

Effect of Ozonation Treatment on Methomyl, Oxamyl and Carbosulfan Residues Removal in Tomato Juice

Maher Mahmoud Al-Dabbas¹, Asma Mohammed Shaderma², Tawfiq Mustafa Al- Antary³

¹ Faculty of Agriculture, Department of Nutrition and Food Technology, The University of Jordan, Amman, 11942 Jordan

² Ministry of Agriculture, Amman, Jordan

³ Faculty of Agriculture, Department of Plant Protection, The University of Jordan, Amman-Jordan
m.aldabbas@ju.edu.jo

Abstract: The effect of ozonation treatment for 3, 5, 10, 15 and 30 min at concentration of 0.4 ppm on methomyl, oxamyl and carbosulfan pesticides residues removal in spiked tomato juice was studied. In our previous work on monitoring of carbamate pesticides residues in tomato juice, we found that methomyl residues was the most prominent residues, while oxamyl and carbosulfan residues were not detected in any of the studied tomato juice samples. Ozonation of spiked tomato juice samples at different concentration levels of methomyl, oxamyl and carbosulfan was found to be an effective treatment in removal of carbamate pesticides residues. Complete removal of carbosulfan and oxamyl pesticide from spiked tomato juice was achieved after 15 and 30 min of ozonation, respectively, regardless of the spiked concentrations studied. Removal percentage of methomyl, oxamyl and carbosulfan pesticide residues from spiked tomato juice samples was highly affected by residues initial concentration and ozonation time.

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1. Introduction

Modern agricultural activities are closely associated with intensive use of pesticides to control plant pests, to increase the yield of cultivated areas, to keep the cost of food production low and to maintain an abundant, affordable supply of fruits and vegetables in the market. However, a public concerns from potential adverse health effects and possible cancer hazards due to high consumption of fruits and vegetables that contain pesticide residues have been much discussed (Engel *et al.*, 2005; Ragin *et al.*, 2013; Laden and Hunter, 1998; Welp *et al.*, 1998; Ahlborg *et al.*, 1995).

Tomatoes, one of the major produced crops in Jordan, have been treated intensively with pesticides to control pests especially *Tuta absoluta* and white fly in large quantities (Ministry of Agriculture, 2011). Carbamate was found to be an effective group of pesticides to control plant pests by contact or systemically (Worthing and Hance, 1991). The produced tomatoes are consumed locally as fruits, salads or processed like tomato paste, tomato soup and ketchup. In 2010, Jordan produced 2310 tons of tomato processed products, the total consumed amount of tomato processed products including imported tomato juice in local market was 6181 tons/year (Department of Statistics, 2010). Furthermore, the per capita consumption of processed tomato products in Jordan was about 1 kg/year (Department of Statistics, 2010).

Food and Agricultural Organization (FAO) database showed that in 2010 around 5297.71 tons of carbamate pesticides were used in different regions of the world (FAO, 2010). Of these pesticides, methomyl and oxamyl were classified by the World Health Organization (WHO) as highly hazardous (class IB), and carbosulfan classified as moderately hazardous (class II) (WHO, 2009). Carbamates are absorbed through skin and from the gastrointestinal tract. They are also readily absorbed by inhalation when vapors are formed. Once absorbed, the carbamates are distributed rapidly into tissues (Krieger *et al.*, 2002). The acute toxicities of the carbamate pesticides ranged from high to very low by the following oral LD₅₀ values to the rats; 32, 2.8, and 218 mg/kg for methomyl, oxamyl, and carbosulfan, respectively (Worthing and Hance, 1991).

Carbamates have been observed to cause oxidative stress by the generation of free radicals in rat tissues; these free radicals play an important role in toxicity of pesticides (Banerjee *et al.*, 1999; Kamboj *et al.*, 2006). Carbamates also have the ability to inhibit AChE in the nervous system, the enzyme responsible for breakdown and termination of the activity of ACh by catalyses the hydrolysis of the neurotransmitter ACh to choline and acetic acid (Hassall, 1996). When carbamate pesticides enter the nervous system it will compete with ACh for its active site, leads to the accumulation of ACh in the synapses (Krieger *et al.*, 2002; Hassall, 1996).

Lehotay *et al.* (2005) showed that methomyl, methomyl-oxime, oxamyl and oxamyl-oxime had recoveries greater than 90% upon using QuEChERS method for extraction and using GC-NPD (Gas Chromatography with Nitrogen Phosphorous Detector) for determination of these carbamate pesticides from different food matrices. Soler *et al.* (2007) showed that LC-MS-MS (Liquid Chromatography Equipped with Tandem Mass Spectrometry) was an efficient technique to determine carbosulfan and its seven degradation products sensitively and accurately at low detection limits of 10 µg/kg.

Ozone is a powerful and strong oxidizing agent that have been used in food industry in many countries including the USA, Japan, Australia, France and Canada since it was approved by United State Food and Drug Administration (USFDA) as an food additive for direct contact with foods for all types of treatments including; washing in water containing ozone, storage in ozone rich atmosphere and direct addition of ozone in fluid food (FDA, 2001). Ozone could be used in an aqueous phase and in a gas phase. In addition, ozone usage in food processing has become increasingly important as a result of its affirmation as Generally Recognized as Safe (GRAS) chemical in 1997 (Gerham *et al.*, 1997).

Ozonation of organic compounds present in food is a complex mechanism involving a variety of possible chemical reactions and considered as a novel technique to remove pesticide residues from fruits and vegetables (Zang *et al.*, 2011; O'Donnell *et al.*, 2012; Chen *et al.*, 2012; Lau *et al.*, 2007; Lkeura *et al.*, 2010; Mico *et al.*, 2010).

Chen *et al.* (2012) investigated the efficiency of a novel machine to remove permethrin, chlorfluazuron and chlorothalonil pesticide residues from Chinese white cabbage using ozone in a domestic-scale vegetable cleaner. The average percentages of pesticides reduction after 15 min of treatment at ozone output rate of 150 mg/h were 51.8%, 55% and 60% for permethrin, chlorfluazuron and chlorothalonil, respectively. However, as the time of treatment increased to 30 min, the percentages of reduction increased up to reach 67% and 64% for chlorfluazuron and chlorothalonil, respectively.

Ozone is considered a strong oxidizing agent that is easily decomposed into oxygen because it is not stable compound. It does not affect the flavor of vegetables or fruits, and has a minimal or no effect on nutritional quality of food (Ölmez and Akbas, 2009; Chen *et al.*, 2014; Tiwari *et al.*, 2010).

Lin and Hay (1990) found that the processing of tomatoes could not eliminate carbamate oximes, since they found oxamyl residues in washed tomato, whole canned, wet pomace, juice, paste, ketchup, puree and

dry pomace, in concentrations of 0.2, 0.11, 0.06, 0.18, 0.54, 0.36, 0.24 and 0.02 ppm, respectively. Therefore ozone can be used as a safe process for the removal of pesticides residues.

In the recent years, the word attention has focused on the removal of pesticide residues by different treatments like; cooking, ozonation, UV-radiation, washing and peeling. It is noticed that these treatments are of great benefits to have safe and healthy food and met the standards for pesticide residue limits in foods.

The objective of this study is to examine the effect of ozonation using domestic home ozonation unit at concentration of 0.4 ppm for different periods of time on the recovered amounts of methomyl, oxamyl and carbosulfan insecticides of spiked tomato juice samples at different concentration levels.

2. Material and Methods

Chemical Reagents and Standards

Anhydrous magnesium sulphate (MgSO₄, assay 99%) (Sigma-Aldrich, Saint Louis), Acetonitrile (CH₃CN, HPLC-grade, assay 99.8%) (LAB-SCAN analytical sciences, Dublin), Acetic acid (CH₃COOH, assay 99%) (J. T. Baker, USA), Acetone (C₃H₆O, GC-grade, assay 99.8%) (LAB-SCAN analytical sciences, Dublin), Sodium chloride (NaCl, assay 99.9%) (AVONCHEM, Cheshire), Primary Secondary Amine (PSA) sorbent, with 40 – 60 µm particle size (Agela Technologies, Wilmington). Standards of oxamyl (C₇H₁₃N₃O₃S), Carbosulfan (C₂₀H₃₂N₂O₃S) and ditalimifos (C₁₂H₁₄NO₄PS) pesticides standard materials were obtained from (Dr. Ehrenstorfer-GmbH, Augsburg) with certified purity of 97%. Methomyl pesticide (C₅H₁₀N₂O₂S, assay 99.5%) was purchased from (Sigma-Aldrich, Saint Louis, USA).

Tomato Juice Samples

Forty five tomato juice samples were collected from the Jordanian local market and analysed for methomyl, oxamyl and carbosulfan residues. The size of each sample requested for pesticides residues analysis was (0.5L) as recommended by Codex Alimentarius sampling guidelines (FAO/ WHO, 1999).

Effect of Spiked Tomato Juice Ozonation at 0.4ppm on the Stability of Methomyl, Oxamyl and Carbosulfan

To investigate the removal pattern of methomyl, oxamyl and carbosulfan pesticides residues in tomato juice, five tomato juice samples (1 L each) (free from carbamates residues) were spiked with five different concentrations (0.1, 0.5, 1, 5 and 10 ppm) from each of methomyl, oxamyl and carbosulfan. Each sample was treated with 0.4 ppm ozone for 3, 5, 10, 15 and 30 minutes using Zaet fruits and vegetables Washer (Zhengao Environmental Protection Industrial Co., Ltd., Guangdong, China). The effect of ozone

treatment on methomyl, oxamyl, and carbosulfan were evaluated by analysing tomato juice samples before and after the treatment. The spiked tomato juice samples were held inside the cleaning chamber during ozone treatment. Samples were taken separately after 3, 5, 10, 15, and 30 minutes for each pesticide determination. Each sample was extracted by QuEChERS method and analysed using GC-NPD to determine the recovered amounts of methomyl, oxamyl and carbosulfan in order to evaluate the efficiency of ozonation on the removal percentages of methomyl, oxamyl and carbosulfan with time.

Control Samples

Five control tomato juice samples were spiked with 0.1, 0.5, 1, 5 and 10 ppm of methomyl, oxamyl and carbosulfan and kept under room conditions for 30 min to investigate the effect of natural light exposure and room temperature on methomyl, oxamyl and carbosulfan reduction percentages, samples were taken after 3, 5, 10, 15 and 30 min for each pesticide determination.

Extraction of Pesticides

The method used for extraction of pesticide residues from tomato juice samples was QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe). It is based on the extraction of pesticide residues from food by acetonitrile followed by partitioning with anhydrous magnesium sulphate (Anastassiades *et al.*, 2003). Homogenized tomato juice samples were extracted by taking ten grams into 50 ml Teflon centrifuge tube followed by addition of 10 ml of acetonitrile acidified with 1% acetic acid. The mixture is then shaken by Vortex mixer for 1 min at low speed and loaded with 4 g of anhydrous MgSO₄ and 1 g of NaCl, then vortexed again for 1 min. Ditalimifos at concentration of 0.5 ppm was then added to the mixture as an internal standard. Finally, sample was vortexed for 30 s and centrifuged at 3000 rpm for 5 min. Sample extract by the end of this step was ready for clean-up.

Samples Clean-up

For clean-up, 1 ml of the upper acetonitrile layer for each sample was transferred into 10 ml centrifuge tube containing 25 mg Primary Secondary Amine (PSA) as sorbent and 150 mg anhydrous MgSO₄, then it was vortexed for 30s. As a final step the centrifuge tube was centrifuged at 3000 rpm for 5 min then the extract transferred into 2 ml GC vial. Since acetonitrile is not compatible with NPD detector, it was replaced completely with acetone after flushing with nitrogen gas. After that samples were analysed with GC-NPD to determine the residues of methomyl, oxamyl, and carbosulfan.

Detection Limits and Recovery percentages

To assess the efficiency of the extraction method, detection limits and recovery percentages

were determined for each pesticide included in this study. To determine the minimum detection limit for methomyl, oxamyl and carbosulfan six independent blank tomato juice samples were extracted and injected using GC/NPD. The DL for methomyl, oxamyl, and carbosulfan were calculated according to the following equation (Muir and Sverko, 2006):

$$DL = \bar{X} + (3 \times SD)$$

After determination of DL for each pesticide, a blank sample was spiked with this concentration and determined by GC-NPD. On the other hand five free tomato juice samples of any pesticide were spiked with different standard concentrations for each of methomyl, oxamyl and carbosulfan to determine its recovery according to the following equation:

$$\text{Recovery percentage (\%)} = \frac{(\text{ppm pesticide detected})}{(\text{ppm pesticide added})} \times 100$$

Methomyl Determination by GC-NPD

The chromatographic system consisted of a gas chromatography (Agilent Technologies 6890N, USA) with nitrogen phosphorous detector, splitless injector and the HP-5 capillary column (30 m X 0.32 mm, 0.52µm). The carrier gas was helium. The operating conditions were: injection volume was 1 µl. The temperature program was: injector temperature 250°C, and detector temperature 300 °C (Delgado *et al.*, 2001). The oven temperature program was modified to get the desired response for methomyl as follows: initial temperature 60 °C for 1 min; 5 °C min⁻¹ to 90 °C for 1 min; 20 °C min⁻¹ to 150 °C for 1 min; 6 °C min⁻¹ to 270 °C for 1 min (Delgado *et al.*, 2001). For data acquisition ChemStation software was used.

Oxamyl and Carbosulfan Determination by GC-NPD

The same instrument used for determination of methomyl was used for determination of both oxamyl and carbosulfan but with different oven temperature program as follows: initial temperature was 70 °C for 1 min; 12 °C min⁻¹ to 280 °C for 15 min (Delgado *et al.*, 2001). For data acquisition Chem-Station software was used.

Statistical Analysis

The design of the experiment was Complete Randomised Design (CRD) with three replicates. Mean values and standard error were calculated and analysed. The obtained data were subjected to statistical analysis using MSTAT-C programme version 1.4, were Least Significant Difference test (LSD) was used at 0.01 probability level. The obtained results from this experiment were summarised in tables in the results section.

3. Results and discussion

Detection Limits (DL)

The results for the analysis of three blank tomato fruits samples showed that the minimum detection limits were 0.0032, 0.0039 and 0.0063 ppm for

methomyl, oxamyl and carbosulfan, respectively, using QuEChERS method for extraction and GC-NPD for determination. Delgado *et al.* (2001) found that the detection limits of methomyl and carbofuran were 0.006 and 0.003 ppm, respectively, using same method of extraction and determination of these carbamate pesticides from powdered potatoes. In addition, similar results were reported by Berger *et al.* (1993), who showed that carbamates were directly and selectively detected using gas chromatography equipped with NPD detector with detection limits ranging from 0.003 to 0.06 ppm.

Recovery Test

As shown in Table 1, the mean recoveries percentages from blank tomato homogenized samples of methomyl, oxamyl and carbosulfan were ranged from 96.4% to 98.2% for methomyl, 92.8% to 94.3% for oxamyl and 85.4% to 87.3% for carbosulfan.

Methomyl, oxamyl and carbosulfan recoveries were found in the range of 96.4% to 98.2% for methomyl, 92.8% to 94.3% for oxamyl and 85.4% to 87.3% for carbosulfan using GC-NPD and QuEChERS method for extraction. In agreement with these results, Lehotay *et al.* (2005) found that the recoveries for methomyl and oxamyl were > 90% for different commodities. Moreover, Glauner (2012), achieved 98.9% and 103.3% recoveries for methomyl and oxamyl, respectively, from tomato fruits samples in a study performed to validate QuEChERS method for extraction of 313 compounds in different commodities.

Effect of tomato juice ozonation

As shown in Figure 1, 2, 3 and 4 carbosulfan reduction percentages after ozonation at 0.4 ppm for 3, 5, 10, 15 and 30 min were higher than that of oxamyl and methomyl for all of the spiked concentration levels. After 3 min of ozonation, carbosulfan maximum reduction percentage was 81.82% when spiked juice concentration was 0.1 ppm (Figure 1), while for oxamyl and methomyl were 76.92% and 63.27%, respectively. Carbosulfan reduction percentage reached 100% after 5 min of ozonation treatment, while oxamyl reduction percentage reached 100% after 10 min, and methomyl reduction percentage reached 100% after 15 min at spiking level of 0.1 ppm. After 30 min of ozonation, oxamyl and carbosulfan reduction percentages increased to reach 100% for the spiked concentration levels of 0.1, 1, 5 and 10 ppm (Figures 1-4). The reduction percentages for methomyl after 30 min of ozonation for the spiked concentration levels of 5 and 10 ppm increased to reach 98.77% and 92.13%, respectively (Figure 3 and 4). The results of the statistical analysis showed that there were significant differences ($P \leq 0.01$) between methomyl, oxamyl and carbosulfan reduction percentages at 3, 5, 10, 15 and

30 min after ozonation treatment for all the spiked concentration levels.

Table 1. Recovery percentages and retention time of methomyl, oxamyl and carbosulfan pesticides from tomato juice samples spiked with different concentration levels, using GC-NPD.

Pesticide: retention time (min)	Spiked amount (ppm)	Recovery %*± SE
Methomyl : 3.749	0.1	96.7 ± 0.9
	0.5	97.2 ± 1.2
	1.0	96.4 ± 1.0
	5.0	96.9 ± 1.6
	10.0	98.2 ± 0.4
Oxamyl : 6.510	0.1	92.8 ± 0.9
	0.5	93.3 ± 1.2
	1.0	93.6 ± 0.5
	5.0	94.2 ± 1.5
	10.0	94.3 ± 1.8
Carbosulfan : 19.329	0.1	85.4 ± 0.4
	0.5	86.0 ± 0.7
	1.0	86.4 ± 0.6
	5.0	86.7 ± 0.6
	10.0	87.3 ± 0.7

Methomyl, oxamyl and carbosulfan recovered amount decreased significantly with time after ozonation treatment at 0.4 ppm to reach a concentrations that are below the EU-MRL after 30 min of treatment (Eu, 2005). Methomyl, oxamyl and carbosulfan reduction percentages were increased with increasing ozonation exposure time. More than 90% reduction percentages were achieved after 15, 10 and 5 min for methomyl, oxamyl and carbosulfan, respectively. The ability of ozonation in reduction of these pesticides amount is related to the ability of ozone to generate hydroxyl radicals in aqueous solution, which are highly effective to decompose methomyl, oxamyl and carbosulfan, so as the time of exposure increased hydroxyl radicals continued to be generated throughout the treatment, and more residues degraded.

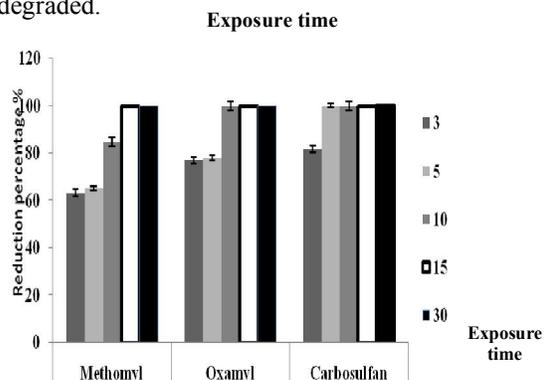


Figure 1. Effect of tomato juice ozonation on degradation of methomyl, oxamyl and carbosulfan at 0.1 ppm for different exposure time.

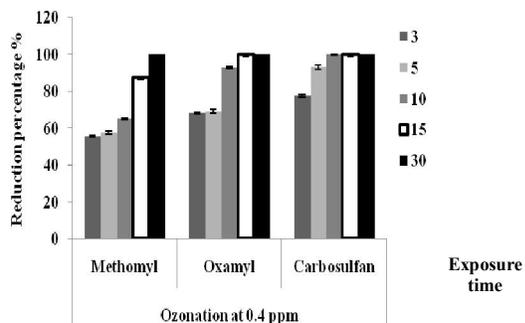


Figure 2. Effect of tomato juice ozonation on degradation of methomyl, oxamyl and carbosulfan at 1 ppm for different exposure time.

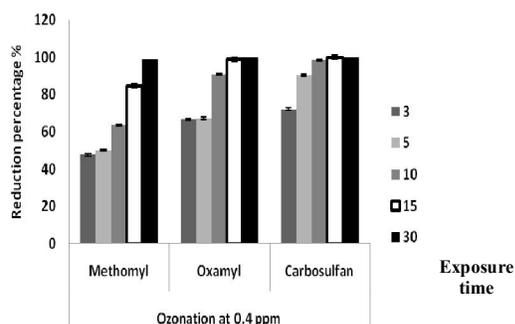


Figure 3. Effect of tomato juice ozonation on degradation of methomyl, oxamyl and carbosulfan at 5 ppm for different exposure time.

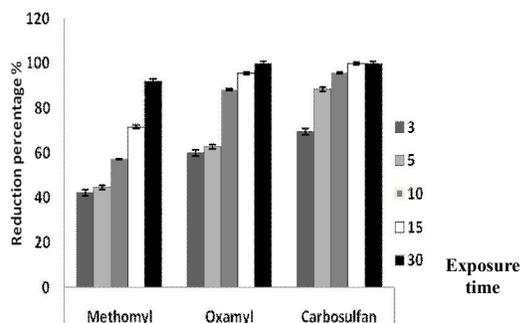


Figure 4. Effect of tomato juice ozonation on degradation of methomyl, oxamyl and carbosulfan at 10 ppm for different exposure time.

The present results agreed with the results obtained by several authors (Chen *et al.*, 2012; Lau *et al.*, 2007; Lkeura *et al.*, 2010; Mico *et al.*, 2010). The authors concluded that ozonation treatment could be considered as an efficient treatment to remove high concentrations of pesticide residues if ozone generated continuously for a sufficient time of treatment. The study of the effect of ozonation at 0.4 ppm on spiked tomato juice results showed that ozonation was an effective treatment to reduce methomyl, oxamyl and carbosulfan spiked amounts significantly below the maximum residue limits, and it is time dependent.

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Corresponding Author:

Dr. Maher Mahmoud Al-Dabbas

Faculty of Agriculture, Department of Nutrition and Food Technology, The University of Jordan, Amman, 11942 Jordan

E-mail: m.aldabbas@ju.edu.jo

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