OPPs residue and percentage recovery rates for all pesticides ranged from 61.9% to 88% (Munoz et al., 2003). Arrebola et al., (2003a) tested tomato, cucumber and pepper with recovery rates ranged from 70.3% and 126.9% for 72 OPPs and OCPs pesticide. Similar observations made by Stajubar and Zupancia-Kralj (2003) in fruits and vegetables and determined 24 pesticide residues (OCPs, OPPs, Carbamates and pyrethroids) with recovery rates of 70-110% for most of the pesticides. Further, pesticides in fruits and vegetables and residue concentration ranged from 0.01 to 0.50mg/kg and relative standard deviation 10% for the majority of pesticides analysed.

The vegetables and fruit ranged from 70-100% with pesticide residues of Benzamidazoles, carbamates and OPP<sub>s</sub> (Johnsson et al., 2004). 67.4% of the total samples contained the residues below the detectable limit and concluded that fruit samples (34.6%) having more detectable pesticide residues compared to vegetable samples (29.0%) (Gebara et al., 2005). Ju-Mei Chang et al., (2005) showed only four samples out of 1999 contained pesticide residue which exceeded the MRL (0.02%) and Liu et al., (2005) determined carbamate and OPP<sub>s</sub> in 25 samples of root vegetables, leafy vegetables, bean vegetables, bulb vegetables and fruits collected from supermarkets of China and reported 30% of samples contained multiresidues of one or the other pesticides. Azinophos methyl and malathion widely reported in all types of vegetables and fruits. Amoah et al., (2006) showed the lettuce vegetable samples from the markets of Accra, Kumasi and Tamale and found to contain 78% chlorpyrifos, 31% lindane, 36% endosulfan, 11% lamda-cyhalothrin and 33% DDT. Market food samples (cereals, vegetables and fruits) from Shanxi area, China and 18 out of 200 samples analyzed contaminated with different OPP<sub>s</sub> like dichlorvos, dimethoate, parathion and primphos-methyl with concentration ranging from 0.004mg/kg to 0.257mg.kg with recoveries ranging from 88-107% (at 0.1% mg/kg) and 89-108% (at 0.5% mg/kg) (Bai et al., 2006). Twenty samples of different veg-

etables (green bean, cucumber, pepper, tomato and egg plant) collected from Spain and exhibited values ranging from 73 and 110%. Cabbage, Cole and spinach from china showed recovery rate of 90% to 109% and the RSD value of 1.5, 2.5 and 3.7% obtained respectively (Xiao-Zhou et al., 2006). Recovery rates in the range 70-110% with RSD values lower than 19% at 12-50g/kg spiking level obtained in fatty vegetable matrices like Avacado (Moreno et al., 2006). In the 101 pesticides analyzed in different fruit and vegetable samples like green pepper, tomato, cucumber and orange and noticed that 82% of the samples contaminated with at least two pesticides and only 15% of the residues had content higher than MRL (Helen Botisi et al., 2007). Jose et al., (2007a) determined 39 pesticides in pepper and tomato of Spain and recovery studies performed at 0.05, 0.1 and 0.02 mg/kg fortification levels ranged from 70.1 to 128.5% with RSD lower than 7%.

Huskova et al., (2008) detected 61 multiple, multiclass pesticide residues in apples grown with and without the treatment of dichlorvos, methamidophos, diphenyl, acephate, chlorpropham, captan, pyridaben belonging to pesticide classes OPP<sub>s</sub>, OCP<sub>s</sub>, Pyrethroids and carbamates in the concentration range of 1.00µg/kg to 21.47µg/kg with RSD of 20%. Dietary intake of OPP residues through vegetables (Tomato, egg plant and pepper) from Kumasi, Ghana and reported that malathion residue concentration beyond MRL values 90.1mg/kg) and in tomatoes (0.120±0.101mg/kg) and pepper (0.143±0.042mg/kg). The recoveries achieved for tomato, egg plant and pepper were 88-102%, 90-105% and 91-98% respectively (Darko and Akota, 2008). Gonzalez- Rodriguez et al., (2008) estimated 23 insecticide and fungicide residues in 75 green and leafy vegetables (Swiss chards, spinach and lettuce) collected from qurense, Spain. Pesticide values were above the MRL in 20% of the analyzed samples. The maximum concentration of 12 mg/kg of fungicides (procyimdone) and 6mg/kg of insecticides (cypermethrin) was present in lettuce and swiss chard respectively. Pan et al., (2008) analyzed the leafy vegetables from the local super market of Hefei (Anhui province), China for multi pesticide residues of OPP<sub>s</sub> with recovery rate over 83%. OPP<sub>s</sub> residues were monitored in vegetables potato, onion, red pepper, green onion and lettuce from Venezuela. 48% samples contaminated with residue value 16.7% of the samples higher than MRL values and recovery rate 72-110% (Quintero et al., 2008). Recovered pesticides vary from 80-115% with RSD less than 15% and concentration range of 0.030-0.360mg/kg in 107 pesticides analyzed in cabbage and raddish samples from South Korea (Thanh et al., 2008). Fresh vegetables shanghai green, Chinese cabbage, carrot and spinach collected from agriculture markets of Nanjing, China and analysed for eight OPP<sub>s</sub>. Vegetable samples contaminated with all the pesticides except fonofos and fenthion and LOD ranged between 0.05 to 0.2g. Average recovery rate of 61.8 to 107% for all pesticides was achieved (Wang et al., 2008).

54 pesticides in vegetables (pepper and tomato) and citrus fruits (orange and lemon) from Murcia, Spain and average recovery varied from 65.5%-114.5% and RSD between 2.3 and 8.3%. Vegetables of Al-qassim region Saudi Arabia were analyzed and residue found in 55.6% of the samples and 33.1% samples had residues above the MRL. The highest concentration was found in lettuce, followed by tomato, cabbage, carrot, green pepper and egg plant (Jose Fenoll et al., 2010; Osman et al., 2010).

Vegetables collected from supermarkets in Beijing, China

exhibited recovery rate higher than 74-111% with variation coefficients of the repeatability typically less than 20% (Tao et al., 2009). Ahna et al., (2009) noticed the recovery of methamidophos (108.6%) and malathion (98.5%) was maximum among the vegetables analyzed. Banana purchased from the local markets of canary island, Spain and observed that 50 sample contained malathion, 4 fenitrothion and 1 bufrofezin. Most of the pesticides remained in the peel (0.87mg/kg) compared to pulp (0.07mg/kg to 0.12mg/kg) (Hernandez-Borges et al., 2009). Residue levels of organo-chlorine pesticides (HCH and DDT) determined in 34 samples of 19 varieties of vegetables collected from Dayang city, China and residues of DDT were 94.12% and HCH 91.8% (Odhiambo Joshua Owago et al., 2009). 33% of samples are contaminated and 80% of residues had residues higher than MRL in egg plant, pumpkin, okra collected from Punjab in Pakistan.

The fruits of Accra Metropolis was analyzed for various pesticide residues and revealed that 32.8% of the fruit samples contained residues of the monitored insecticides above the accepted MRL and 48.7% of the samples with residues below the MR (Crentsil and Augustino, 2011). The concentration of pesticide residues in fruits and vegetables from markets from Kumasi for organochlorine and pyrethroid and only 19% of the samples gave results with levels of insecticide residues above the MRL (Crentsil Kofi Bempah et al., 2011). Fruits, vegetables, herbs and spices availed from Egyptian local market with contamination reached 45.45% and only 8.4% of samples contained pesticide residues above MRL (Farag et al., 2011). Approximately 9% of the samples tested positive for pyrethroids (Residue range from 0.004-0.573 mg/kg) in 345 vegetable samples produced in Sonara, Mexico tested for the presence of Cyhalothrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin. Vegetable samples of Pakchoi cabbage, legumes and leaf mustard procured from Xiamen, China in which pesticide residue was most frequently detected with 17.2%, 18.9% and 17.2% of samples exceeding the MRL respectively and most commonly observed pesticide was cypermethrin found in 18.7% of the samples analyzed (Chen et al., 2011). Three pepper, one tomato and one cucumber samples had residues above the maximum allowable residue (0.01mg/kg) in vegetables from Almeria (Spain) and mean recoveries ranged from 80% for thiometon to 116% for haptenphos with relative standard deviations lower than 20% for all components (Camino et al., 2011). 34% samples found to have residue above the MRL and most frequently found pesticides were carbaryl followed by biphenyl and carbofuran in vegetable samples of four super markets located in Al-qassim region, Saudi Arabia. The precision ranged from 2-12% for all fresh vegetables and recovery values ranged from 81 to 115% which are considered as acceptable (Khaled et al., 2011).

#### Pesticide detection in fruits and vegetables: Indian scenario

Residue levels of selected OPP<sub>s</sub> (Methyl parathion, malathion and chlorpyrifos) in different seasonal vegetables such as spinach, cucumber, brinjal, cauliflower and cabbage from the fields of Agra district, India. The recovery rates in the range of 70-110% with RSD less than 8%. 63% found contaminated with pesticide and 46% of contaminated samples contain pesticide residues more than MRL as given by FAO/WHO (Parveen et al., 2005). Vegetables collected from Agra, India during winter showed slightly higher concentration of lindane, endosulfan and DDT in summer vegetables. But the concentration of these organochlorine pesticides was well below the established

tolerances both in summer and winter vegetables (**Bhanti and Tanuja, 2005**). Among the organochlorines, HCH, DDT, endosulfan detected in all the samples of vegetables (Ber, grapes and guava) and residues of HCH and DDT in ber followed by grapes and guava where as residues of endosulfan was maximum in guava followed by grapes and ber. All the fruits showed the presence of residues with one or the other groups of pesticides but below the respective MRL values (BeenaKumari et al., 2006). It was observed that winter season vegetables are highly contaminated and concentration of malathion was maximum during all the seasons and methyl parathion minimum during summer and rainy seasons (**Bhanti and Taneja, 2007**). 10 multiclass pesticide residues analyzed in fresh grape samples and mean fortification recoveries obtained at the levels of 0.010-0.100mg/kg were 78-104% for all compounds with RSD < 5%. The results revealed that the concentrations of the studied pesticide residues in grape samples were within the permissible limits except for monocrotophos (**Pada-lavenkateswaralu et al., 2007**).

HCH residues in various food matrices such as vegetables, leafy vegetables, fruits, wheat, pulses and medicinal plants collected from Lucknow, Uttar Pradesh and reported the recoveries for the spiked samples ranged from 93% to 103% and RSD between 5%-10%. The limit of detection of  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  HCH was 3, 6, 4 and 5ng/g respectively (**Abhilash et al., 2009**). Brinjal, cucumber, okra, ridge gourd and tomato and water samples collected from Andhra Pradesh, India showed the presence of chlorpyrifos in four samples (6.8%) and cypermethrin in two samples (3.4%) [**Ranga Rao et al., 2009**]. 42 samples were found to be contaminated with low but measurable amount of residues belonging to three major chemical groups namely OC, OP and SP but found below their maximum residue limits in 50 farm gate samples of cauliflower in punjab (**Kousik and Balwinder, 2010**). Some fruits accumulated more than residue limit in grapes collected from Bijapur district, Karnataka (**Pujeri et al., 2010**). **Gouri et al., (2011)** screened 72 pesticides in fruits and vegetables of Delhi, India with a recovery of 35 matrices at 0.025, 0.050 and 0.100 mg/kg. Recovery ranged between 72-114% with RSD < 20%. Contrastingly 13 OCPs and 17 OPPs pesticides recorded by **Doyeli et al., (2011)** in soil, spinach and egg plant with mean recovery in the range of 70-120% and median (CV%) less than 10%. cyhalothrin and procymidone in 120 tomato samples, revealed residue levels ranged from 0.001 to 0.400mg/kg for dicofol, from 0.003 to 0.170 mg/kg for procymidone, from 0.001 to 0.250 mg/kg for chlorothalonil, from 0.050 to 0.500mg/kg for bifenthrin and from 0.003 to 1.123mg/kg for endosulfan. European MRL for endosulfan exceeded by 6.6% and deltamethrin by two samples (1.6%) in tomato (Salghai et al., 2012). 120 samples of four different fresh vegetables (Brinjal, cabbage, tomato and lady finger) from UP, India and found that the pesticide residues was not present in 58.33% samples and 13.33% samples exhibited greater MRL values (**RashiBankar et al., 2012**). Residues in vegetable samples (Brinjal, okra, tomato, sweet pepper, cabbage and cauliflower) from five different districts of Uttarakhand and showed endosulfan residues above MRL values Eight pesticide (bifenthrin, chlorothalonil, cypermethrin, deltamethrin, dicofol, endosulfan,  $\lambda$ -followed by carbendazim, chlorpyrifos, imidacloprid and cypermethrin. Among the vegetable samples cauliflower and tomato had carbendazim residues higher than the recommended MRL while cabbage had endosulfan contamination higher than the recommended MRL value (**Shailendrasinghchauhan et al., 2012**).

### Conclusion:

Pesticide residue analysis is an important step in determining the safety of using certain pesticides. Residue analysis provides a measure of the nature and level of any contamination within the environment and its persistence. Producers of agro-food products are required to follow good agricultural practices. Prolonged use of pesticide will promote pest resistance, each time when higher doses are applied. Continuous monitoring for pesticide residue in food crop is desirable in order to protect the end user from health hazards and generate baseline data upon which, future plans to be envisaged.

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