HAZARD ANALYSIS OF CRITICAL CONTROL POINTS (HACCP) OF SOME POST HARVEST PESTICIDE IN ORANGE FRUIT

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The present work was conducted in one of an Egyptian food processors company with the purpose of identifying critical control points (CCP's) and reducing pesticide residues contaminating incoming raw orange throughout the manufacturing steps. This would certainly improve the quality and ensure the safety of the final food products.

The results revealed that the criteria to determine loss relative to initial and successive steps of post harvest residues in treated orange raw material along different manufacturing procedures. Sodium ortho-phenyl phenate 36% (SOPP), Imazalil 80% and thiabendazole 98% (TBZ) were added to orange raw material in packinghouse with application rate 2 %.

In case of SOPP and Imazalil application the washing and drying steps 4 and 5 could be considered as the CCP's along orange fruit processing line. The loss percentages of residue relative to initial step were 53.8 ± 1.67 %, 30.63 ± 2.3 % at step 4 . However, SOPP and imazalil percentages of loss were 60.1 ± 1.7 % and 39.47 ± 3.19 % at step 5 respectively. The pattern of TBZ residues suffered dissipation after drying (step 5) 15.27 ± 8.85 % loss relative to initial. Washing and drying steps certainly decreased the initial residues in the end product.

تحليل المخاطر لنقاط التحكم الحرج لبعض مبيدات ما بعد الحصاد فى ثمار البرتقال.

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المعمل المركزى لتحليل متبقيات المبيدات والعناصر الثقيلة فى الاغذية مركز البحوث الزراعية

تم إجراء هذه الدراسة فى خطوط معالجة وتعبئة ثمار البرتقال فى احد المصانع المصرية يهدف هذا البحث الى تعيين نقطة التحكم الحرج وخفض متبقيات المبيدات التى تتم معاملة البرتقال بها قبل التعبئة الى أقل مستوى مما يؤدى الى تحسين جودة المنتج النهائى وتأكيد سلامته.

وقد اوضحت الدراسة العوامل التى تؤدى الى خفض متبقيات المبيدات التى تتم معالجة ثمار البرتقال بها بعد الحصاد خلال مراحل التجهيز والتعبئة المختلفة حيث يضاف كل من orthophenyl - sodium phenate ٣٦% (sopp) و imazalil ٨٠% و thiabendazole ٩٨% الى ثمار البرتقال الخام والمعده للتعبئة فى محطات التعبئة والتجهيز بنسبة٢% .

تبين من النتائج ان مرحلة الغسيل (الخطوة الرابعة) تعتبر هى نقطة التحكم الحرج حيث انه يتم التخلص من نسبة كبيرة من sopp ، imazalil حيث بلغت ٥٣,٨ % ، ٣٠% على التوالى . كما اوضحت الدراسة ايضا أنه فى المرحلة الخامسة يتم فقد ٦٠% ، ٣٩% من sopp وimazalil على التوالى وقد وجد ان متبقى مركب TBZ عند التجفيف (المرحلة الخامسة) ينخفض بنسبة ١٥,٢٧% وبذلك تكون مرحلتى الغسيل والتجفيف تؤدى الى خفض متبقيات هذه المركبات بصورة واضحة فى المنتج النهائى.

INTRODUCTION

Due to increasing extent of industrialization and technological development and their growing entanglement with degradation of

environmental quality of human, animals, plant and materials, the awareness of environmental problems has spread through almost societies not only in industrialized nations but also in developing countries (Codex, 1984).

The Hazard Analysis critical control point (HACCP) system identifies hazards and measures for their prevention and control to ensure the safety of food. HACCP is a tool used to asses hazards, estimate risks and establish specific control ensures that emphasize prevention and control rather than reliance an end product testing and traditional inspection methods. The HACCP system is capable of accommodating change, such as advances in equipment design, improvement in processing procedures and technological developments related to product. In addition to enhance food safety, the benefits of applying HACCP include better use of resources and more timely response to production problems.

Pesticide residues tolerance established by US Food and drug administration USDA apply to the raw agricultural commodities. The low simply provides that no action will be taken against manufactured or processed food if the residues are with in tolerance and if pesticide compound have been removed to the extent possible in good manufacturing practice.

The intent of regulatory agencies and food manufacturers is to minimize the exposure of the public to pesticides compounds that remain at harvest (Edwared, 1986).

The purpose of the present study is to increase the quality of manufactured food through the determination of critical control points, establishing corrective action when there is a deviation in critical control points and the loss percentages of pesticide residues during manufacturing steps to improve the quality and ensure the safety of final food products. SOPP, Imazalil and TBZ pesticides residues were subjected for analysis that have been recommended to be use at packaging and preparing of orange for exportation to avoid a wide range of fungal diseases e.g. powdery mildews, storage diseases of citrus fruit

MATERIALS AND METHODS

Sampling

Orange fruits were treated with SOPP 36 % , Imazalil 80% and TBZ 98% as post harvest pesticides with application rate 2 % .Samples of oranges were taken from each step of six steps along processing line for residue analysis

Three represented samples 5 kg each were collected from each six steps along processing line of orange in order to determine CCP's. Two kg from each sample was prepared according to Codex Guidelines 1993.

Sampling was performed according to the generally recommended method of sampling to achieve a representative part of the material to be analysed Codex 1993.

The analysis of samples was carried out immediately on their arrival to the laboratory or they were stored at 0-5 oC

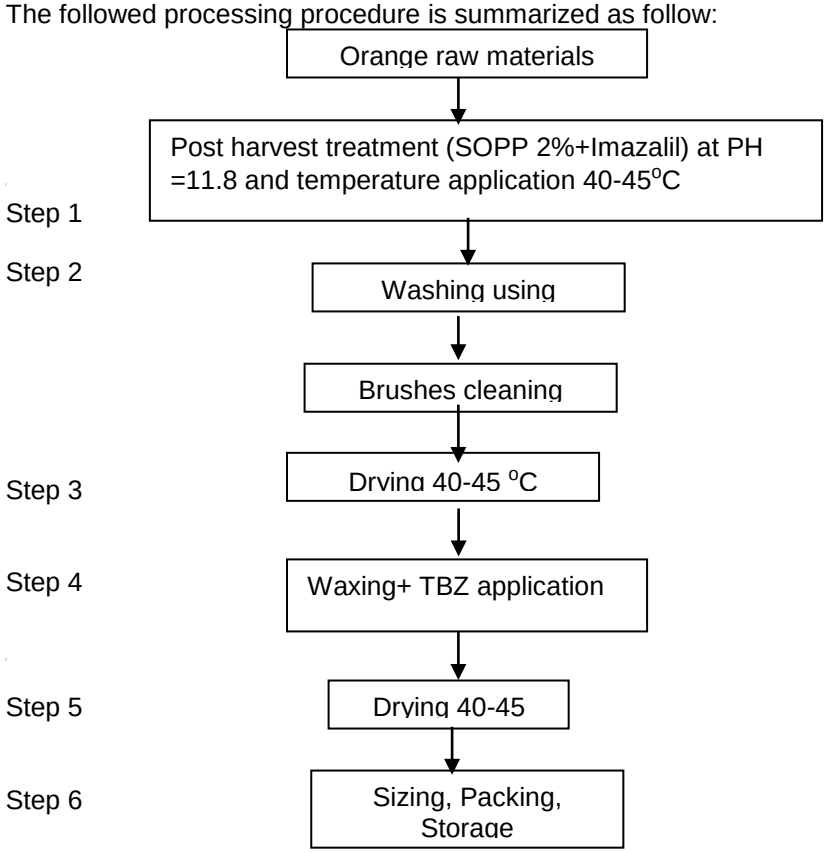
Extraction and Cleanup

Two methods were used in analysis; multiresidue method for imazalil, SOPP and the second for TBZ analysis.

1- Multiresidue method: -

According to the method described by Luke et al, 1981, residues are extracted from orange samples by blending with acetone. The pesticides are transferred from the aqueous filtrate into organic phase by shaking with petroleum ether and dichloromethane after drying, organic phase is concentrated just to dryness and dissolved in hexane /acetone for GC determination. The method allows the determination of imazalil and SOPP residues.

The followed processing procedure is summarized as follow:



2- Thiabendazoles (TBZ) analysis:-

Spectrophotometric method that described by Mesteres et. al 1977 was followed. This method allows determination of TBZ, the sample was made alkaline and residues extracted with ethyl acetate. The clean up was made by liquid-liquid partitioning with diluted HCL and alkaline ethyl acetate. TBZ was collected in 0.1 N HCL saturated with ethyl acetate and detected by UV spectrophotometer, Dogheim et al 2001 .

Determination

1- Imazalil

Gas chromatography with electron capture detector (ECD) was used in identification. The detection and confirmation of presence of residues of imazalil in orange samples depends on the use of chromatography columns of different polarities. Quantitative determinations were made using internal standard technique. Aldrin was used as an internal standard used with electron capture detector (ECD).

2- SOPP

Samples were injected in GC-MS after extraction with the previous proposed method (the multiresidue method). Different concentrations of SOPP, 0.1, 0.3, 0.5 and 1 ug/ml was used to establish the standard curve. External standard technique was followed in identification.

3- TBZ

UV spectrometer was used in identification of TBZ using external standard technique. TBZ was measured at wavelength, 302 nm. A solution of 0.1 N HCL saturated with ethyl acetate was used as blank.

Quality assurance procedure

The criteria of quality assurance of the Codex Committee were followed to determine the performance of the followed method. All analytical methods and instruments were fully validated as part of a laboratory quality assurance system and were audited and accredited by FINAS (Centre for Metrology and Accreditation) Helsinki, Finland. This quality system is referred to ISO guide 25, EN- 45001.

The spike levels, average recoveries and standard deviations were demonstrated. Imazalil and SOPP were exhibit validation work described in table (1)

Table (1): Recoveries, limit of determinations and coefficient variances % of Imazalil, SOPP and Thiabendazole on orange fruits.

Compound	Spiking level mg /kg	LOD mg/kg	Matrix	No. of samples	Average recovery %	CV %
Imazalil	1	0.3	Orange	36	106	7.4
SOPP	0.1	0.1	Orange	10	84	3.2
Thiabendazole	0.1	0.1	Orange	7	93	8
	0.2			18	88	16
	4			5	80	1.4

CV= coefficient variance (relative standard deviation divided by mean)LOD= limit of determination

Apparatus

1- Gas chromatography. – Hewlett Packard (HP) 5890 (USA) equipped with double Electron Capture Detector (ECD) with two capillary columns., injector 225 oC , detector 300 oC .
Operating conditions: Nitrogen carrier gas 2.5 ml/min, 75-90 ml/min (carrier + make up), column head pressure 82 Kpa.

2- Mass Spectrometer: Hewlett Packard (HP) 5890 plus series II equipped with mass detector (USA)

3- Spectrophotometer UV: Shimadzn, double beam Unicam SP 1800.

Chromatography Columns

(1) PAS-5 tested ultra 2 silicon, 25m x 0.32 mm, and film thickness 0.52 um

(2) PAS - 1701 tested 1701 silicon, 25 m x 0.32mm, film thickness 0.25 um. Both column are used for ECD

(3) PAS-5 MS tested ultra 2 silicon, 30m x 0.32 mm, and film thickness 0.52 um

Temperature programmes of ECD and Mass GC instruments were; initial temperature 90 oC for 2 min, ramp (1) 20 (oC / min) to 150 oC, ramp (2) 6 (oC/min) to 270 oC hold 15min.

Solvents

-Acetone, dichloromethane, n-hexane, petroleum ether, Ethyl acetate (Pestiscan chromatography grade or similar quality)

-Hydrochloric acid Merck

-Anhydrous sodium sulphate (Riedel-de Haen), sodium chloride, sodium hydroxide (Merck) and ammonia solution (Merck).

Reagents

-0.1 N HCL, 0.1 N sodium hydroxide, 2 N sodium hydroxide and concentrated ammonia solution.

Pesticide standard reference

Imazalil , SOPP, Thiabendazoles reference materials are certified standard provided by Dr. Ehrenstorfer Gmbh, Gogginger Str. 78 D- 8900 Augoburg Imazalil and SOPP prepared in n-hexane /acetone mixture, TBZ is prepared in 0.1 N HCL.

RESULTS AND DISCUSSION

Despite lack of information in the magnitude of health and environmental problems associated with pesticides use in Egypt, the few incidents that are brought to public attention in recent years clearly demonstrate the need for a nation wide commitment for the safe handling of these hazardous chemicals.

This study demonstrates that SOPP, Imazalil and TBZ residues can be removed during the washing and processing operations that intervene between harvest and use.

Orange fruits were treated with SOPP 36 %, Imazalil 80% and TBZ 98% as post harvest pesticides with application rate 2 %. Samples of oranges were taken from 5 steps along processing line for residue analysis. The levels

of dissipation are illustrated in fig (1), while the percentage of loss are summarized in table (2)

SOPP treatment:

The pattern of SOPP dissipation along the orange processing in samples received from the packinghouse was indicating that samples did not contain excessive residues hazardous to consumers (The MRL of SOPP in citrus fruits is 5 mg/kg) table (2).

Step 4 could be considered as the (CCP) Critical Control Point along orange fruit processing line. However, the loss percentage of residue relative to initial step was 53.8% Whereas, 25.8% of SOPP residues was eliminated due to this step. The data obtained showed that the percentage of residue loss in the end product at step 5 is 60.1% of the initial residues while this step remove only 13.6% of SOPP residues figure (1). fig1 من الأصل table2 It was proven that , washing step (step 4) is the more effective than drying (step 5) and consider that this is the CCP of SOPP.

Imazilil treatment:

The results of determination of imazalil residues in oranges samples collected throughout the different processing steps are demonstrated in Table (2). The analysis was conducted following supervised post harvest treatment with imazalil 80% at rate of 2%.

The data demonstrated that the drying process at 40-45C (step 5) of orange fruits is eliminated 39.5% of imazalil residue relative to initial step. The loss percentages (12.7%) represents the most percentages of loss along processing steps. Washing also contributed to 30.6% rate of loss relative to initial step. As for CCP, washing (step 4) and drying (step 5) had contributed to the reduction of Imazilil level table(2).

TBZ treatment:

The results in table (2) demonstrated that the pattern of Thiabendazol 98% (TBZ) treated in orange fruits as post harvest with rate of 2% suffered dissipation after drying (step 5) 15.3% loss relative to initial. Previous studies, El-Marsfy, 1995 found that washing of treated orange fruit leads to 100 % elimination of TBZ residue. However, TBZ appeared in orange peel after blanching, this indicate that TBZ dose not penetrate into the pulp but only into peel. It was concluded that the amount of residue completely disappeared after washing, reappeared after blanching, then vanished completely after mashing. As far as CCP washing step was considered as critical control point.

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Table (2): Loss percentage of SOPP, Imazalil and TBZ at different processing steps after treatment at recommended doses

1- Initial treatment with SOPP 2% and imazalil 2% with
2- Loss percentage of relative to initial step
3- Loss percentage of between successive step