

# PESTICIDE RESIDUE ANALYSIS OF DATE PALM FRUITS BY GAS CHROMATOGRAPHY MASS SPECTROPHOTOMETRY

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## ABSTRACT

Pesticides are being used indiscriminately to control insect pests of date palm (*Phoenix dactylifera*) such as red palm weevil, dubas bug, and mealy bug. The commercial formulation of several pesticides usually applied on date palm as root treatment, or injection into trunk, or as spray on foliage during flowering and fruiting stages to control insect pests. Green fruits of date palm were used for the extraction of pesticides using different solvent extraction procedures. Pesticides extracted from fruits were analyzed on Hewlett Packard gas chromatograph-mass spectrophotometer. Pesticides were identified by using retention time of their reference standard and reconfirmed by HPPEST computer mass spectral library coupled with gas chromatograph-mass spectrophotometer. The residues of dimethoate (0.44 mg/kg fruits) were found 15 days after injection reaching to maximum 1.98 mg/kg after 45 days followed by sharp decline. The trend of accumulation of dimethoate in Aflix insecticide was found similar to that applied alone.

## INTRODUCTION

Date palm (*Phoenix dactylifera*) is an important agricultural crop in Arabian Peninsula and many other countries. The red palm weevil, *Rhynchophorus ferrugineus* Oliver, is considered one of the most economically important pests in many date producing countries. In the Sultanate of Oman, destruction caused by red palm weevil insects in Mahdah, Bureimi and Musandam regions is significant. Chemical control of red palm weevil is still practiced as one of the preferred method throughout the Gulf region and other parts of the world.

Commercial formulations of systemic and non-systemic pesticides are being used indiscriminately to control insect pests worldwide. Many of these

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pesticides tend to have residual effect and may pose serious threat to the health of the consumers. The present investigation was undertaken to analyze the pesticide residues in date fruits collected from plants treated with insecticides to control red palm weevil.

## MATERIALS AND METHODS

Commercial formulation of different insecticides after dilution with water in 1:1 ratio was used on selected date palm trees in Bureimi region for the control of red palm weevil. Three holes 12 – 15 cm deep were made making a triangle on the trunk of the each tree using a micro drill machine. 10 ml of insecticide was injected in each hole. The first injection was made on date trees when fruits were small and green. For each insecticide at least three plants were used for injection. Fruits (200 g) from trees treated with insecticides were collected at an interval of 15 days up to 120 days. The insecticides selected for residual analysis were Dimethoate 40EC, Aflix 38.5EC (mixture of dimethoate and endosulfan), Nogos 50EC (dichlorvos) and Marshall 25EC (carbosulfan).

**Extraction Procedures:** Fifty grams of fruit were sampled and used for the extraction of each insecticide. Different solvents were used to extract the insecticides to maximize the recovery. For dimethoate samples were macerated with 2 x 100 ml of acetone, aflix in petroleum ether: acetone mixture (1:1), nogos in methylene chloride and marshal with hexane: 2-propanol mixture (2:1) in commercial blender. Extracts were pooled, filtered, and concentrated at 35 °C. 100 ml of saturated NaCl was added to each extract. Liquid – liquid partitioning was performed twice with 100 ml of chloroform for dimethoate, and aflix, ethyl acetate for nogos and hexane for marshal. Extracts were pooled separately, dried over anhydrous sodium sulfate and reduced under vacuum at 40 °C. Extracts containing insecticides were passed over 2 x 15 cm glass column packed with Florisil and overlaid with 1 cm activated charcoal for clean up. Eluted extract was concentrated under vacuum at 35 °C and re-dissolved in 5 ml of hexane for GCMS analysis. The method of extraction for different insecticides was followed with slight modifications as described by Misra et al. (1992) for Dimethoate, Duhra and Hameed (1990) for Aflix, Anonymous (1986) for Nogos, and Martin (1985) for Marshal.

Extracted insecticides were analyzed and quantified using Hewlett-Packard Gas Chromatograph (HP5890) equipped with automated sampler

and HP5989B mass detector. The operating conditions of gas chromatograph were: 30 m x 0.320 mm capillary column; temperatures, oven 50 – 280 °C with a rate of 6 °C per minute, injector 250°, detector 275°. Helium was used as carrier gas with a rate of 30cm/sec linear velocity. Mass detector was auto tuned for electron impact ionization mode using PFTBA. Temperatures of ions source and quadrupole were set at 200 and 100 °C, respectively. Individual insecticides were identified by comparing retention time with their reference standard, and reconfirmed by mass spectral library of pesticides (HPPest library). Using the capabilities of the HP system, the quantitation of insecticide residues was automatically performed by peak area integration using dichlorobiphenyl as internal standard.

## RESULTS AND DISCUSSION

Various methods of extraction and cleanup are available in literature for organophosphate and organochlorine insecticides (Braun and Stanek, 1982). Because of the different chemical structure of the insecticides used in present study, the use of different procedure for extraction was adopted. The individual insecticides were quantified by peak area integration against dichlorobiphenyl as internal standard and recalculated to yield mg/kg fresh weight of date fruits. Results on the quantification of residues and the persistence of the active ingredients of different insecticides injected in trunk in March 1999 and repeated in 2000 are summarized in Table 1. Treatments with dimethoate provided maximum residues in date fruits either applied alone or with other formulation (Aflix). The accumulation of dimethoate (0.44 mg/kg fresh wt) was evident in first sample, which was collected 15 days after injection and continued until 60 days (0.14 mg/kg fresh wt). However, the maximum dimethoate residue was recorded after 45 days of injection (1.98 mg/kg) followed by a sharp decline in sample collected afterwards and disappeared in 75 day sample and later. Al-Samarraie et al. (1988) have reported residue level of date fruits sprayed with fenitrothion, chlorpyrifos, and primiphos-methyl as 3.9, 1.9 and 1.5 mg/kg, respectively. Other insecticides, such as nogos (dichlorvos), endosulfan (in aflix) and carbosulfan (marshal) were not detected in any samples. There are no reports seems to be available on use of insecticides by trunk injection of date palm, the present findings on residue accumulation in date fruits after injection into trunk appears to be the first.

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Table 1: Persistence of residues of some insecticides on date fruits.

Insecticide	Persistence of insecticide residues at different days after injection (mg/kg fresh weight of fruits)							
	15	30	45	60	75	90	105	120
Dimethoate 40EC	0.44	0.638	1.98	0.14	0	0	0	0
Nogos 50EC	0	0	0	0	0	0	0	0
Dimethoate (Aflix)	0.68	0.75	1.09	0.24	0	0	0	0
Endosufan (Aflix)	0	0	0	0	0	0	0	0
Marshal 25EC	0	0	0	0	0	0	0	0

Data are average of three replicates.