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## Determination of Pesticide Residues In Potato Tuber Samples Using QuEChERS Method With Gas Chromatography.

<sup>1</sup>Mohamed A.I. Ahmed, <sup>2</sup>Nasr S. Khalil and <sup>2</sup>Tarek A. Abd El Rahman

<sup>1</sup>Plant Protection Department, Faculty of Agriculture, Assiut University, Assiut 71526. Egypt.

<sup>2</sup>Central Agricultural Pesticides Laboratory, Agricultural Research Center ARC, Dokki, Giza, Egypt.

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### ABSTRACT

**Background:** Pesticide residue testing is an important tool for monitoring the residues in vegetables. However, it is well known that over-use of pesticides without any regulations, could lead to serious and dangerous levels of hazardous chemical that enter the environment, especially food chain. Furthermore, vegetables, such as potato tubers, are being consumed in increasing quantities which considered fresh production that is most susceptible to pesticide residues. **Objective:** to detect and analysis the pesticide residue of major pesticide groups organophosphates (OPs), organochlorines (OCs), and Synthetic pyrethroids (PYs) from randomly collected nine potato tuber samples from Assiut, Elminia, Kalubia, Cairo, and Giza cities in Egypt using Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method with the quantification method by Gas Chromatography-Flame Photometric Detector (GC-FPD) for OPs and Electron Capture Detector (GC-ECD) for OCs and PYs. **Results:** The recovery varies from 75.72% to 99.43%. However, the results showed that OCs and OPs have the highest values of contamination and violation. The detected pesticides were: Chlorpyrifos, Fenitrothion, p,p-DDE, and Gama-HCH. However, the level of pesticide residues was either below or slightly below the maximum residues limits (MRLs). The highest significant values were found in Assiut, Kalubia, Cairo, and Giza for OPs pesticide residues and in Giza for OCs pesticide residues. The PY pesticide residues were not detectable (ND) in the samples. Furthermore, washed, washed and salted, and peeled methods shown the most effective methods in reducing the pesticide residues. **Conclusion:** we have proposed that QuEChERS method with (GC-FPD) and (GC-ECD), was best testing tools in analysis the pesticide residues in potato tuber samples which important to ensure that the vegetable production will meet the regulatory, healthy, and safety standard level for consumers. However, further investigation must be done to improve and develop advanced methods in the field of pesticide residues analysis.

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## INTRODUCTION

In recent years, analysis of pesticide residues in food has become an essential requirement for consumers, producers, and food quality control authorities (Ahmed et al., 2014; Ashutosh et al., 2011). In Egypt, organophosphates (OPs), organochlorines (OCs), and pyrethroids (PYs) are considered the most common used pesticides in plant protection. However, pesticide residues analysis of food is considered a time-consuming process that required several post extraction cleanup steps (Cairns et al., 1993; Lee et al., 1991; Christer et al., 2004). Moreover, the use of organic solvents such as acetone and acetonitrile for extraction provided high recovery percentages and further cleanup required before gas chromatography (GC) analysis which pretend the magnitude of time, cost, and potential efforts in analytical methods (Lehotay, 2000). Thus, using appropriate detectors in GC which is important in reduced the amount of cleanup necessary in that it is excellent tool in removal the interfering co-extracted components in the analysis of pesticide residue procedures (Lehotay, 2000). To meet this trend, Flame photometric detector (FPD) and Electron capture detector (ECD) considered sharp degree of selectivity which usually counted as strength of selective detectors among the other detectors (Lehotay, 2000). Recently, the QuEChERS method for pesticide residue analysis was introduced by Anastassiades et al (2002), which provided high quality results in fast, easy, and an inexpensive approach for analysis the pesticide residues in food and other environmental commodities such as vegetables, fruits, water, and soil. Yet, Follow-up studies have further validated the method for greater than 200 pesticides (Lehotay et al., 2005). In this study, we analysis the amount of pesticide residues in potato tuber samples collected from

**Corresponding Author:** Mohamed A. I. Ahmed, Plant Protection Department, Faculty of Agriculture, Assiut University, Assiut 71526, Egypt  
Phone: +201113991177; Fax: +20882331384; Email: maiaf2000@yahoo.com

different cities of Egypt using (GC-FPD) and (GC-ECD). The study also included the application of QuEChERS method for the estimation of the residue of major pesticide groups' OPs, OCs, and PYs in the samples.

## MATERIAL AND METHODS

### *Samples:*

Nine samples were collected randomly from nine local markets in five cities in Egypt (Table 1).

**Table 1:** Random markets from Egypt which the samples obtained from.

Market	City
Alzahraa	Assiut
Abo-Teg	Assiut
Naela Khatoon	Assiut
Alwelidia	Assiut
Der-Mwas	Elminia
Shobra-Elkhema	Kalubia
Elmaadi	Cairo
Eldokki	Giza
Elharam	Giza

### *Sample Preparation:*

Three kilograms of potato tubers were taken for each sample in polyethylene bags labeled by name of market and city then transferred immediately to the Lab. Samples were completely homogenized then divided into three portions consisting of 1 Kg each.

Samples homogenization was done following the guidelines of Codex Guide vol.2-section 4 Anonymous, (1993) as follow:

One-kilogram sample of potato tubers was completely homogenized, three replicates of 100 g each were taken, two for extraction and the third was kept in the deep freezer at -20 °C. Extraction was carried out as soon as possible.

The samples were comminuted (10 g) of each was then placed into 50 ml polyethylene tube. Samples were extracted and cleaned up immediately after sampling using QuEChERS methodology (Anastassiades *et al.*, 2002). 15 ml of acetonitrile was added into each tube. The samples were well shaken using a vortex mixer at maximum speed. Afterwards, 6 g of anhydrous magnesium sulfate and 1.5 g of sodium chloride were added, then extract by shaking vigorously on vortex for 5 min and centrifuged for 10 min at 4,000 rpm. An aliquot of 4 ml was transferred from the supernatant to a new clean 15 ml centrifuge tube containing 100 mg PSA and 600 mg anhydrous magnesium sulfate. The samples were again vortexed for 3 min and then centrifuged for 10 min at 4,000 rpm. Sodium Chloride Saturated solution used for washed and slated method.

### *Pesticides Detected:*

Thirty pesticides were studied for identification and quantification, the detected OP residues included: chlorpyrifos, chlorpyrifos-methyl, cadusafos, diazinon, ethoprophos, pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, fenitrothion, fenamipho and triazophos. Monitoring OC pesticides included: alpha-HCH, beta-HCH, gama-HCH, heptachlor, heptachlor-epoxide, aldrin, dieldrin, p,p-DDE, endrin, o,p-DDT, p,p-DDD, p,p-DDT. Synthetic Pyrethroid PY included fenpropathrin, permethrin, lambda-Cyhalothrin, cypermethrin, fenvalerate and deltamethrin. The average recoveries percentage of pesticides for 3 spiked levels (0.05, 0.01 and 0.001mg/kg) in Potato tuber samples were conducted (Table 2).

**Table 2:** The average recovery percentage of OC, OP, PY pesticides in potato tuber samples.

Pesticide groups	Pesticides	Average Recovery %
OPs	chlorpyrifos	96.81
	chlorpyrifos-methyl	86.99
	cadusafos	87.42
	diazinon	97.32
	ethoprophos	90.51
	fenitrothion	87.43
	fenamiphos	87.47
	phenthoate	88.52
	pirimiphos-ethyl	85.64
	pirimiphos-methyl	91.57
	profenofos	94.56
	prothiofos	90.86
	triazophos	96.92
OCs	Alpha-HCH	75.72
	Beta-HCH	88.53

	Gama-HCH	90.51
	Heptachlor	87.43
	Aldrin	87.47
	Heptachlor-Epoxyde	82.21
	Dieldrin	89.95
	P,P-DDE	88.52
	Endrin	85.64
	O,P-DDT	91.57
	P,P-DDD	94.56
	P,P-DDT	90.86
PYs	Fenprothrin	98.82
	Lambda-Cyhalothrin	96.92
	Permethrin	85.72
	Cypermethrin	89.11
	Fenvalerate	99.43

OC= organochlorinate pesticides.

OP= organophosphate pesticides.

PY= pyrethroid pesticides.

### GC-FPD and GC-ECD

The pesticide residues analysis was detected by Gas chromatography (GC) Hewlett Packard (HP) serial 6890 equipped with Flame photometric detector (FPD) and Electron capture detector (GC-ECD). The columns that were used in the analysis of the samples to determine the different pesticide groups are shown in Table 3. The detection and confirmation of presence of residues in potato tuber samples depended on the use of chromatography columns of different polarities. For OP pesticide residues, the GC instrument was adjusted as followed,

Injector temperature = 250 °C, Detector temperature = 250 °C, Flow rate of hydrogen =75 ml/min, Flow rate of air =100 ml/min, and Flow rate of nitrogen =11.7 ml/min. the Oven temperature program for GC adjusted for OP pesticides was shown in Table 4. The Total run time: 35 min. For OC and PY pesticide residues, The GC instrument was adjusted as followed, Injector temperature = 320 °C, Detector temperature = 320 °C, Flow rate of hydrogen =75 ml/min, Flow rate of air =100 ml/min, and Flow rate of nitrogen =3 ml/min. the oven temperature program for GC adjusted for OC and PY pesticides was shown in Table 5. The Total run time: 43 min.

**Table 3:** Columns that used in analysis the pesticide residues to determine different pesticide groups

	Column A	Column B	Column C
Name	PAS-5	PAS-1701	DB-17
Film thickness	0.52um	0.25um	0.25um
Length	25 m	25 m	30m
Column ID	0.32mm	0.32mm	0.32mm
Determined pesticides	OP	OP or OC+PY	OC+PY.

**Table 4:** Oven temperature program for GC adjusted for OP pesticides.

Level	Rate (°C/ min)	Temp.( °C)	Time( min)
1	-	160	2
2	5	210	3
3	5	240	1
4	2	250	8

**Table 5:** Oven temperature program for GC adjusted for OC and PY pesticides.

Level	Rate (°C/ min)	Temp.( °C)	Time( min)
1	-	170	2
2	3	260	11

## RESULTS AND DISCUSSION

The results of OP pesticide residues analysis in potato tuber samples are shown in Table 6. However, the detected OP pesticides were Chlorpyrifos, Fenitrothion. The highest significant values were found in Assiut (Alwelidia market), Kalubia (Shobra-Elkhema market), Cairo (Elmaadi market), and Giza (Elharam market) and

the level of pesticide residues were 0.009, 0.009, 0.008, and 0.04 mg/kg, respectively. The presence of OC pesticide residues were given in Table 7. Meanwhile, two pesticides were detected p,p-DDE and Gama-HCH, with values 0.009 and 0.007mg/kg. The highest value was in Abo-Teg market (Assuit Governorate) and the level was 0.009 mg/kg. It is interesting to note that p,p-DDE and Gama-HCH which is banned for long times were found in the samples. Further, PY pesticide residues analysis has not shown in any samples. The three cleanup methods, washed, washed and salted, and peeled were considered best methods in reducing the residue of all pesticides that detected in this study. The low level of some markets such as Alzahraa, Der-Mwas, and Abo-Teg markets, in this study, was promising indication of changing in usage and dealing of pesticides behavior. Many studies reported the residues of OCs, OPs, and PYs in vegetables samples (Kumari *et al.*, 2002; Kumari *et al.*, 2003a; Kumari *et al.*, 2003b; Kumari *et al.*, 2006; Wang *et al.*, 2008). One of the reasonable causes for obtaining low level of residue in some samples was that the conscious use of pesticides with appropriate waiting period followed by farmers in vegetable planting crops. Whereas the reason that pesticides were shown in some samples because of the heavy use and the persistence of these pesticides which is indicated that not all farmers follow the legal practices and sending the vegetable samples to analysis from the residues. For instance, OC pesticides mainly enter and accumulate into human body through the consumption of contaminated food and may produce toxicological hazard effects not to mention the negative effects on the environment (Matsumura, 1985). To sum up, a periodical and restricted monitoring of pesticide residues are the recent and important need for the producers, consumers, and food quality control and appropriate agricultural legislation must be applied.

**Table 6:** Organophosphate pesticides residue analysis in potato tuber samples.

Market	Pesticide found	MRL (mg/kg)	unwashed	washed	Washed and Salted	Peeled
Alzahraa	Chlorpyrifos	0.05	0.03	ND	ND	ND
Alwelidia	Chlorpyrifos	0.01	0.009	ND	ND	ND
Der-Mwas	Chlorpyrifos	0.05	0.01	ND	ND	ND
Shobra-Elkhema	Fenitrothion	0.01	0.009	ND	ND	ND
Elmaadi	Fenitrothion	0.01	0.008	ND	ND	ND
Elharam	Chlorpyrifos	0.05	0.04	ND	ND	ND

**Table 7:** Organochlorine pesticides residue analysis in potato tuber samples.

Market	Pesticide found	MRL (mg/kg)	unwashed	washed	Washed and Salted	Peeled
Abo-Teg	P,P-DDE	0.05	0.009	ND	ND	ND
Eldokki	Gama-HCH	0.01	0.007	ND	ND	ND

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