Residue and Dissipation Dynamics of Tetraconazole in Tomato Fruit Using QuEChERS Methodology

A. M. Abdellseid, and Tarek. A. Abd El Rahman

***Abstract*—**An effective analytical method for the residue analysis of tetraconazole and its dissipation in tomato were studied. Tetraconazole residues were extracted from tomato samples and the extract was cleaned up according to QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method and determined by Gas chromatography (GC) equipped with detector, electron capture (ECD). At fortification levels of 0.1, 0.5, and 1.0 mg/ kg in tomato, it was shown that recoveries ranged from 89.4 % to 95.6 %. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.02 and 0.01 mg/ kg, respectively. The dissipation half-life time of tetraconazole residues in tomato was 5.02 days. According to maximum residue limit (MRL) 0.5 mg /kg, the pre harvest interval (PHI) of tetraconazole on tomato was 4 days after the treatment. Based on the results of this study and the relevant residue regulation, tetraconazole residue levels will be acceptable when applied to tomato in Libya.

***Keywords*—** Tetraconazole, Residue, tomatoes, Dissipation, Half-life and Libya.

I. Introduction

TETRACONAZOLE fungicide ((±)-1-[2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy) propyl]-1H-1,2,4-triazole, is abroad spectrum systemic triazole fungicide (1). 1t has been registered in various European countries and in Libya. This fungicide is a steroid de methylation inhibitor, acting mainly on the vegetation stages of fungi by blocking the mycelia growth either inside or on the surface of the host plant. Tetraconazole is effective in controlling a broad spectrum of diseases such as powdery mildew and scab on fruits, powdery mildew on vines and cucumbers, powdery mildew and rust on vegetables and powdery mildew, brown rust, Septaria and Rhynhasparium spp. on cereals (2). In Libya, tetraconazole (Domark 10%EC) is a broad-spectrum systemic fungicide with protective, curative and eradicant properties. Absorbed by the roots, stem and leaves with translocation a cropetally to all parts of the plant, including subsequent growth. Uses control of powdery mildew and rust on vegetables (3). Governments and international organizations are regulating the use of pesticides and are setting the acceptable MRL When these compounds are applied according to good agricultural practices, MRL are not exceeded, but there in correct application may leave harmful residues, which involve possible health risk and environmental pollution. Teratogenic, carcinogenic and toxic properties of these compounds have been reported by (5). Tomato (Lycopersicon esculentum Mill.) belongs to the solanaceae family and is one of the most widely grown vegetables in the world. Tomato is one of the basic component of the Mediterranean and Asian diet and is used almost daily in several countries, raw, home – cooked or processed as a canned product, Juice or paste a pesticides are widely used in tomato because its susceptibility to insect and disease attacks [6].

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This Study Aimed To:

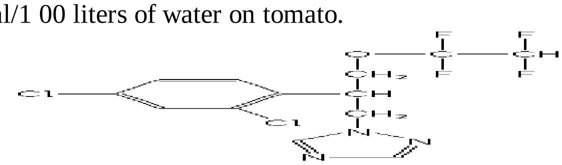
-The behaviour of tetraconazole in and on tomato fruits grown in open field.

-Determine the dissipation rate, half-life values (RL50) and pre-harvest interval (PHI) for the tetraconazole.

II. Material And Methods

A. Pesticides used

Tetraconazole (Domark 10% EC); (RS)-2-(2,4,dichlorophenyl)-3-(1H-1,2,4-triazol-1-yl) propyl 1,1 ,2,2-tetrafiuorethylether. Tetraconazole was used at the rate of 50 ml/1 00 liters of water on tomato.



Structure

B. Chemical and reagents

All organic solvents were of HPLC grade and supplied by Merck, USA. Primary and secondary amine (PSA, 40 lm Bondesil) was purchased from Supelco (Supelco, Bellefonte, USA). Anhydrous magnesium sulphate was of analytical grade, purchased from Merck, USA, and was activated by heating at 250oC for 4 h in the oven before use and kept in desiccators. A stock standard solution (100 g /ml) was

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prepared with methanol and stored at -20oC. The standard working solutions were prepared from stock solution by serial dilution with toluene at 0.01, 0.05, 0.1, 0.2, 0.5, 1.0 and 2.0 g /ml and were stored at 4ºC before use.

C. Field experiments

The experiments were carried out tomato in private farm, El-Beida city, Libya, to determine the residues of tetraconazole in and on tomato fruits. The experimental area was divided into plots of 175 m2 (1/24 Fed). The tested pesticide was applied on May 2 th 2010. The pesticide was applied using a knapsack hand sprayer fitted with one nozzle boom. Untreated plots were left as control check. Three randomized plots were treated by tetraconazole, and one untreated plot was left to serve as control. Sampling was performed by random collection from various places of the experimental plots according to the (7) recommendations.

D. Sampling

Samples of tomato with similar ripening stage, size, and shape were located and tagged. Samples about 1.0 kg were taken 1 h after the pesticide application. Subsequent samples were taken 1, 3, 5, 7, 10, 14, and 21 days after treatment. During the experiment, a control sample was taken in each sampling time. Immediately after collecting the samples, all the samples were packed in polyethylene bags and transported to the laboratory in an ice box. The samples were homogenized using a food processor (Thermomix Vorwerk). The homogenate of each sample was done where three representative samples of 15 g were taken. Samples were then placed into polyethylene 50-ml centrifuge tube and frozen at -20 °C until the time of analysis.

E. Extraction and clean up

Samples were extracted and cleaned up immediately after sampling using QuEChERS methodology (8) .About 15 g of the homogenized samples were weighted in a 50-mL centrifuge tube and 10 ml of acetonitrile (1% acetic acid) were added, the screw cap was closed and the tube vigorously shaken for 1 min using a vortex mixer at a maximum speed. Next 1 g sodium chloride and 4 g anhydrous magnesium sulfate was added, the sample was vortexed for 30 s. The extracts were centrifuged for 5 min at 3800 rpm and 40 oC. An aliquot of 4 ml was transferred from the supernatant to new clean 15 ml centrifuge tube and cleaned up by dispersive solid-phase extraction with 100 mg PSA, 20 mg GCB and 600 mg MgS04. The sample was again vortexed for 1 min and then centrifugation was carried out as mention above. Then, 1ml of the supernatant was taken, mixed with 2ml toluene and evaporate to dryness. The residues were redissolved in 1ml of toluene, filtered through 0.22 um PTFE filter (Millipore, USA) and transferred into a 1.5 ml glass vial for GC-ECD analysis.

F. Instrumental determination

Gas chromatography (GC) Hewlett Packard (HP) serial 6890 equipped with detector, electron capture (ECD) was used. Analysis of the pesticide was performed on capillary column, DB-35 (35%-Phenyl-methylpolysiloxane). The dimensions of each column were 30 m length x 0.25 mm inner diameter and coated with 0.25 μm film thickness of the stationary phase. Nitrogen was used as a carrier gas at a flow rate of 5ml/min. The temperature of injector was 280°C.the oven temperature was 240 °C and detector temperature was 300 °C. Recovery studies were carried out by spiking 3 replicates of untreated date samples (control) with , 0.01, 0.5 and 0.1 mg / kg of tetraconazole. Samples were analyzed using their prescribed procedure and mean values of the three replicates were calculated. Recovery percentages were satisfactory for the tetraconazole and ranged from 89.4 % to 95.6 % .The minimum detection limit of tetraconazole was 0.005mg/kg.

The rate of degradation (K) and half-life (t1/2) values were obtained from the following equation of (9).

Rate of degradation (K) =2.303 X slope

Half-life (t1/2) =0.693/(K)

Data were statistically evaluated by one-way analysis of variance (ANOVA). All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

III. RESULTS AND DISCUSSION

The dissipation trends of tetraconazole in tomato fruit were shown in Table 1.and Fig.1. Tetraconazole dissipated rapidly after application. The concentration of tetraconazole 1 h after treatment was 0.92mg/kg. The residues amount decreased to 0.76 mg/kg, in tomato fruit within the first 24 h after application. Following that period, tetraconazole residues in/on tomato fruit decreased to0.66, 0.45, 0.16, 0.09 and 0.04mg/kg, at 3, 5,7, 10,12 and 15 days after treatment, respectively . Samples taken 21 days after treatment contained no detectable amount of tetraconazole in tomato fruit. The dissipation rate of tomato fruit exhibited a first order kinetics. The half-life of tetraconazole calculated in tomato fruit treated at recommended dose was 5.02 days (Table I and Fig.1). The dissipation of the pesticide residues in/on crops depends on environmental condition, type of application, plant species, dosage, and interval between application, the relation between the treated surface and its weight and living state of the plant surface, in addition to harvest time (10). European Union MRL for tetraconazole in tomato is 0.5 mg/kg. It can thus be concluded that the preharvest interval (PHI) of tetraconazole on tomato was 4 days after the last treatment. Our finding agree with (11- 14).

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TABLE I
DISSIPATION OF TETRACONAZOLE RESIDUES (MG KG−1 ± SD) IN/ON TOMATO FRUIT

Time (days)	Residue level (mean ± SD)	% Dissipation
Zero time	0.92±0.052	0
One day	0.76±0.0024	17.35
3days	0.66± 0.0023	28.26
5days	0.45± 0.022	51.05
7days	0.16±0.03	82.62
10days	0.09 ±0.007	90.21
15days	0.04± 0.018	95.69
21 days	n.d	n.d
MRL	0.1	
T 0.5	5.02	
PHI	4	

IV. CONCLUSION

A modified capillary gas chromatographic and QuEChERS method were described for the determination of residues of tetraconazole. The method is useful for quantitative analysis of real samples. The tech¬nique developed for sample extraction and clean-up was applied to monitor the residues of the studied pesticides in tomatoes.. The half-life time of tetraconazole residues in tomato was 5.02 days. The pre harvest interval (PHI) of tetraconazole on tomato was 4 days after the treatment.

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