

Determination of Diazinon and Carbofuran Residue Levels in Apples Kept in Cold Storage Depots in Karaman Province, Turkey

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In this study, two pesticides *viz.*, diazinon and carbofuran residue levels that is used in agricultural spraying in apple samples that were harvested in 2014 harvest season and kept in cold storage in Karaman province, were examined by gas chromatography-mass spectrometer (GC-MS) and gas chromatography-flame-ionisation detector (GC-FID) method. The samples that were taken from 6 different cold storages in the region at 5 different time zones, were kept in laboratory in refrigerator at + 4 °C. The residue levels of diazinon and carbofuran pesticides in apple samples were determined. In order to identify pesticides residues at least three apple samples that were chosen randomly, were homogenized by homogenizator. In extract of samples QuEChERS method was used since it is fast, easy, low-cost, effective and reliable method. The residues of pesticides were taken from this homogenate with acetonitrile and given to GC-MS equipment in a suitable way. According to the results, carbofuran and diazinon pesticides types that are forbidden in Turkey, were determined in large amount of samples.

Keywords: Apple, Pesticides, Medicine residue, Carbofuran, Diazinon.

INTRODUCTION

Despite important benefits of pesticides in agricultural production, they are more or less toxic compounds and consuming of food having pesticides residue over permitted level, forms risk on human health [1,2]. Pesticides involve all chemicals that are classified as insecticide (insect killer), herbicide (weed destroyer), rodenticide (rodent killer) *etc.* [3]. Pesticides with chemical and biological variation products (metabolites) attract attention not only with their biocide effects but also with their targets and effects in total ecosystem. There are more than 10000 insects, 600 weeds, more than 1500 plant disease and 1500 type nematods that can be harmful to people, animals and plants at various levels [4]. Pesticites or pesticides derivatives on or in the product are called "pesticides residue". The limit of this residue that does not form a risk in terms of human and animal health is generally defined as maximum residue limit (tolerance, MRL) [5]. Do not using agricultural pesticides at exact dose or on time affects human and environmental health negatively. Measuring of residue levels of active materials becomes important in Turkey as it is in all over the World since they are toxic, mutagenic, carcinogenic and teratogenic in terms of human and environmental health. Apart from accidents the harm for human comes out in stages such as transportation,

storage, using and consumption of food involving pesticides residues. According to the U.S. Environmental Protection Agency, pesticides have been linked to developmental problems in children [6] and may act as carcinogens or negatively affect the endocrine system. Pesticides can be roughly classified as hydrophilic (water soluble) or hydrophobic (water insoluble). It is well known that the soluble pollutants on the surface of products are easily washed off with water, whereas insoluble pollutants persist on food and potentially threaten human health. In addition to insoluble surface pesticides, pesticide residues that are physically inside food products also persist after washing. Numerous studies have reported that food processing (including washing, peeling, boiling and juicing) can largely reduce the levels of pesticide residues in food [6-8]. Many studies have been carried out on the removal of pesticide residues from apples during home preparation and commercial processing [8-11]. Fruit and vegetable compounds that pesticides are applied and their shelf life change according to pesticides group, climatic conditions, their formulation forms and structure of fruits and vegetables. Generally the compounds of organic phosphoric pesticides spoil or clear away in short time without leaving residue. On the other hand, organic chloride pesticides stay long on fruit and vegetable. That is why organic chloric pesticides are not preferred in

usage. As pesticides usage changes between 1.2-13.8 kg/ha in European Union countries, it is between 490-700 g/ha in Turkey [12,13]. These values show that Turkey use rather low level of pesticides according to European Union countries. However according to residue analysis results conducted in Turkey although very few risky product number in terms of pesticides residue are reported, according to EU Fast Alarm System results the existence of pesticides residue on products sent from Turkey to EU is spectacular. As the number of party is 141 in products exported to EU countries in 2001, they increased to 202 in 2003 [13]. Pesticides left on soil after plant and soil applications can reach under ground water and other water sources with rain water as runoff or flow down. Carried pesticides due to slope, vegetation, formulation, soil type and rainfall cause the death of fish and other invertebrate water organisms in these waters. The pesticides residues in these organisms enter food chain of people as well as chronic toxicity by consumption of these contaminated waters. Since pesticides lose their effects in short time after their usage, disinfection is needed again. When this process is repeated one or twice, it leaves a little residue on product. Pesticides show toxicity by making cumulation in body. When they are taken to body they are spoiled by the effect of enzymes and some part of it is discarded from body [14]. Poisoning in human happens by taking pesticides to body *via* skin, respiration or digestion. When exposed to pesticides for a long time, some defaults happen in nervous, respiration, cardiac, vein, stomach, digestion and circuit systems, in inner organs such as liver, kidney *etc.*, skin and eyes. Also it has got serious effects such as cancer, tumour, irritation and wounds on skin, preventing recovery of wounds and cell renewal, deterioration of immune system and causing mutation by causing DNA failure in cells. According to Turkish Food Codex (TGK) pesticides maximum residue regulation dated 25 August 2014, its usage in Turkey was banned [15]. According to 2011 TGK regulation MRL values of carbofuran diazinon are given in Table-1 [16]. According to 2013 TGK regulation pesticides the carbofuran and diazinon usage was banned, are placed in pesticides list.

TABLE-1
MAXIMUM RESIDUE LIMIT VALUES OF PESTICIDES
(mg/kg) (REGULATION OF MAXIMUM RESIDUE
LIMITS OF TGK PESTICIDES, 2011) [Ref. 16]

Pesticides	MRL value	Explanation
Carbofuran	0.02*	Prohibited Pesticide
Diazinon	0.01*	Prohibited Pesticide

*The lowest analytically detectable limit

For pesticide residue analysis in different kind of matrices, liquid chromatography (LC) and gas chromatography (GC) are commonly used. Gas chromatography, coupled to different detectors, is used for the analysis of volatile and semi-volatile pesticides. However, the mass spectrometer detector is the most widely used due to its high selectivity and sensitivity and capability to detect compounds with different chemicals [17-19].

Over the last 40 years, various methods have been developed to investigate multiresidues of pesticides in food, given the variety of products applied to crops. In the QuEChERS method (quick, easy, cheap, effective, rugged and safe) samples

are extracted with acetonitrile, magnesium sulfate and sodium chloride, followed by clean-up using dispersive solid-phase extraction with primary and secondary amine [20,21]. Gas or liquid chromatography coupled with mass spectrometry is normally used to quantify the residues. In addition to acetonitrile, other solvents can be used for pesticide extraction, including ethyl acetate [22-25], which is more suitable for GC analysis than acetonitrile, as it is less polar and provides a smaller liquid-to-gas expansion volume [26]. In this study a method using QuEChERS extraction and GC-MS was developed for the analysis of two frequently applied pesticides in apple. The studied pesticides were representative of two of the most commonly used classes, *e.g.*, carbamates (carbofuran) and organophosphorous (diazinon). The proposed method was validated according to European guidelines. In addition, the expanded uncertainty was evaluated taking into account the different sources of uncertainty that affect the process.

EXPERIMENTAL

Analysis of the pesticides was carried out on Agilent Technologies 7890A GC-MS instrument. In addition, the MS detector (Agilent Technologies 5975C VL MSD with triple-axis detector, US 11398601), FID detector (Agilent Technologies 5188-5372 FID detector), pure water device (Millipore ultra pure water device, FONA81849), Mixer (Waring Commercial, 8010ES), Injector (Genject, 20002), analytical balance (Mettler Toledo JB1603 C/FACT with 10⁻⁴ sensitivity), centrifuge (Sigma 2-16 KC and Zentaifugen), homogenizer (IKA T 18 Basic Ultra-Turrax). The chemicals used are in the form of magnesium sulphate (Merck, 106067), acetic acid (Merck, 100063), acetonitrile (Merck, 1.00003) and Primer-Sekonder Amine (Thermoscientific, 60105-203). Pesticide standards were obtained from Sigma-Aldrich.

Ninety apple sample among harvested products in 2014 and kept in 6 different cold storage depot at 5 different time period in Karaman province, were collected according to random sampling method and they formed the material of research.

Preparation of standards: Certificated Sigma-Aldrich brand standards that their concentrations are clear, were used. Standard stock solutions of various concentrations were prepared in acetone and stored at 4 °C (purity > 95 %). From 1000 mg/kg stock standards working standards that their concentration were indicated below, were prepared. Diazinon: 0.1, 0.5, 1.0, 1.5 µg/kg; carbofuran: 0.1, 0.5, 1.0, 1.5 mg/kg with acetonitrile were completed to 100 mL. As an example calibration curve of diazinon standard is shown in Fig. 1.

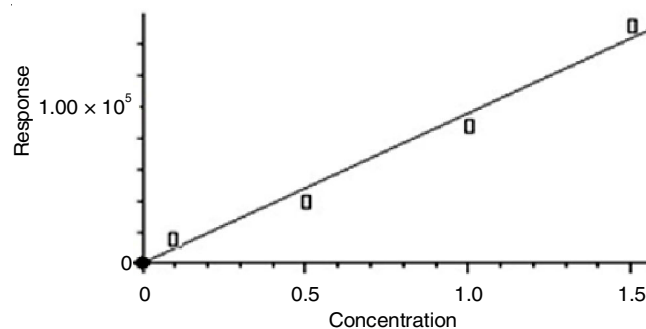


Fig. 1. Calibration curve of the diazinon standard (µg/kg)

System conditions: GC-MS analysis was carried out using an Agilent 7890A GC system integrated with an Agilent G4513A series auto sampler and a 5975C VL mass selective detector (MSD). The analytes were separated a 30 m × 0.25 mm × 0.25 μm film thickness HP-5MS fused-silica capillary column. The injector was set at 250 °C and the carrier gas was helium at a flow rate of 1 mL/min. The oven temperature was initially at 70 °C for 2 min, increased at a rate of 40 °C min⁻¹ upto 150 °C; held for 4 min; increased at a rate of 9 °C min⁻¹ up to 200 °C; increased at a rate of 24 °C min⁻¹ up to 280 °C and held for 15 min. The ion source, quadrupole and transfer line temperature were set at 230, 150 and 280 °C, respectively. The mass spectrometer was operated at 70 eV in electron impact (EI) mode. Solvent delay was 8 min and the injection volume was 1 mL. The GC-FID analysis was performed using an Agilent 6850 series gas chromatograph equipped with a flame ionization detector. Separations were performed on a 30 m × 0.25 mm × 0.25 μm film thickness HP-5MS fused-silica capillary column. The injector and detector temperatures were 250 °C and 300 °C, respectively. The injection port was operated at a 1:15 split. Flow rate of carrier gas nitrogen was set at 5.0 mL min⁻¹. Total run time was 27.347 min.

Preparation of examples to analysis: The samples taken from cold storage were brought to laboratory in transparent bags and kept in refrigerator at + 4 °C until analysis. Efficient amount was used from samples kept for analysis. Three apple samples were made homogeneous by grinding completely with mechanical grinders. The amounts for extraction were taken from these homogeneous samples by weighing.

Extraction: In extract of samples QuEChERS method that is widely used in pesticides analysis was used since it is fast, easy, cheap, effective, certain and reliable method [17]. 10 g were taken from samples grinded in 50 mL centrifuge tubes and after adding 10 mL acetonitrile with 1 % acidity, 4 g MgSO₄ and 1 g sodium acetate and were shaken by hand. Later the samples were centrifuged in a centrifuge working at 9000 rpm for 2 min. 2 mL of centrifuged samples were taken from upper phases and transferred to 30 mL glass tubes. 0.6 g MgSO₄ and 0.2 g PSA (primary secondary amine) was added. The samples were centrifuged at 5000 rpm for 1 min. Sufficient amounts from upper phases of centrifuged samples were taken and put into vials so solution ready to be analyzed in GC-MS and GC-FID equipment was obtained [20].

Method validation: The validation of the analytical method was performed by the following parameters: linearity, precision and limit of detection and limit of quantification. The method has been validated according to EC SANCO/10684/2009 directive [27]. The calibration curves of the compounds in the matrix were obtained by plotting the peak area against concentration of the corresponding calibration standards at four calibration levels between 0.1 and 1.5 mg kg⁻¹. The limit of detection (LOD) and the limit of quantification (LOQ) were determined by considering the slope of the calibration curve and the residual standard deviation of the regression line, calculated with the equations described elsewhere [28].

RESULTS AND DISCUSSION

Carbofuran and diazinon, obtained from 90 samples from 6 different cold storages (Ayaz, Babaođlu, Cavsa, Kirefe,

Yildizbas, Tasbas) randomly in Karaman province at 5 different time periods, in solutions obtained by QuEChERS method were measured by GC-MS equipment. According to the findings, pesticides residues were identified in most of 90 analyzed samples. GC-MS, GC-FID chromatograms and mass spectrums of carbofuran and diazinon standard are shown in Figs. 2-4. GC-MS chromatograms of the carbofuran and diazinon materials obtained in apple samples are shown in Fig. 5. Chromatographic parameters of carbofuran and diazinon materials are given in Table-2. The linearity data (equation, correlation coefficient, R²), LOD, LOQ are given in Table-3. Average values

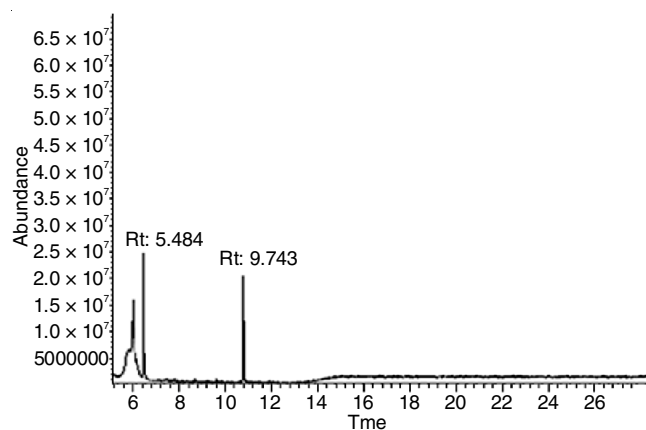


Fig. 2. GC-MS chromatogram of the carbofuran and diazinon standard (total ion current)

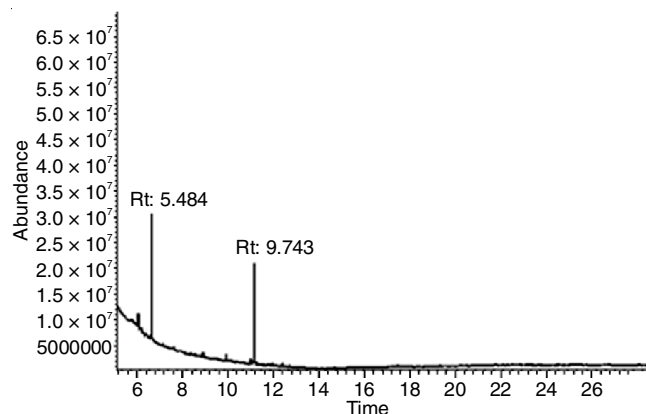


Fig. 3. GC-FID chromatography of the carbofuran and diazinon standard

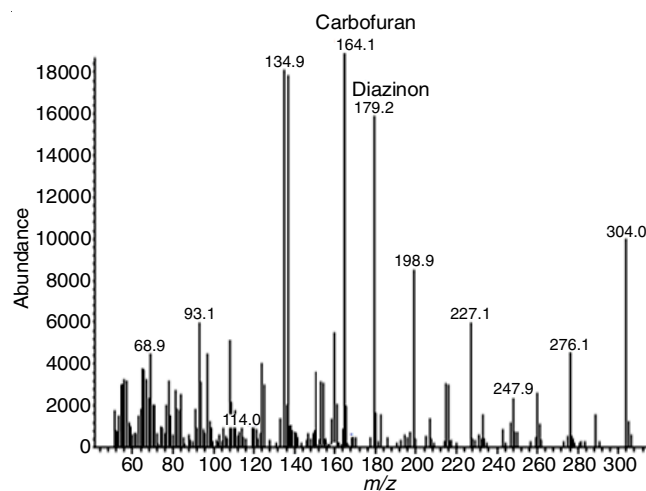


Fig. 4. GC-MS mass spectra of the carbofuran and diazinon standard

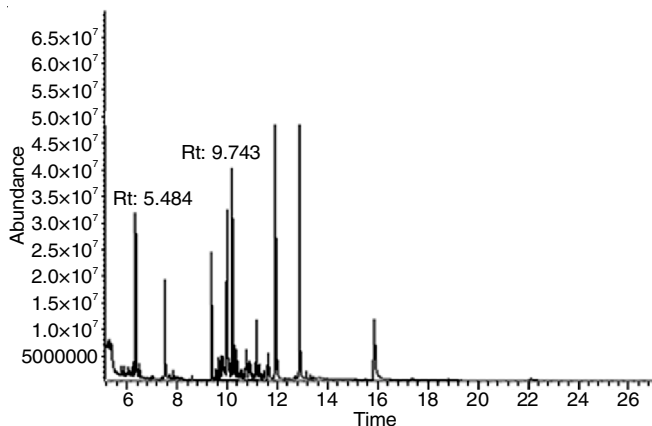


Fig. 5. GC-MS chromatogram of the carbofuran and diazinon material of the apple sample

TABLE-2
CHROMATOGRAPHIC PARAMETERS FOR THE
SELECTED COMPOUNDS ANALYZED BY GC-MS

Pesticide	m.f.	m.w. (g/mol)	Target ion (<i>m/z</i>)	Retention time (min)
Carbofuran	C ₁₂ H ₁₅ NO ₃	221.26	164.1	5.484
Diazinon	C ₁₂ H ₂₁ N ₂ O ₃ PS	304.35	179.2	9.743

of carbofuran and diazinon in apple samples taken from cold storage is given in Table-4. Graphics of average values are shown in Figs. 6 and 7.

The residue levels of diazinon and carbofuran in apple samples were determined. In order to identify medicine residues at least three apple samples that were chosen randomly, were homogenized by homogenizer. In extract of samples QuEChERS method was used since it is fast, easy, cheap, effective, certain

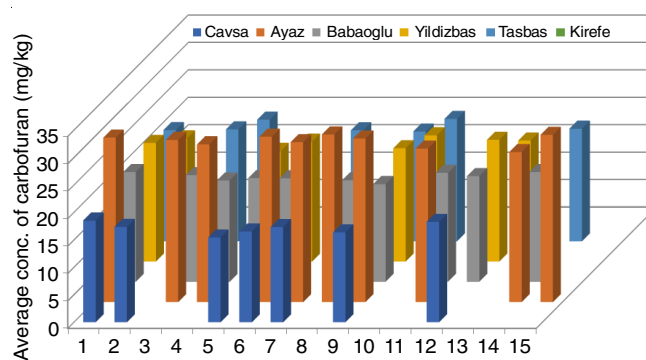


Fig. 6. Average amounts of carbofuran in the samples (mg/kg)

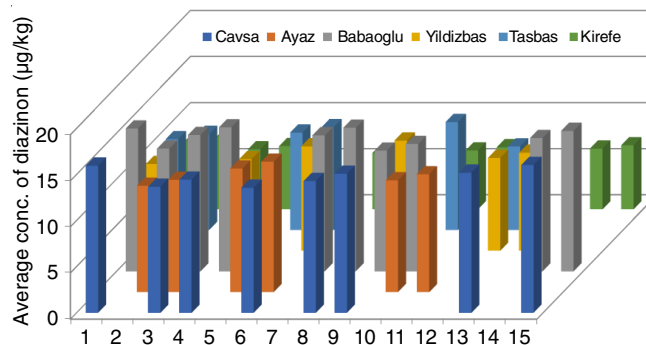


Fig. 7. Average amounts of diazinon in the samples (µg/kg)

and reliable method. The residues of pesticides were taken from this homogenate with acetonitrile and given to GC-MS equipment in a suitable way. According to the results, the carbofuran and diazinon are forbidden in Turkey, were determined in large amounts of samples.

TABLE-3
LINEARITY DATA (EQUATION AND CORRELATION COEFFICIENT, R²), LIMIT OF DETECTION; LIMIT OF QUANTIFICATION

Pesticide	Linearity range	Regression equation	R ²	Limit of detection	Limit of quantification
Carbofuran	0.1-1.5 mg/kg	y = 13011x + 32579	0.997	0.03 mg/kg	0.10 mg/kg
Diazinon	0.1-1.5 µg/kg	y = 12775x + 10251	0.994	0.60 µg/kg	1.70 µg/kg

TABLE-4
AVERAGE AMOUNTS OF CARBOFURAN AND DIAZINON IN THE SAMPLES

	Carbofuran (mg/kg)						Diazinon (µg/kg)					
	Cavsa	Ayaz	Babaoglu	Yildizbas	Tasbas	Kirefe	Cavsa	Ayaz	Babaoglu	Yildizbas	Tasbas	Kirefe
1	18.54	29.98	20.02	21.64	20.28	ND	15.96	ND*	15.50	9.40	9.85	7.50
2	17.40	ND	ND	22.46	ND	ND	ND	11.54	13.32	ND	10.42	7.92
3	ND	29.56	19.44	ND	20.42	ND	13.68	12.18	14.80	ND	ND	6.50
4	ND	28.76	18.48	ND	22.18	ND	14.44	ND	15.62	9.92	ND	6.86
5	15.44	ND	18.9	20.18	ND	ND	ND	13.40	ND	ND	10.56	ND
6	16.56	30.14	18.86	21.86	ND	ND	13.56	14.14	ND	11.32	11.14	ND
7	17.36	29.14	ND	ND	20.24	ND	ND	ND	14.76	ND	ND	6.10
8	ND	30.56	18.50	ND	ND	ND	14.30	ND	15.58	ND	ND	6.44
9	16.40	29.80	17.82	20.66	20.02	ND	15.08	ND	13.10	11.94	ND	ND
10	ND	ND	ND	23.02	22.32	ND	ND	12.12	13.82	ND	11.70	6.38
11	ND	27.96	19.86	ND	ND	ND	ND	12.78	ND	ND	ND	6.72
12	18.28	ND	19.26	22.20	ND	ND	ND	ND	ND	10.06	9.06	ND
13	ND	ND	ND	22.06	ND	ND	15.20	ND	ND	10.62	ND	ND
14	ND	27.34	20	ND	20.54	ND	ND	ND	14.46	ND	ND	6.58
15	ND	30.48	ND	ND	ND	ND	16.04	ND	15.24	ND	ND	6.94
Average	17.14 ±	29.37 ±	19.12 ±	21.76 ±	20.86 ±	ND	14.78 ±	12.69 ±	14.62 ±	10.54 ±	10.46 ±	6.795 ±
± SD	1.092	1.073	0.734	0.933	0.966		0.948	0.951	0.931	0.948	0.932	0.549

ND = None detection

Conclusion

When studies in world wide are examined, voluminous quantity of pesticides are used to increase productivity. One of the most important reasons of pesticides usage is to struggle with plant mites in order to compensate food demand of increasing population. Also pesticides are used to lengthen shelf life of products. As all these are taken into consideration, producers continue pesticides usage until harvest season. That is why it is possible not to comply with waiting period of pesticides. Turkey has given serious importance to especially agriculture and stock breeding subjects during EU orientation period. Foremost among them innovations such as prescription system in agricultural medicines. Also with farmer provision system (CKS) big steps were taken in controlled production of producers. Consulting programmes given by agricultural engineers were supported and residual analyses were standardized routinely. The usage of 2 pesticides in apple (carbofuran and diazinon) examined in this research, are in prohibited pesticides list according to EU standards and Turkish Food Cortex Pesticides Maximum Residue Regulation. According to results finding prohibited pesticides in most of the apple samples show how important this study is in terms of human health. According to these results it is suggested that our farmers do not have sufficient knowledge about applying pesticides. Although agriculture has great place in economy of our country, Karaman province has an important place in exporting apple. Most of the apples harvested in Karaman are kept in cold storage depots in the province. The apples are both sold in the country and exported to mainly Arab countries, EU and Russia. In previous studies carbofuran and diazinon residues were obtained as a result of analysis in most of the apples in cold storage. Turkish Food Cortex Pesticides Maximum Residue Regulation was published in 2014. According to this, prohibited carbofuran and diazinon were identified in most of the samples. Pesticides usage should be done consciously and controlled in order to provide food security of our people and protect our environment and foreign trade. In EU and USA low risk or environmental friendly pesticides are given priority. However in Turkey environmental friendly pesticides are not given priority both in registration and supporting of consumptions. That is why, notably human health, precautions should be taken to prevent refusal of production exported to EU and Russia. In terms of protecting the health of our people, sometimes pesticides analysis of domestic products should be done as well as producers and tradesmen should be warned and raised awareness. Immediate precautions should be taken by government agencies about this subject.

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