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Effect of γ- ray, Microwave Heating and Solar irradiation of Apple Juice on Organochlorinated Pesticides Residues

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Abstract: This study was conducted to evaluate the effect of solar radiation, microwave heating and γ-irradiation on the Organochlorinated Pesticide (OCP′s) in apple juice. The solar radiation caused a destruction of 20% after 20 hr exposure to sunlight compared to 12% reduction for the tested OCP's after microwave heating for 10 min. On the other hand, the use of γ- irradiation leads to a degradation percentage of 30% after treatment with 25 kGray, while the irradiation with 5 kGray was found to produce insignificant effect on OCP's residues when compared with the control treatments. The degradation was found to increase with increasing exposure time and all treatments were found to be not effective in complete destruction of OCP's.

Key words: OCP's, organo-chlorinated pesticide, γ ray, microwave

INTRODUCTION

Pesticides, natural or synthetic, are chemical compounds that are widely used in the production of most agricultural products to eradicate pests and/or to increase the plant's resistance against them[1]. Therefore, pesticide residues are normally found in various food stuffs, which may, indirectly, cause problems for human health[2-3]. Although, the major source of pesticide residues could be fruit and vegetables, they can also be taken indirectly through the consumption of meat or dairy products. The introduction of these pesticides into animal products will take place through the utilization of feed contaminated with chlorinated pesticides which are usually found in food and food products given to animals. These pesticides vary in their stability in the produced food products. The chlorinated pesticides: p-p DDT, aldrin, endrin, heptachlor (the most fat-soluble) show a higher degree of accumulation in animal tissues (meat and meat products) and in milk fat[4]. The chlorinated pesticide residues are considered to be toxic and carcinogenic compounds. The toxicity of Organo-Chlorinated Pesticides (OCP's) is expressed as Lethal Dose (LD50). The LD_{50} is the amount of toxicant that is needed to kill 50% of test animal whether it is given orally or through the skin. Chlorinated pesticide residues could be affected by many factors such as processing, heat treatment and storage conditions. Processing of fruit and vegetables into juice may causes pesticide destruction, chemical changes or lowering pesticide concentration in the produce, which imposes hazards on humans' health. Apple juices could be used as food products such as apple pies, cakes, sweets, muffins and in many recipes of food produce. These food products could be prepared or reheated using microwave heating or radiated with γ-rays as a method of preservation[5] or apples could sun dried to produce apple crisps as well as apples on apple trees exposed for a longer period to sunlight[6,7]. Therefore, the objectives of this study were to find the effect of γ-rays , microwave heating and sunlight on the OCP's residues in the extracted apple juice using a new method of OCP's extraction.

MATERIALS AND METHODS

Reagents and pesticides standards: All of the used solvents used were of gas chromatographic grades. N-hexane, (pest, scan, Dublin), Toluene, HPLC grade (GC grade, Dublin), acetonitril 99.5% (GC grade, Dublin), ethyl acetate (99.8% GC grade, UK) for pesticide residue analysis. Anhydrous sodium sulfate 99% (Scharlau, Spain) was heated at 500ºC for 5 h, cooled

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and stored in oven (Memmert, Germany), sodium chloride analytical grade of 99% (Fluka, Switzerland), Florisil, 60-100 Mesh (Riedel-dehäen,Germany) was activated before use at 550ºC for six hours and stored at 130ºC in oven (Memmerts, west, Germany) and Whatman filter paper of 55mM in diameter. Pure organochloranated pesticide standards: α-BHC, β-BHC, γ-BHC (lindine), δ-BHC, heptach;ore, aldrin, heptachloe epoxide, γ-chlorodine, endosulfan I, α-chlorodine, dieldrine, 4,4'-DDE, endrine, endosulfan II, 4, 4'-DDD, endrine aldehyde, endosulfan sulfate, 4, 4'-DDT and endrine ketone were purchased from Supelco (47426-U, USA). The organchlorinated pesticide were of a concentration 2000 μg mL^{-1} of each component dissolved in hexane: toluene (50:50).

Preparation of pesticides standard solution: A stock solution of the 19 organochloranated pesticides (COP's) that contains 2000 μg mL^{-1} (ppb) of each standard was prepared in hexane: Toluene (50:50 v/v). A working I solution containing 200 μg mL^{-1} of each standard was prepared from the stock solution. Then a working solutions II of concentrations 0.5, 1.12, 12.4, 20 ppb for each pesticide were prepared from the working I. A 1-μL of each standard was injected into GLC (Shimadzu-2010).

Gas chromatograph parameters: A splitless injector mode was used at 250°C. The oven temperature was programmed from 150°C (held for 1 min) to 275°C (at intervals of 5°C/min) and held for 2 min then to 280 at 5°C/min. The total run time was 28 min. The detector temperature was maintained at 310°C.

Sample preparation: Fresh or Apple juice samples were purchased from the local market and filtered through the filter paper No.1 to prepare a homogeneous juice for the treatments. The juice was analyzed directly for chlorinated pesticides using SPE followed by SPME and then gas chromatography analysis was performed to ascertain that this juice is free of chlorinated pesticides.

Preparation and treatment of pesticides spiked apple juice solutions: A sample of 4000 mL of freshly apple juice (free of OCP's as detected by GC analysis) was spiked with 2 mL of the stock solution to obtain a concentration of about 100μg mL^{-1} (100 ppb) of each pesticide. Thirty transparent glass bottles (150 mL capacity) were filled with 125 mL of the spiked apple juice. Fifteen bottles of this juice were irradiated with γ-ray at doses of 5, 10, 15, 20 KGray, nine bottles were heated in microwave for 2, 5 and 10 min and six bottles were exposed to sunlight for 5 and 10 days. Three bottles of the prepared juice were used for each dose or time of each treatment. The remaining 3 bottles were kept as control samples.

Extraction of pesticides: The fleshly prepared or the treated apple juice samples (10 mL) were filtered and passed through 500 mg SPE florisil column (Supelco, USA) previously conditioned by passing 5 mL of hexane through it. The retained pesticides were eluted from the SPE column by 9 mL of 85% hexane/diethyl ether. Solvent were removed under vacuum to dryness the residue was resuspended in 3 mLs of solvent and transferred into 4-mL amber glass vials containing a stirring rod (2 mM length). The resuspended pesticides then, placed on a hot plate with a magnetic stirrer at 40°C and the fiber of solid phase microextractin (SPME) (Supelco, USA) coated with polydimethylsiloxane (100 μm thickness) was immersed into the elute while being stirred for 35 min to extract the OCP's. The extracted OCP's on the SPME fiber was then injected into the GC-ECD.

Recovery test: The recovery test for the selected OCS's was carried out by spiking 25μL of the working solution into 50 of apple juice to obtain a concentration of 100 ppb of each OCP. The OCP's were then re-extracted following the same steps used for their extraction from the treated juice solutions.

Gas Chromatographic analysis (GC): The extracted OCP's on the SPME fiber either from the treated samples or from the recovery test sample was injected into the injector of shimadzo gas chromatograph (Model 2000, Japan) equipped with a split-splitless injector, ^{63}Ni-ECD (electron capture detector) and a rtx.5 capillary column coated with 95% dimethyl olysiloxane (30 m, .25 mm id, 0.1 μL mdf). The oven temperature was programmed from 150 C (held for 1 min) to 275C at rate of 5C min^{-1} and held for 2 min. The injector and detector temperatures were 250 and 310 C, respectively. The concentration of each pesticide was obtained by using standard curves prepared by plotting the average of 3 replicates of the peak area versus concentration. The concentrations used were 0.5, 0.12, 12.4 and 20 ppb for each pesticide. The results obtained were the average of three replicates.

Limits Of Detection (LOD): The limits of detection for chlorinated pesticides were determined by the injection of concentrations less than 1 ppb and increased until we reached the concentration of 20-ppb by successive dilution of the OCP's. The lower

concentration was measured from peak/noise ratio found for the solvent (hexane: toluene). The peak was increased and decreased by two Standard Deviations (±SD) for the 19 mixed OCP's. Then the lower concentration was calculated and injected for four times.

RESULTS

The GC trace of the 19 OCP' is shown in Fig. 1. It is evident that all of the used OCP's were well resolved by non polar (5% dipehnyl, 95% dimethylsiloxan) column. The efficiency of the SPME for extracting the 19 selected OCP's was evaluated using an apple juice that has a concentration of 100 ppb of these pesticides in three separate runs. The recovery percentages of these OCP's were presented in Table 1 and found to be between 97 and 99% with standard deviations between 0.83 and 2.03 as shown in Table 1. The degradation levels of the 19 OCP's used in this study and added to the apple juice at concentration of 100 ppb for each and exposed to; γ-radiation, at 5, 10, 15, 20, 25 KGray, microwave heating for 2,5,10 min, and sunlight exposure for 10 and 20 h were evaluated and the results are presented in Table 2. The effect of treatment of OCP's on the degradation percentages were ranged from 8 to 30 % for γ-radiation, 2 to 12 % after 10 min of microwave heating, and 10 and 20% reduction percentage after 10 h exposure to sunlight (Table 2).

DISCUSSION

The reproducibility (defined as the relative standard deviation of retention times of 15 replicates) of each of the 19 OCP' and the precision (defined as the relative standard deviation of the peak area of 15 replicates) for each of the OCP's were less than 4.2%. The minimum detectable level of each OCP's was found to be 0.5 ppb. The linear regression and the correlation coefficient of the 19 OCP's selected in this study showed linear response in the range of 0.5-20 μg kg^{-1} (ppb), since the R values were between 0.980 and 0.991.

For instance the R values for α-BHC and heptachlore were 0.999 and 0.987, respectively. These results for both linearity rang and the high correlation values were in agreement with those obtained by Moreno *et al*.[8] who found that the values for β-BHC (Lindine), Aldrin, p, p'-DDE and O, p'-DDT were between 0.9971 and 0.9990. The time of the analysis was reasonable and relatively short (17.4 min).

The efficiency of the SPME extraction method: The results demonstrated that the recovery percentages of these OCP's were ≤ 99% and standard deviation of less than 2.03 as shown in Table 1. These results agreed with the results obtained by Moreno *et al*.[8], Waliszwski, *et al*.[9], Mallatou *et al*.[10], Ganzhang, *et al*.[11] and Beseler *et al*.[12].

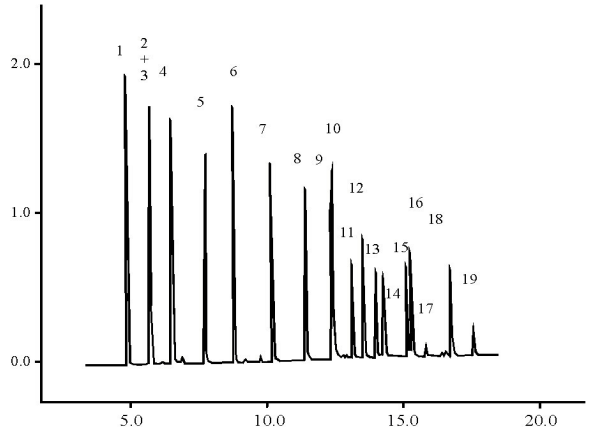

Fig. 1: OCP's standard chromatogram analyzed by GC/ECD .(where: 1-α-BHC, 2- β-BHC, 3- γ-BHC (lindine), 4- δ-BHC, 5-heptachlore, 6-aldrin, 7-heptachlore epoxide, 8- γ –chlorodine, 9-endosulfan I, 10-α- chlorodine, 11- dieldrine, 12-4,4'-DDE, 13-endrine, 14- endosulfan II, 15-4, 4'-DDD, 16- endrine aldehyde, 17-endosulfan sulfate, 18- 4, 4'-DDT, and 19-endrine ketone

Table 1: Chlorinated pesticides recoveries percentage from apple juice samples spiked with 100 ppb OCP's

ID	Name	Retention Time	OCP's Conc. (ppb)	% Recovery
1.	α-BHC	5.5010	100±1.0	99±1.20
2.	β -BHC	6.2640	100±1.0	99±0.96
3.	γ- BHC(Lindance)	6.3120	100±1.0	99±0.87
4.	δ- BHC	7.0520	100±1.0	99±1.00
5.	Heptachlore	7.3810	100±1.0	98±2.00
6.	Aldrin	8.1380	100±1.0	99±1.60
7.	Heptachlore epoxide	9.1390	100±1.0	99±0.86
8.	gama-chlorodine	10.4520	100±1.0	99±0.80
9.	endosulfan I	11.5810	100±1.0	99±0.98
10.	alpha-chlorodine	12.4530	100±1.0	99±0.98
11.	Dieldrine	12.5510	100±1.0	98±1.07
12.	4,4'-DDE	13.1580	100±1.0	98±1.17
13.	Endrine	13.5520	100±1.0	99±1.00
14.	Endosufan II	13.9920	100±1.0	98±1.90
15.	4,4'-DDD	14.2350	100±1.0	97±2.03
16.	Endrine aldehyde	15.0290	100±1.0	99±0.83
17.	Endosulfan sulfate	15.1950	100±1.0	99±0.90
18.	4,4'DDT	16.5740	100±1.0	98±1.33
19.	Endrine ketone	17.3390	100±1.0	99±1.33

Values are means of four replicates (n = 4) ± SD

Table 2: Effect of γ -irradiation, microwave heating and solar radiation of apple juice on Chlorinated pesticide residues concentration

	Treatment								
	γ- Irradiation					Microwave heating (min)		Solar Irradiation (hr)	
	% Reduction (± SD)								
Name	5(kGray)	10(Kgay)	15(kGay)	20(kGay)	25(kGay)	2	5	10	20
α-BHC	1±0.12	8 ± 0.2	20 ± 0.18	30±1.1	30±1.1	<0.5	10 ±0.2	12±0.30	20 ±0.8	20±1.8
β-BHC	1±0.12	8 ± 0.2	20 ± 0.18	30±1.1	30±1.1	<0.5	9±0.2	9±0.30	20 ±0.8	20±1.8
γ-BHC(Lindance)	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	9±0.2	9±0.30	20 ±0.8	20±1.8
δ- BHC	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	9±0.2	9±0.30	20 ±0.8	20±1.8
Heptachlore	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	9±0.2	10±0.24	20 ±0.8	20±1.8
Aldrin	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	2±0.1	3±0.30	20 ±0.8	20±1.8
Heptachlore epoxide	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	2±0.1	3±0.30	15 ±1.1	20±1.8
gama-chlorodine	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	2±0.1	2±0.13	20 ±0.8	20±1.8
endosulfan I	1±0.12	8 ±0.2	20 ±0.18	30±1.1	30±1.1	<0.5	7±0.3	7±0.30	18 ±0.8	20±1.8
alpha-chlorodine	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20 ±0.8	20±1.8
Dieldrine	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20 ±0.8	20±1.8
4,4'-DDE	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20 ±1.5	20±1.8
Endrine	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	12 ±0.8	20±1.8
Endosufan II	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20 ±0.8	20±1.8
4,4'-DDD	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	4±0.28	5±0.26	10 ±0.8	20±1.8
Endrine aldehyde	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20±0.8	20±1.8
Endosulfan sulfate	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	18 ±0.8	20±1.8
4,4'DDT	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20 ±1.8	20±1.8
Endrine ketone	1±0.12	8 ±0.2	8 ±0.2	30±1.1	30±1.1	<0.5	8±0.3	8±0.30	20 ±1.2	20±1.8

Values are means of four replicates (n = 4) ±SD

Effect of γ-radiation, microwave heating and sunlight on degradation level of OCP's: The results indicated that the effect of γ-radiation on the degradation level of the OCP's was to some extent dose dependent, since the reduction percentage of these pesticides gradually increased from 1 to 5% at 5 KGray to 30 at 25% KGray treatment.

Effect of γ-radiation, microwave heating and sunlight on degradation level of OCP's: The results indicated that the effect of γ-radiation on the degradation level of the OCP's was to some extent dose dependent, since the reduction percentage of these pesticides gradually increased from 1 to 5% at 5 KGray to 30 at 25% KGray treatment. Furthermore, it is evident that all of the selected OCP's were subjected to the same degree of degradation, regardless of their chemical nature (Table 2).

It is worth to mention that the highest dose of γ-radiation that commonly used for food preservation is between 1 up to 5 KGray and the maximum allowed dose set by WHO is 10 KGray. This dose resulted in 8% reduction of the selected OCP's, which reflect their high stability at these doses. The results obtained is in agreement with the results obtained by Mallatou *et al.*[10], Ganzhag *et al.*[11], Benard *et al.*[1] and Basa *et al.*[13] who found the use of heat treatment has only little effect on OCP's when compared with the use of γ-radiation at 25 KGray. Acreo *et al.*[14] reported that degradation of pesticides by γ-radiation resulted from the generated high-energy photons which break molecular bonds in organic molecules and produces-OH radicals that drive photon-oxidation process.

In case of the microwave heating, the data in Table 2 exhibit that the heat treatment for 2 min was of insignificant effect on all selected OCP's, since their degradation level was below the detection limit of the method (<0.5 ppb). However, their degradation levels after 5 min microwave heating was variable and ranged between 2% for aldarin, heptachlore epoxide and γ-chlorine and 10% for α-BHC. Extending the heat treatment for further 5 min affect aldarin, heptachlore, 4, 4'-DDT and α-BHC, since the increase in their degradation level was 50, 50, 25 and 20% of that observed after 5 min of heating. Whereas, the other OCP's did not affected by extending the heat treatment for 5 min.

The effect of sunlight exposure on OCP's for 10 h was also variable and ranged between 10 and 20% as shown in Table 2. The degradation level for 4, 4;-DDD, endrin, heptachlor, endosulfan I and endosulfan sulfate were 10. 12 and 15, 18 and 18%, while for the other OCP's was 20%. Exposure of the selected pesticides to sunlight for 20 h affected only 4, 4;-DDD, endrin, heptachlor, endosulfan I and endosulfan sulfate, since their degradation levels reached 20%. The increase in the degradation levels of these five pesticides were 100, 67, 33, 11 and 11% respectively of degradation levels after 10 min of sunlight exposure.

The results obtained from microwave heating and sunlight exposure revealed that the effect of these two treatments on OCP's degradation was not time

dependent, since the degradation reached a maximum value then remains constant during the rest period of the experiment. This finding needs further studies to verify the mechanism by which the OCP's degraded by these two treatments.

CONCLUSION

The SPME methods for analyzing OCP'S was found to be an excellent alternative method in multiresidues analytical technique and it is equivalent to those obtained by the conventional method which involved extraction, clean-up (SPE or Florisil). Therefore, the SPME is a precise and fast method for OCP's determination to be used as a method of choice. The γ-irradiation, microwave heating and solar radiation has limited effect on the levels of OCP's in food products. The increase in the types of fruit juices imported from abroad and the threat that could be imposed on human health from chemical residues particularly from OCP's that considered as a carcinogenic compounds urges the use of SPME which provides a good solution for OCP's analysis as fast and low cost monitoring tools with detection limits of ≥0 .50 ppb. On the other hand, the fate of pesticides residues must be studied before recommending the use of radiation dose or microwave heating in food processing, because the treatment of apple juice with either the γ -ray or heating in a microwave caused ~ 30% degradation which might lead to generation of harmful chemical degredants.

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