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RESIDUE DITECTION OF CHLORPYRIFOS AND FENITROTHION IN TOMATO

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ABSTRACT

The present study regarding pesticides residue analysis was made during the period of September, 2015 to March, 2017. The residue detection (the estimation of active ingredient i.e. A.I. content) of chlorpyrifos and fenitrothion from tomato fruit using Gas Chromatography (GC) was carried out in the Pesticide Analysis Laboratory, Department of Chemistry, University of Dhaka, Bangladesh. The quantity of chlorpyrifos was gradually decreased with increasing days after spraying (DAS) and it was below MRL at 7 DAS (0.279 ppm). Residue of fenitrothion determined by GC-FID at 0 DAS (two hours after spraying) was 8.341 ppm and it was also gradually decreased with increasing days after spraying (DAS) and it was below MRL at 6 DAS (0.281 ppm).

Key words: Pesticide, chlorpyrifos, fenitrothion, residue, tomato.

Introduction

The detection and monitoring of pesticide residue particularly in vegetable and fruits is being done in regular basis in many countries (Kumar *et al*., 2004; Rajeswaran *et al*., 2004). Many developed countries have set maximum residue limit (MRL) for crops and acceptable daily intake (ADI) of food items for the safe guard of consumers and environment (Anon. 1993). If ADI is exceeded than FAO/WHO recommendation that should be hazardous for consumers. It has reported that organophosphorus pesticide are being widely used to control insect-pests of vegetables, but their actual residue status under Bangladesh condition is not known. Though pesticide residue data on vegetables are important to the public in general because of potential hazard to health. Study on pesticide residue analysis in Bangladesh is considerably new; so far very little informations are available. Pesticide manufacture, formulation, repackaging, unitization and storage etc. play important role for the control of pest problems in the country. But, no systematic study has yet been performed, no questions of ensuring the utilization of pesticides in the farmer's field or at farm level. The proposed study assured the residual situation commonly used organophosphorus pesticides in tomato.

Materials and Methods

The present study was carried out during the period of September, 2015 to March, 2017.

Detection of residues of chlorpyrifos and fenitrothion in tomato fruit: Residue detection of chlorpyrifos and fenitrothion compounds from pesticide treated tomato fruit, were conducted at the Pesticide Analysis Laboratory, Department of Chemistry, University of Dhaka, Bangladesh with developed procotols (Anon. 1996; Akerblom, 1995). Reference grade pesticides were used from the stock of the Laboratory.

Sampling and processing of tomato fruit samples for residue analysis: The collected representative of pesticide (chlorpyrifos and fenitrothion) treated (at 0, 1, 3, 5, 6 and 7 days after spraying) tomato fruits samples were preserved at -10 °C in a deep freezer. Then kept out of the deep freezer for residue analysis until they reached at room temperature.

Extraction, separation and clean up of tomato fruit samples: Collected tomato fruit samples ($\geq$ 250g) were chopped by knife and mixed well. A sub sample of 20 g was taken into a wide mouth jar then 100 ml of hexane was added to it. Sodium sulphate (Na_2SO_4) was also added with sample until water was removed from the sample. The mixture was then macerated with high speed homogenizer (Ultra-turrax, IKA T18

basic, Germany) for 2 minutes. The homogenized materials was then poured into 20 ml conical flask and placed into the shaker (refrigerated Shaker, Rexmed, Sweden) for 12 hours continues shaking. After shaking, the slurry was filtered through whatman filter paper no.40 and a Buchner funnels with suction. The flask and filter cakes were rinsed with 25 ml of hexane each. The filterate was then transferred into 250 ml round bottom flask and was dried to around 5-7 ml by evaporation using a rotary vacuum evaporator (Laborota-4001, Heidolph, Germany). Then the concentrate filtrate was collected in a centrifuge tube adjusted at 10 ml volume which was then centrifuged at 16500 rpm for 10 minutes with Laboratory Refrigerated Centrifuges, Sigma-3k30, Germany. After centrifuge, supernatant was collected and cleaned up by Super Phase Extraction (SPE) cartridge. Then the final volume was kept in 10 ml volumetric flask. Before injection this volume was again cleaned up by High Performance Liquid Chromatography (HPLC) filter which was ready for injection.

Instrument parameters for detection and quantification of pesticides: To detect and quantify of organophosphorus pesticides residue (chlorpyrifos and fenitrothion) in tomato GC, Shimadzu-2010 instrumental parameters were used. Prior to injection of the sample extract, standard solutions of different concentrations of pesticides were prepared and injected with the above instrument parameters. Insecticide compounds were qualitatively identified by comparing the retention time of peaks and quantitatively estimated on the basis of area of chromatograms obtained in each test solution with that of the analytical standard. Sample results were expressed in ppm automatically by GC software which represented the concentration of the final volume injected. From this value of actual amount of insecticide residue presented in the sample was determined by using the following formula.

$$\text{Residue in sample (ppm)} = \frac{\text{Conc. Obtained in injected volume (ppm)} \times \text{Quantity of final Volume (L)}}{\text{Amount of sample taken (Kg)}}$$

Results and Discussion

Residues of Chlorpyriphos (Dursban 20 EC) in tomato: The residual situation of chlorpyrifos in tomato fruits at 0, 1, 3, 5, 6 and 7 DAS were determined by gas chromatography. Residues (ppm) of chlorpyrifos at different days after spraying (DAS) in tomato shown in Table 1. The initial quantity of chlorpyriphos obtained by GC-FID at 0 DAS was 11.031 ppm. The quantity of chlorpyrifos was gradually decreased with increasing days after spraying (DAS) and at 7 DAS, it was 0.279 ppm. Chromatograms of residues of chlorpyrifos in tomato at 0, 1, 5 and 7 DAS were presented through Figs. 1-4, respectively.

Residues of Fenitrothion (Sumithion 50 EC) in tomato: The residues of fenitrothion in tomato fruit at 0, 1, 3, 5, 6 and 7 DAS were also determined with by gas chromatography with 8.341, 4.245, 2.170, 0.617, 0.281 and 0.076 ppm, respectively. The residues of fenitrothion at different days after spraying (DAS) in tomato were shown in Table 2. Residue of fenitrothion determined by GC-FID at 0 DAS (two hours after spraying) was 8.341 ppm and it was gradually decreased with increasing days after spraying (DAS). Chromatograms were presented in Figs. 5-8 for 0, 1, 5 and 7 DAS, respectively.

Table 1. Residue of chlorpyrifos (Dursban 20 EC) detected from tomato at different days after spraying (DAS)

Days after spraying (DAS)	Sample wt (g)	Total volume prepared (ml)	Injected volume (µl)	Conc. obtained in final volume (ppm)	Residue of chlorpyrifos left (ppm)
0	20	5	1	44.124	11.031
1	20	5	1	24.512	6.128
3	20	5	1	12.700	3.175
5	20	5	1	5.384	1.346
6	20	5	1	2.468	0.617
7	20	5	1	1.116	0.279

FAO/WHO Codex Alimentarius Commission (1990) recommended, MRL=0.5 ppm, ADI = 0.002 ppm kg^{-1} body wt.

Table 2. Residue of fenitrothion (Sumithion 50 EC) detected from tomato at different days after spraying (DAS)

Days after spraying (DAS)	Sample wt (g)	Total volume prepared (ml)	Injected volume (µl)	Conc. obtained in final volume (ppm)	Residue of fenitrothion left (ppm)
0	20	5	1	33.364	8.341
1	20	5	1	16.98	4.245
3	20	5	1	8.68	2.170
5	20	5	1	2.468	0.617
6	20	5	1	1.124	0.281
7	20	5	1	0.304	0.076

FAO/WHO Codex Alimentarius Commission (1990) recommended, MRL=0.1 ppm, ADI = 0.005 ppm kg^{-1} body wt.

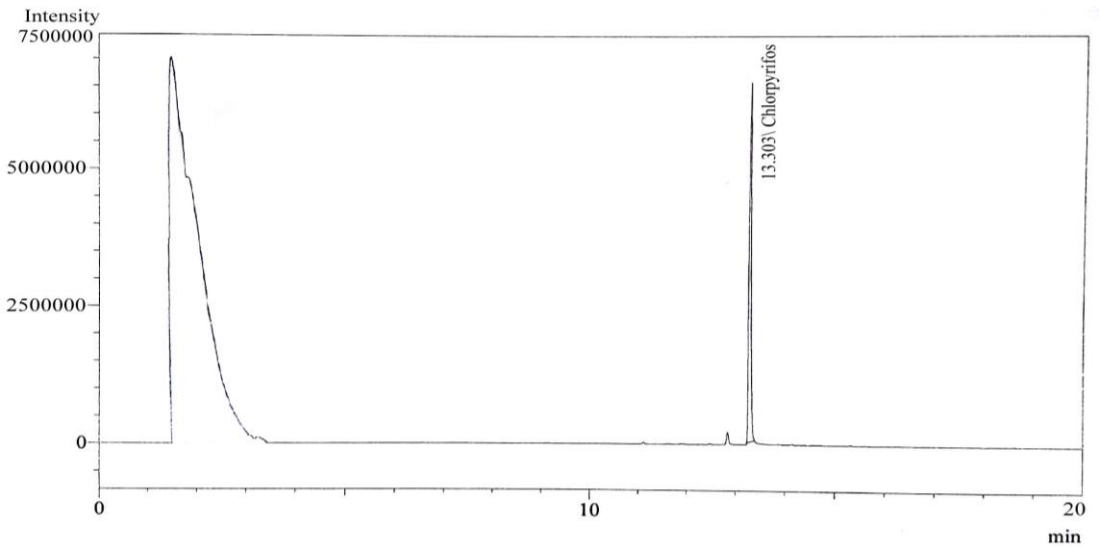

Fig. 1 Chromatogram of chlorpyrifos (Dursban 20 EC) residue in tomato at 0 DAS

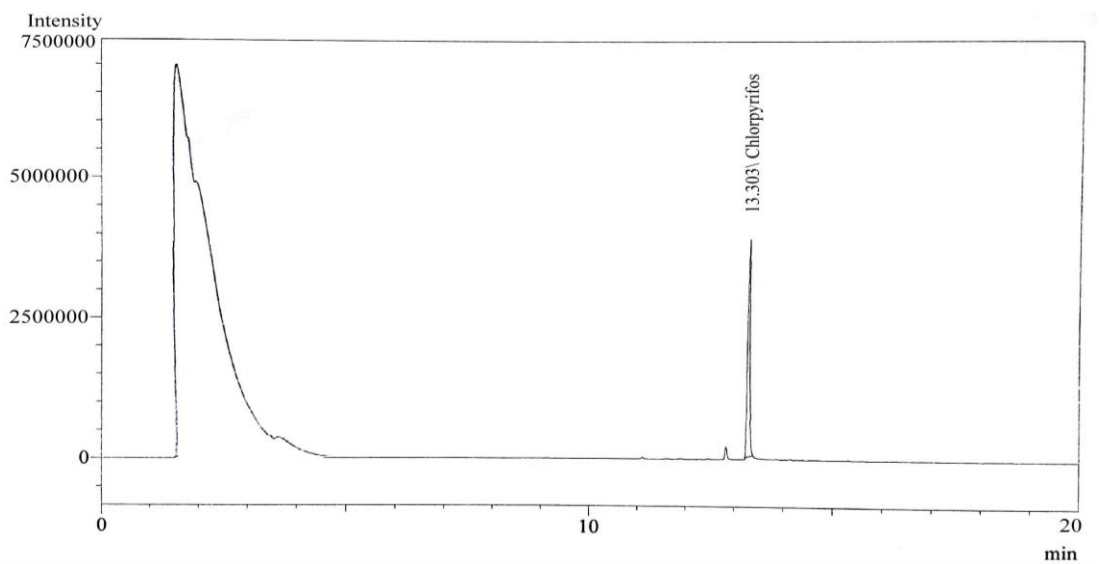

Fig. 2 Chromatogram of chlorpyrifos (Dursban 20 EC) residue in tomato at 1 DAS

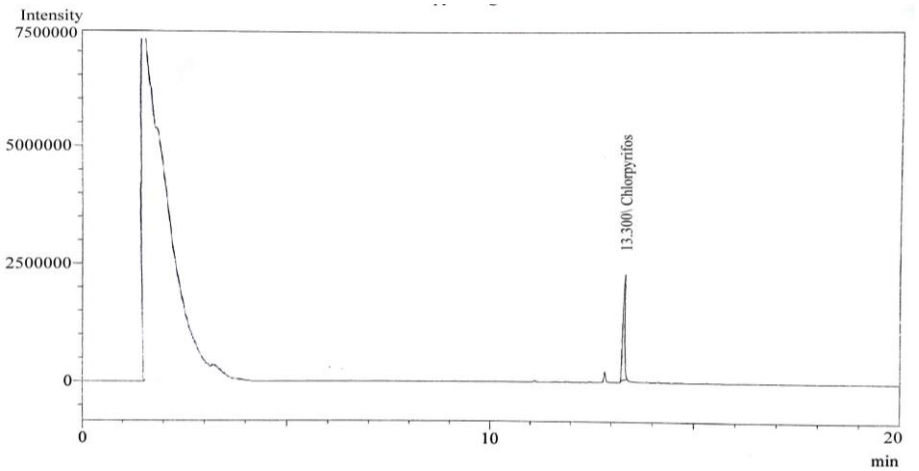

Fig. 3 Chromatogram of chlorpyrifos (Dursban 20 EC) residue in tomato at 5 DAS

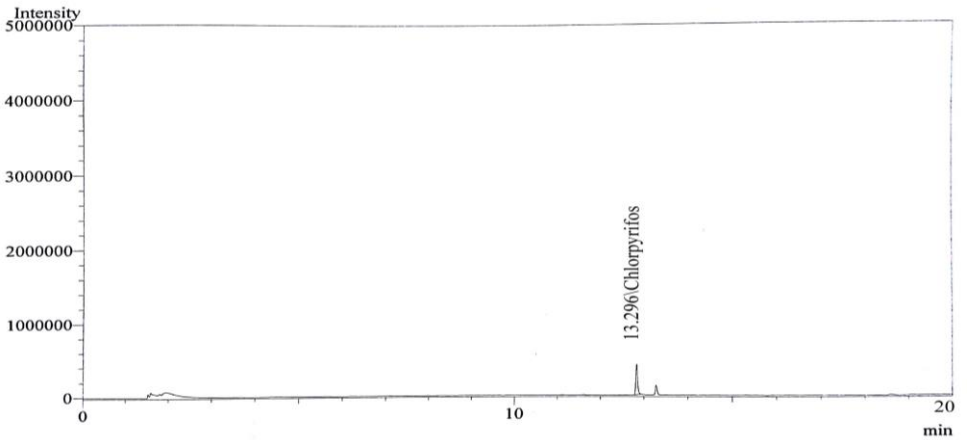

Fig. 4 Chromatogram of chlorpyrifos (Dursban 20 EC) residue in tomato at 7 DAS

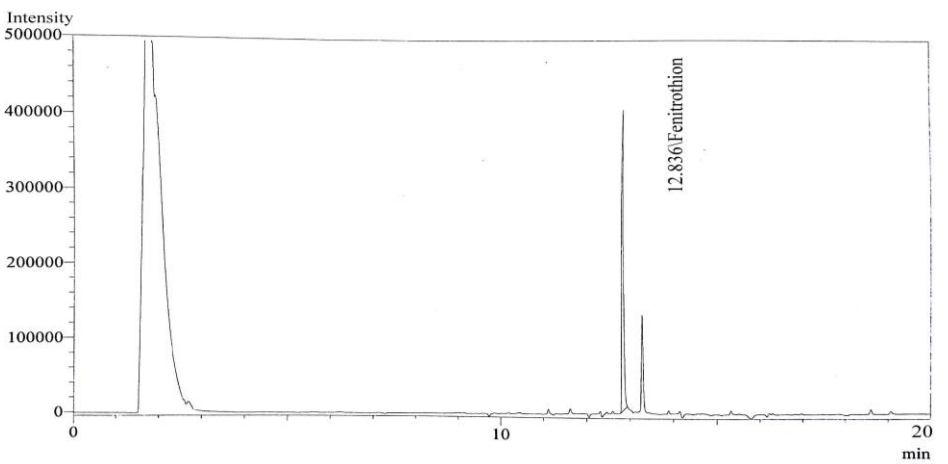

Fig. 5 Chromatogram of fenitrthion (Sumithion 50 EC) residue in tomato at 0 DAS

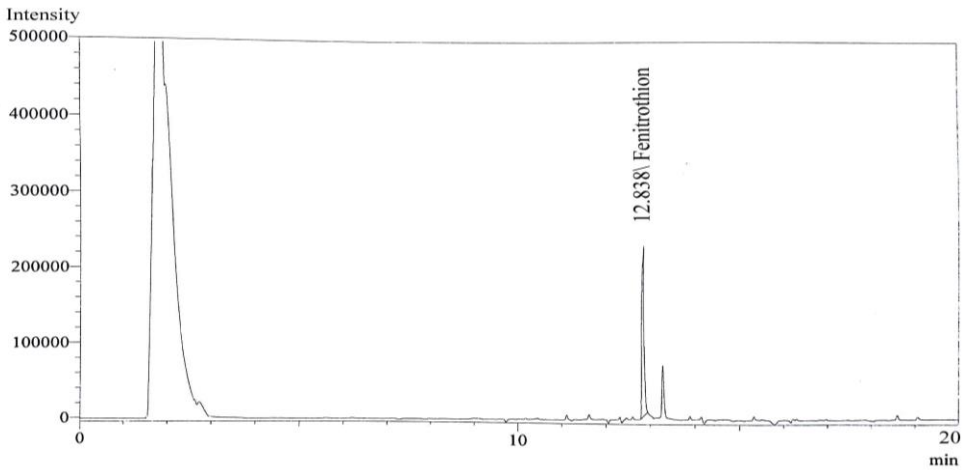

Fig. 6 Chromatogram of fenitrthion (Sumithion 50 EC) residue in tomato at 1 DAS

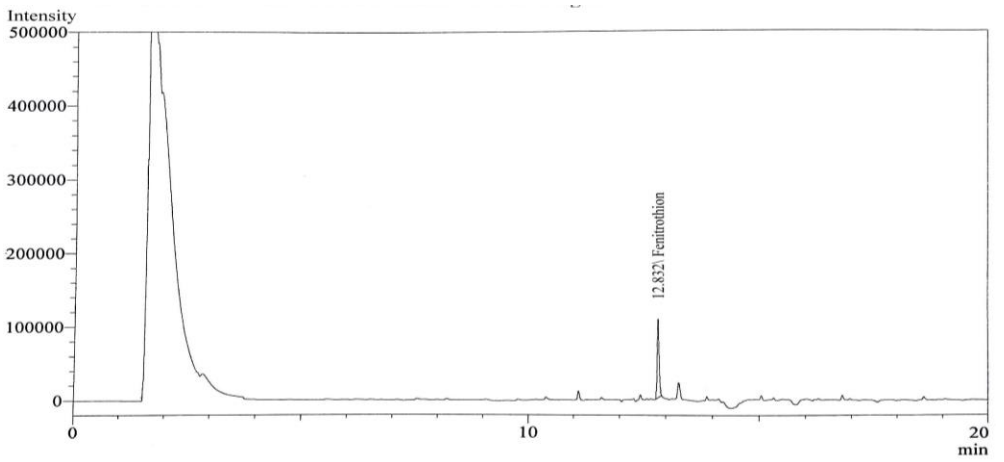

Fig. 7 Chromatogram of fenitrthion (Sumithion 50 EC) residue in tomato at 5 DAS

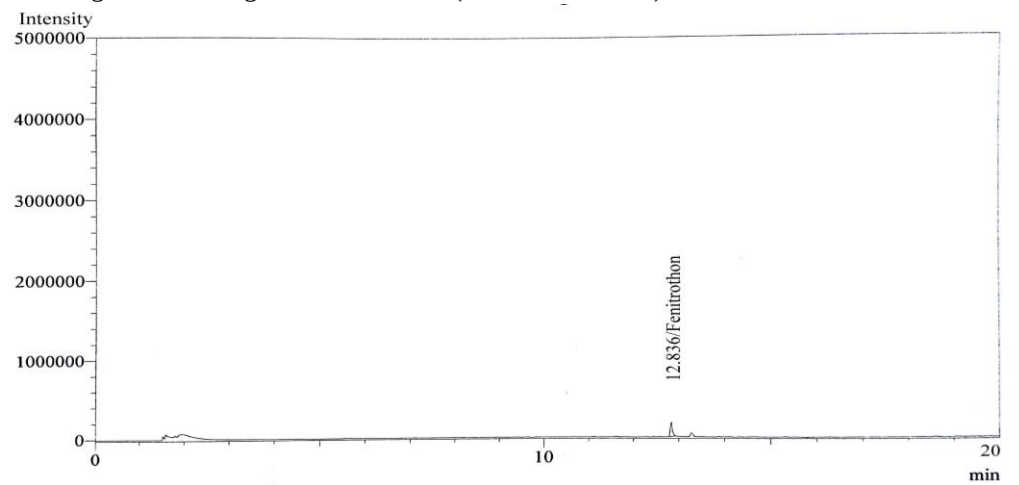

Fig. 8 Chromatogram of fenitrthion (Sumithion 50 EC) residue in tomato at 7 DAS

From the MRL point of view, it was found out that fenitrothion degradated quickly and its residues was above MRL upto 5 DAS. Incase of chlorpyrifos residue was above MRL up to 6 DAS. Moreover, the characteristics of rapid and gradual degradation of organophosphorus pesticides may be the reason for frequent spraying of pesticide for insect pests control effectively. But, their rate of degradation depends upon various factors, such as variety, plant physiology, evapo-transpiration, composition and concentration of pesticide formulation, application techniques, period of interval between pesticide spraying and harvest, temperature, rainfall and humidity of crop growing area etc. (Tomlin, 2003; Anderson, 2004).

Conclusion

The degradation rate of chlorpyrifos was found slower compared to fenitrothion in tomato. It is not safe and wise to harvest the treated tomato fruits within 5 DAS for fenitrothion and that of 6 DAS for chlorpyrifos. From the view point of pre-harvest interval (PHI) of tested pesticides, fenitrothion with 5-6 DAS and chlorpyrifos with 6-7 DAS could be included for tomato cultivation in Bangladesh.

Recommendations

- Situation of quality control system of Bangladesh is very weak so, increase laboratory facilities and efficient manpower both in field and laboratory would be needed.
- To ensure judicious and proper use of pesticides, enforcement and implementation of government rules and orders should be strengthened and may be amended, if necessary.
- A national MRL (maximum residue limit) and ADI (acceptable daily intake) of pesticides should be developed for safety of human health. Therefore, it needed to comply with FAO/WHO recommended MRL's and standards of European Union for the pesticide use in agriculture and public health concern in Bangladesh.

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