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ORIGINAL ARTICLE

Estimation of Methomyl Residues In Tomato Samples In Alwhate City - Libya

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ABSTRACT

In the present study, it is of primary interest to estimate the methomyl residues and then the rate of disappearance of methomyl after application to tomatoes. Samples of tomatoes were collected at random from market in Alwhate city and screened for methomyl residues. Tomato plants were subjected to a single chemical treatment by applying pesticides to a crop of tomatoes as a low-volume spray using an air gun. The rates of insecticide application tested were 0.25 kg/L and 0.50 kg/L, and there were 7 replicates. These doses recommended by the manufacturers. Tomato samples were taken and the pesticide residues were extracted using dichloromethane as solvents and determined by UV- Spectrophotometry. Beer›s law was obeyed in concentration ranges of 0-0.6 mg/L, the limit of detection was 0.03 mg/L. the relative standred deviation at three concentration level were< 3%. Implying good accuracy and precision of the method. The results of the study showed that tomatoes were the crop with the highest number of pesticide residues with the predominant presence of methomyl (0.130-0.243 mg/kg). This results showed that the tested samples contained residues below the MRLs.
Key Words:*Tomato, Pesticides, Methomyl, Residues, UV- Spectrophotometry.*

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INTRODUCTION

Tomato is a second of the most common agricultural products in Alwhate- libya after dates. It is the main component for several dishes in the Libyan people diet. Tomatoes have significant nutritional value; they are a good source of vitamin C, vitamin A and antioxidants [1]. While tomatoes are fruits – botanically classified as berries – they are commonly used as a vegetable ingredient or side dish.Tomatoes have been treated intensively with pesticides to control pests especially Tutaabsoluta and white fly in large quantities [2]. It has been reported that some of the pesticides are being used in the country where no preharvest time frame after application is maintained, for that monitoring pesticides residues, and in particular.

Pesticides are worldwide used to provide a necessary remediation measure for preventing or controlling insects that can adversely affect crops by diseases, fungi or even damage to the plants. They are classified according to the pest they control. However, it has to be noted that only a fraction of the applied pesticides reaches its targets. The remaining part which is still toxicologically active accumulates and remains in the environment. These residues must be removed from the ecosystems to prevent contamination [3]. Most of fruits and vegetables are treated with pesticides on several occasions during the growing season. Pesticides enable farmers to produce some fruits and vegetables in areas that otherwise would not be suitable, increase their yields, preserve product quality, and extend shelf life. Without pesticides, commercial fruits and vegetables production would not be economically viable in many regions of the world. Insecticides and fungicides are likely to remain the major class of pesticides used for crops protection in developing countries [4]. Fungicides are applied to control a considerable number of diseases [5]. At the same time, pesticides can pose risks if they are not applied according to Good Agricultural Practice (GAP). Pesticide levels tend to decline over time as the residues on crops degrade/metabolise during their growing period and following harvest if they are washed and processed before reaching the markets.

Methomyl was introduced in 1966 as a broad – spectrum insecticide. It is extensively used as an acaricide to control ticks and spider and it is employed for foliar treatment of vegetable, fruit and field crops, cotton, and commercial ornamental plants. The pesticide is effective as both a contact and systemic insecticide [6].Methomyl (S-methyl N-methylcarbamoyloxy) thioacetimidate) has been recommended to control these pests and is proving to be a satisfactory treatment. However, incidents of poisoning after consuming fresh vegetables have been reported. These incidents were attributed to growers' misuse of the insecticide or to negligence in observing a safety interval before harvest [7].The European Commission has established that MRL must be 0.2mg/kg for pesticides residues in basic food products and food for children [8]. This compound is a very toxic compound and a major polluting agent for environment because of its high solubility in water [9].Water contamination with methomyl, both surface and deep waters, is caused by its weak absorption in soils. It can be found as an active substance in Lannate 90, Lannate 25WP, Metomex 90SP, etc. It is a carbamate insecticide used to destroy the white fruit-fly in vegetable greenhouses, the solanaceae louse of tomato, and the apple and plum-tree worm. It can also destroy the grape-vine moth and the Californian clover that attacks cucumbers in solariums [10] [11]. The toxic effect of pesticides on humans and animals varies on the basis of their chemical compositions. Smulders et al., have reported that the carbamate pesticides inhibit the brain receptors and affect different subtypes of neuronal nicotinic receptors [12].

The increasing number of environmentally significant pesticides requires development of analytical techniques. Pesticides are among the most regulated products in the world. Because of their importance in terms of consumer safety, pesticide residues have been determined using methods based on gas chromatography – mass spectrometry (GC-MS) [13], liquid chromatography-tandem mass spectrometry (LC-MS/MS) [14] liquid chromatography with UV detection (LC-UV) [15]. The Methomyl residues can be determined by spectrophotometry [16].

The aim of this study is to investigate the occurrence and concentrations of methomyl residues in some fresh tomatoes samples from domestic producers. And the rate of disappearance of methomyl after application to tomatoes was examined to establish a safety interval before harvest in alwahat city. Sensitive, selective, rapid and reproducible UV- spectrophotometric methods are presented for the determination of methomyl in tomato. Unlike the chromatographic methods, the proposed spectrophotometric methods are simple since they use an inexpensive instrument, and easy to perform. The reagents use of are cheap, easily available and the procedures do not involve any critical reaction condition.

MATERIAL AND METHODS

Reagents and solutions

Reagents and materials The reagents used were of analytical grade, and water was always double distilled, methomyl pesticide (C5H10N2O2S) - Dichloromethane were purchased from Sigma and Anhydrous magnesium sulphate (MgSO4) Aldrich Chemical Industries (St. Louis, MI, USA) and charcoal.

Field experiments

Methomyl, formulated as 'Lannate' 900 g kg^{-1} water- soluble powder, was applied at the manufacturer's recommended rate, using a knapsack sprayer fitted with a single-nozzle boom.Tomato plants were subjected to a single chemical treatment by applying pesticides to a crop of tomatoes as a low-volume spray using an air gun. The rates of insecticide application tested were 0.25 kg per L and 0.50 kg per L. these doses recommended by the manufacturers. The samples were taken for analysis at 0, 1, 3, 7, and 14 days after methomyl application.

Sampling

1 kg of tomatoes samples were collected at random from market in alwhate city. The representative samples were taken, chopped, and three representative analytical sub-samples taken for analysis as recommended by Codex Alimentarius sampling guidelines (FAO/WHO, 1999). All samples were kept in polyethylene plastic bags, labelled and refrigerated until analysis [17]. And approximately 1kg tomatoes were collected from farms in alwahat city, maturity was taken from each plot 1, 3, 7, 10 and 14 days after spraying. The samples were frozen immediately and transported to laboratory, where they were stored at approximately -18 °C.

Sample preparation

In this work based on the extraction by dichloromethane and partitioning with anhydrous magnesium sulphate was used for extraction of methomyl residues from tomato fruits [18]. Homogenized tomato juice samples were extracted as described for tomato fruits samples as follows:

0.5 kg of tomatoes were homogenized with 50 ml of distillated water. Each tomato samples were separately homogenized with dichloromethane (150- 200 ml) the down layer were collected and eluted through anhydrous sodium sulfate and charcoal (0.3-0.5 g). The dichloromethane extracts were combined and evaporated to near dryness at room temperature, dissolved in methanol (1ml) and transferred quantitatively to small glass vials for analysis by UV spectrophotometer. To examine the efficacy of extraction, three samples of tomatoes was spiked with known concentration 2 mg kg^{-1} of pure methomyl dissolved in water. Extraction was performed and the average recovery. The results were corrected according to recovery rate.

Measuring

UV- Spectrophotometer that used to detected the quantify methomyl content in tomatoes sample, in our work with UV-radiations and the wavelength corresponding to maximum absorbance, λmax, which is 233 nm for methomyl.

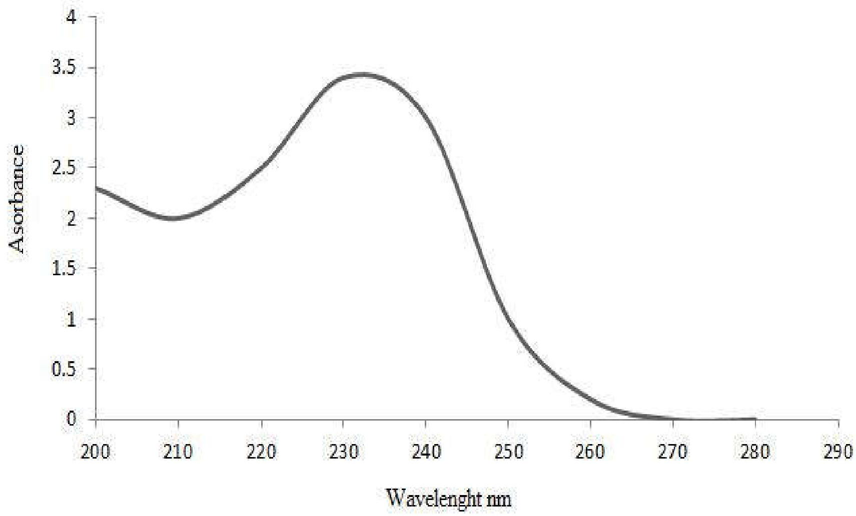

Fig. 1: Maximum absorption for methomyl

Calibration Curve

The concentration of methomyl is determined from a working curve after calibrating the instrument with standards concentration. a standard stock solution of 1 mg/L concentration methomyl,several successive dilutions there have been prepared calibration solutions of the following concentrations: 0.1 mg/L, 0.2mg/L, 0.3mg/L, 0.4mg/L, 0.5mg/L, 0.6mg/L and 0.7 mg/L, in 50mL. Each solution was extracted by dichloromethane. Good linearity was obtained in the range 0- 0.6 mg kg^{-1}.

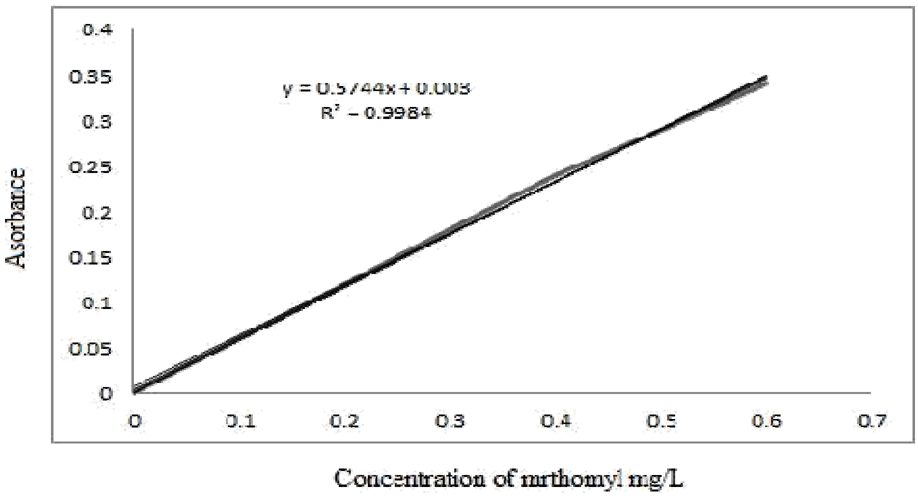

Fig. 2 Calibration curve for methomyl

A linear correlation was found between the absorbance at ʎmax and the methomyl concentration in the ranges 0-0.6 mg kg^{-1} the graphs **Fig. 2** showed a negligible intercept, as described by the regression equation: Y=0.5744X+ 0.003

Where Y is the measured absorbance, X is the concentration in mg/L and m and b are the slope and intercept respectively. Correlation coefficients(r) 0.9984 and the calculated values of limits of detection LOD is 0.03.

The Percent relative standard deviation (%RSD) as an indicator precision and percent relative error (%RE) as a measure of accuracy of the suggested methods were evaluated by replicate determination at three concentration levels. Accuracy by recovery test Pre-analyzed tomato samples was spiked with pure methomyl at three levels and the total was found by the proposed methods. The determination each level was replicated thrice. The results of percent recovery of methomyl which are an indication of accuracy are 87%, 89% and 90%, and demonstrate the methods' freedom from interference. The limit of detection was 0.03 mg/L. the relative standard deviation at three concentration level were< 3%.

RESULTS AND DISCUSSION

The results of 30 analyzed tomato samples which collected from local markets and analysed for methomyl residues are shown in Table 1.The concentration of methomylwere expressed as mg per kg (mg/kg). The mean of methomyl residues were 0.150 mg/kg.

From our result we note, the most examined tomato samples showed undetectable, As shown in Table , was observed a small variations in value , the highest concentration was found in sample 4 (0.243±0.031mg/kg) whereas the lowest concentration was found in sample 3 (0.110±0.010mg/kg). Most samples show us contain a small concentrations of methomyl, but it's not exceed the allowed limit according EU and Libyan standard specification in most samples. But in other samples exceeded the MRL value. That showed in sample 4. The possible reason for this non-compliance is over application and use of pesticides in larg quantities.

Table 1: The Residues of Methomyl detected in tomatoes Samples Collected from City Markets

***Mean of three analyses**		**ND: not detected**
Samples	**Methomyl Conc.* (mg/kg)**	**Mean± SD**
1	0.130	0.132±0.003
	0.150	
	0.130	
2	ND	
	ND	
	ND	
3	0.100	0.110±0.010
	0.110	
	0.120	
4	0.270	0.243±0.031
	0.250	
	0.210	
5	0.125	0.122±0.002
	0.120	
	0.120	
6	ND	
	ND	
	ND	
7	ND	
	ND	
	ND	
8	0.100	0.113±0.014
	0.120	
	0.120	
9	0.170	0.180±0.010
	0.180	
	0.190	
10	ND	
	ND	
	ND	

Methomyl is a carbamate insecticide with restricted use because of its high toxicity to humans. Therefore, the MRL for methomylfor the most of fruits and vegetables is set at the 0.2 mg/kg in the Regulation (EC) 396/2005. The methomyl residues were found in tomato samples from different brands. All of the

detected methomyl residues were less than 0.2 ppm, which is below the maximum residues limits established by the European Union countries (EU, 2005); e.g. UK (0.2 ppm), France (0.5 ppm) and Spain (0.5 ppm). Our results were in agreement with Al-Dabbas et al. (2014) results, the mean values of methomyl residues in tomato fruits grown in open fields ranged from0.078 to 2.468 ppm, but in plastic houses, the mean values of methomyl and residues ranged from 0.073 to 2.602 ppm [19]. In another study conducted byShaderma S et al. (2013) in Jordan, all of the detected methomyl residues were less than 0.2 ppm, which is below the maximum residues limits [20].
The residues of methomyl remaining on treated tomatoes are shown in Table 2.

Table 2: Residues of Methomyl detected in Tomatoes after Foliar Application

Rate	Time (days after spraying)				
	1	3	5	7	14 Days
0.50 mg/Kg	0.33	0.23	0.19	0.06	ND
0.25mg/Kg	0.19	0.05	Trace	ND	ND
0	0	0	0	0	0

From Table explained the average obtained from each rate of methomyl applied. For both sets of results the limit of measurability was 0.50-0.25 mg/kg; a "trace" is a probable residue which was below this value. The residue levels decreased steadily over 10 day study period, the residue level at seven day sampling was below the tolerance level 0.5 mg kg^{-1}. The results reported for the LOD values in this study compared relatively well to previous studies done by this research group for the evaluation of carbamate pesticides. The degradation of methomylresiduses are safe.In a study conducted by Ahmed & Ismail, 1995 [21]. The residue level in tomatoes at the seven-day sampling was 0.2 mg/kg $^{-1}$ which was below the tolerance level of 0.5 mg $kg^{-1}$and the residues of methomyl were 0.6 mg/kg seven days after methomyl had been applied to cucumbers.But in a study conducted by the present preliminary results would suggest that a safety interval in the range of 7-10 days should be allowed after the application of methomyl on tomatoes.

CONCLUSION

The results of the current study showed that the 60% of the samples, that were found to contain residues well below the relevant MRLs. Our investigations showed that tomatoes contained the high methomyl residues in some samples. The presence of methomyl in tomato may due to intensive uses of these pesticides against several agricultural pests in alwahat. The present preliminary results would suggest that a safety interval in the range of 7-10 days should be allowed after the application of methomyl on tomatoes.

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