

## Dissipation of Fenitrothion Residues in Some Fruits and Vegetables Using High-Performance Liquid Chromatography Method

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**ABSTRACT.** High performance liquid chromatographic method was described for the determination of the dissipation of fenitrothion residues in some fruits and vegetables. Crops were sprayed with very dilute solution of fenitrothion, and collected daily one day after spraying for 7 to 13 days, and then extracted with acetonitrile and partitioning in normal hexane. Solid phase florisil cartridges were used for clean up. The analysis was carried out by reversed-phase high performance liquid chromatography (HPLC) with methanol-water (90:10) as a mobile phase. Detection limit is 0.01 mg/kg. The percentage of losses are 89.55, 85.71, 76.01, 93.39, 98.75, and 99.24 for rocket, parsley, lettuce, fig, grape and guava, respectively.

### Introduction

Organophosphorus pesticide came into general use in early 1960s. The growth in use of these compounds as a result of the resistance of insects toward chlorinated pesticides. Fenitrothion (o,o-dimethyl 4-nitro-3-methyl-phenylphosphonothionate) [C<sub>9</sub>H<sub>12</sub>NO<sub>5</sub>PS] is an organophosphorus insecticide. It is used almost worldwide for such crops as rice, fruits, vegetables, cotton, cereals and soybeans. It is also used in public health, principally as residual spray in houses for control of mosquitoes. It has low toxicity to mammals<sup>[1]</sup>. The toxicity is much lower than many similar insecticides. LD<sub>50</sub> the amount or concentration of a toxicant required to kill 50% of the test animal population under a standard set of conditions is 800 mg/kg<sup>[2]</sup>. Maximum Residue Limits (MRL's) permitted by Food Agriculture Organization (FAO) is 0.5 ppm<sup>[3]</sup>. Gas chromatography (GC) is the basic technique for analysis of several multiresidue pesticides in

plants<sup>[4-6]</sup>. (HPLC) is the most important alternative to GC for pesticide residue analysis<sup>[7-10]</sup>. Liquid-liquid partitioning and adsorption chromatography have been traditionally applied for clean-up<sup>[11,12]</sup>. Head space solid-phase micro-extraction was used in strawberries and cherries<sup>[13]</sup>. Fast supercritical fluid extraction and high-resolution gas chromatography with electron-capture and flame photometric detection was used for multiresidue screening of organochlorine and organophosphorus pesticides in Brazil's medicinal plants<sup>[14]</sup>. Supercritical fluid extraction was also used for removal of organophosphate pesticides from waste water by supercritical carbon dioxide extraction<sup>[15]</sup>. This paper describes the dissipation of fenitrothion in six crops, which are rocket, parsley, lettuce, fig, grape and guava over a period of time. Florisil cartridges were used for clean-up prior to analysis by High-Performance Liquid Chromatography (HPLC).

## Experimental

The study was carried out at the Agricultural Research Center, King Abdulaziz University, Faculty of Meteorology, Environment, and Arid Land Agriculture, at Hada Alsham region. The study included spraying the pesticide on three types of fruits (fig, grape, and guava) and three types of vegetables (lettuce, rocket, and parsley).

### *Pesticide Spraying*

Pure or undiluted pesticides are highly toxic to both animals and plants, so they must be diluted before spraying. According to a procedure used in the farm where 4.5 g of fenitrothion dissolved in 5 liters of water to form liquid emulsion, then placed in the sprayer (Honda Electronic Ignition GX 270). Five basins of vegetables and three trees of fruits were sprayed with the emulsion (one of each remains without spray as blank).

### *Crops Sampling*

Twenty-four hours after spraying, the first batch was collected from each plant and transferred to the laboratory, this process was followed regularly to the end of the period (7-13 days).

### *Extraction and Clean-up Procedures*

The sample extraction was based on the method described by Sastry and Vijaya<sup>[10]</sup>. A 25 g sample of each of lettuce, rocket, parsley, fig, grape, and guava was homogenised with acetonitrile (50 ml) in a blender. The extract was filtered through a Buchner funnel by suction and washed twice with 10 ml of acetonitrile. The combined filtrate was used for partitioning in a separatory funnel

with 50 ml n-hexane with strong shaking for 5 minutes. Then 50 ml deionized water and 5 ml saturated sodium chloride solution were added and the contents were shaken slowly in a horizontal direction for one minute. The lower aqueous layer was discarded and the upper organic layer containing the pesticides was collected and washed twice with 25 ml deionized water. The extract was dried using a minimum amount of anhydrous sodium sulphate, and filtered. Then, the filtrate was concentrated to 5 ml with rotary evaporator under vacuum at 40°C. The organic extracts were cleaned up prior to HPLC analysis using florisil cartridges, which were rinsed with 20 ml of n-hexane for conditioning. The sample was applied to the cartridge by syringe. Finally the analyte was eluted from the sorbent using 10 ml of a mixture of n-hexane and acetone in the ratio of 80:20.

### ***Reagent and Standard***

HPLC-grade acetonitrile, methanol, n-hexane, acetone and analytical grade sodium sulfate and sodium chloride were obtained from BDH, (England). Water purified using Milli-Q Plus Sytem (Millipore, Bedford, MA, USA) was used for solution preparation. Fenitrothion pesticide standard was obtained from Allied Signal, (Riedle-deHaen, Germany).

### ***HPLC Instrumentation***

A Beckman HPLC system consisting of 114 multisolvent delivery system, programmable 165 variable wavelength detector, 7725i Rheodyne injector fitted with 20 µl-sample loop. The column was Ultrasphere C-18, 5 µm, 250 × 4.6 mm, Beckman. The column effluent was monitored at 254 nm and 0.01 absorbency unit full scale. The mobile phase was composed of methanol-water (90:10) and the flow-rate was 1.0 ml/minute. The solvent used was of HPLC grade and filtered through 0.45 and 0.5 µm Millipore filter paper and degassed with Ultrasonic (Brasonic 2210 R- DTH) before using.

## **Results and Discussion**

The dissipation of fenitrothion from the six plants is shown in Table 1. The initial concentration in the first day after spraying in ppm for fenitrothion on rocket, parsley, lettuce, fig, grape and guava are 2.017, 3.397, 0.4581, 0.7575, 2.303 and 19.40, respectively. Then decrease gradually reaching 0.2108 ppm after 12 days in rocket the percentage of losses being 89.55%. For parsley the final concentration is 0.4854 to reach 85.71% after 13 days. In lettuce the period of experiment is only 7 days that gives 76.01% of residue losses. On the other hand for the fruits the initial concentration in figs is 0.7575 ppm and the final concentration after 12 days is 0.0500 ppm and percentage losses is 93.39%. For

grape the initial concentration is 2.3030 and the final concentration is 0.0287 ppm after 11 days and the percentage losses is 98.75. Finally the guava has the highest initial concentration in the first day 19.40 ppm, while in the final day the concentration was 0.1474 ppm. Figure 1 shows the dissipation of fenitrothion in the six crops used in this study.

TABLE 1. The dissipation of fenitrothion from the six plants in ppm.

Day	Rocket	Parsley	Lettuce	Fig	Grape	Guava
1	2.017	3.397	0.4581	0.7575	2.303	19.40
2	1.635	3.231	0.4154	0.5666	0.8589	3.145
3	1.041	2.864	0.3995	0.4936	0.8209	2.226
4	1.019	2.233	0.2190	0.4687	0.6582	0.6754
5	0.849	1.926	0.1767	0.4414	0.6569	0.6782
6	0.844	1.319	0.1586	0.3539	0.4425	0.4140
7	0.6880	1.270	0.1099	0.3375	0.4184	0.0372
8	0.6875	1.254	–	0.3066	0.3916	0.3446
9	0.5975	1.154	–	0.2505	0.3265	0.2642
10	0.5281	0.794	–	0.2218	0.2590	0.1638
11	0.2787	0.788	–	0.0952	0.0287	0.1602
12	0.2108	0.7444	–	0.0500	–	0.1474
13	–	0.4854	–	–	–	–
% of loss	89.55%	85.71%	76.01%	93.39 %	98.75 %	99.24 %

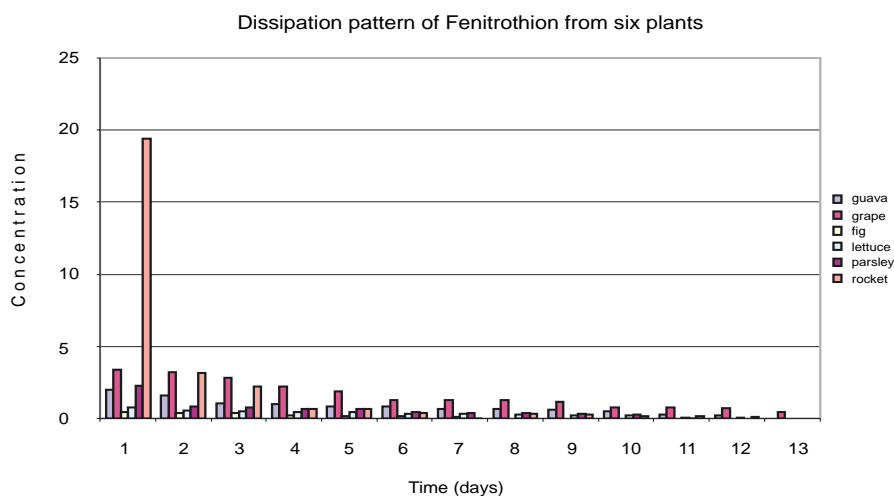


FIG. 1. Dissipation of fenitrothion residues in the six crops used in this study.

Solid-phase extraction reduced the analysis time and solvent consumption compared with traditional methods such as liquid-liquid extraction. The present data indicate that solid-phase extraction using florisil cartridges is capable of effecting rapid clean-up of fenitrothion from hexane extracts of vegetables and fruits. The peak areas of the monitoring fenitrothion on the chromatograms were measured, and the concentration of pesticide residue was determined from the calibration curve.

### Conclusion

Periodic analysis of the treated vegetables and fruits over 7-13 days showed progressive dissipation especially in the first days. Sep-Pack solid-phase florisil cartridges were used for clean-up. Reversed-phase high performance liquid chromatography at wavelength of 254 nm was used for the determination. The detection limit is 0.01 ppm. The period of study was suitable for dissipation of pesticide from crops to reach less than maximum residue limit permitted by Food Agriculture Organization (FAO) and World Health Organization(WHO)<sup>[16]</sup>.

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## تبدد بقايا الفينثرون في بعض الفواكه والخضراوات باستخدام الكروماتوجرافي السائل عالي الكفاءة

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المستخلص. تم في هذا البحث وصف طريقة لتقدير تبدد بقايا مبيد الفينثرون في بعض الفواكه والخضراوات باستخدام جهاز الكروماتوجرافي السائل عالي الكفاءة. حيث ترش المحاصيل بحلول مخفف من مبيد الفينثرون ثم تقطف جزئياً بعد يوم واحد من بداية الرش، وتستمر عملية القطف لمدة تتراوح من ٧ إلى ١٣ يوم. يستخلص المحصول بمذيب الأسيتونيتريل، ويتم توزيع المبيد بمذيب الهكسان العادي، ثم يمرر الهكسان على أنابيب صغيرة تحتوي على الفلورسيل الصلب، وذلك لتنقيتها من الشوائب. تجرى عملية التحليل باستخدام جهاز الكروماتوجرافي السائل عالي الكفاءة باستخدام تقنية الطور العكسي، حيث يتكون وسطه المتحرك من ٩٠٪ ميثانول : ١٠٪ ماء. وقد وجد أن حد الكشف للجهاز ٠,٠١، ٠,٠١ مليجرام / كجم. ووجد أن نسبة الفقد للمبيد في الفواكه والخضراوات هي ٨٩,٥٥، ٧١,٨٥، ٧٦,٠١، ٣٩,٩٣، و ٩٨,٧٥، و ٢٤,٩٩ في الجرجير و البقدونس والخس والتين والعب والجوافة على التوالي.