



Residue Analysis of Etoxazole in Red Pepper using Gas Chromatography: Application to Dissipation Pattern



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Abstract

A major modification of the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method was developed to analyze etoxazole in red pepper using gas chromatography coupled with nitrogen-phosphorus detector (GC-NPD). Etoxazole was extracted with acetonitrile, partitioned with magnesium sulfate, and purified with a solid phase extraction (SPE) cartridge. The method showed good linearity with a determination coefficient (R^2) of 0.998 for the 0.02–2.0 mg/L concentration range. The method was validated using blank red pepper spiked at 0.2 and 1.0 mg/kg, and the average recovery rate was 74.4–79.1% with relative standard deviations < 5% for intra- and inter- day precision. The limits of detection (LOD) and quantification (LOQ) were 0.007 and 0.02 mg/kg, respectively. The developed method was successfully applied to field incurred samples, and etoxazole residues were confirmed using gas chromatography/mass spectrometry (GC/MS).

Keywords : Etoxazole, red pepper, QuEChERS, residue analysis; gas chromatography

Introduction

Etoxazole, 2-(2,6-difluorophenyl)-4-[4-(1,1-dimethylethyl)-2-ethoxyphenyl]-4,5-dihydrooxazole (Figure 1), is one of the oxazoline compounds belonging to the chemical class of 2,6-difluorophenyl group which commonly used in commercial greenhouses.

It is publicly introduced in 1994, and commercialized in 1998 as an insecticide whose targeted main pests are tetranychid spider mites such as *Panonychus* spp. and *Tetranychus* spp.

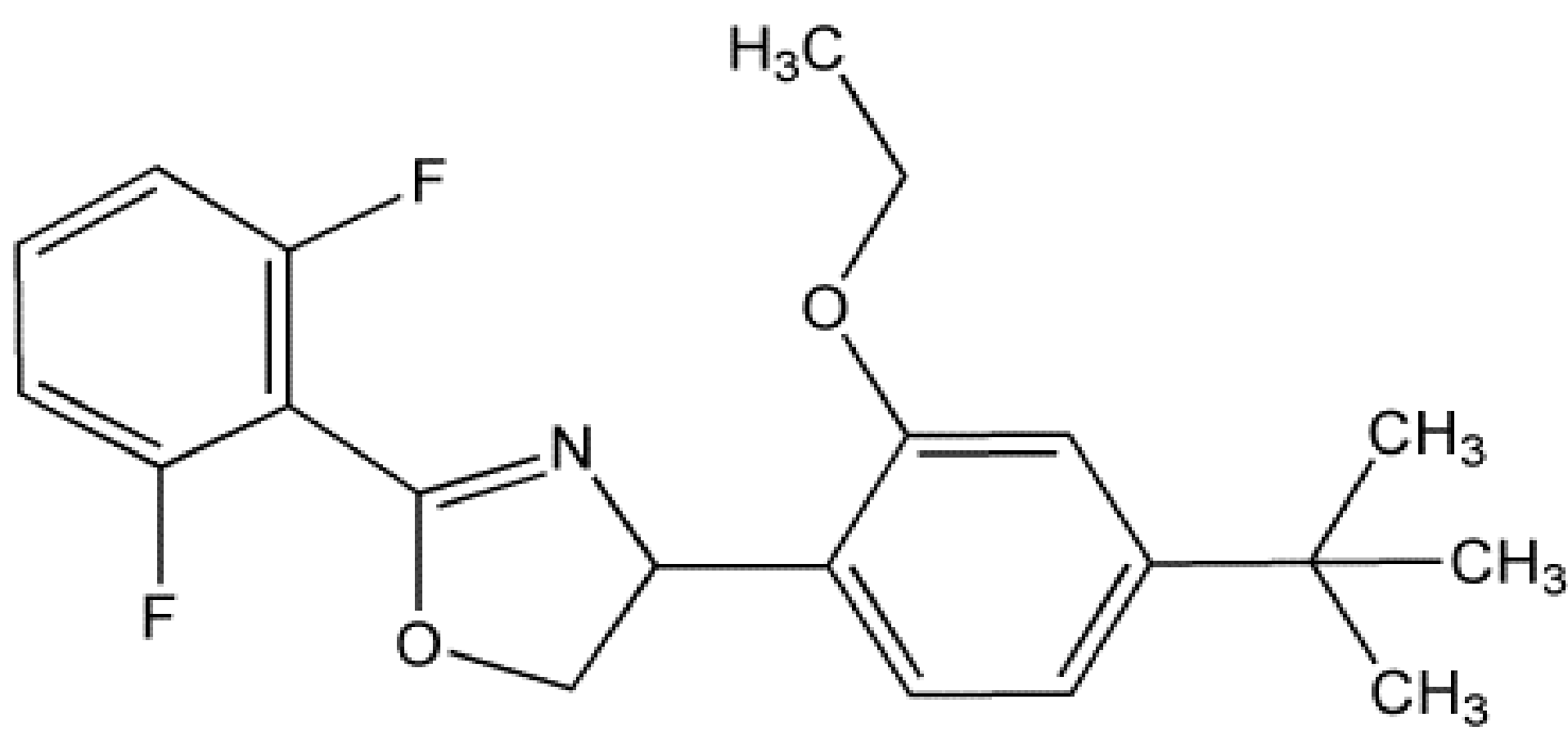


Figure 1. Structural formula of etoxazole.

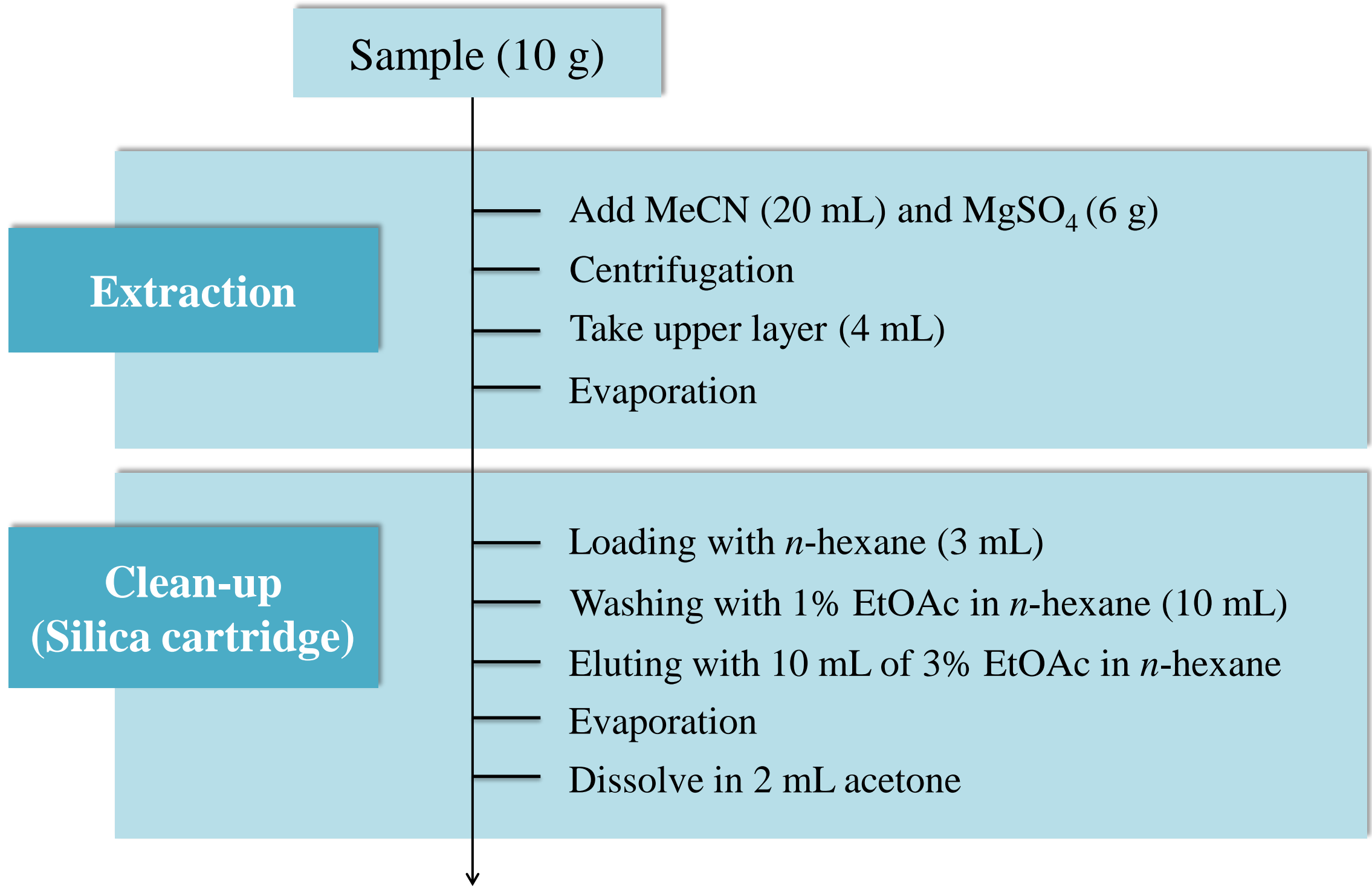
Objective

The purpose of the present work was to find out the dissipation patterns of etoxazole in red pepper

Materials and Methods

- Sample
Red pepper
- Standard
Etoxazole
- Reagents
Acetone, acetonitrile (MeCN), *n*-hexane, magnesium sulfate (MgSO₄)

Extraction method



GC-NPD analysis

Instrumental conditions

Table 1. Analytical conditions of GC-NPD for etoxazole in red pepper					
Model	Agilent 6890 equipped with NPD				
Column	DB-17 capillary column (30 m × 250 μm i.d., 0.25 μm film thickness, Agilent, CA, USA)				
Temperature	Oven	<div><div></div><div>270 °C (10 min)</div><div>150 °C</div><div>30 °C/min</div></div>			
	Injector	250°C			
	Detector	280°C			
Flow rate	Column (N ₂)	1.0 mL	Air	60.0 mL	
	Makeup (He)	4.0 mL	H ₂	4.0 mL	
Injection volume	2 μL (Splitless)				
Retention time	8.9				

Results

Table 2. Determination coefficient (R^2), limit of detection (LOD, mg/kg), limit of quantification (LOQ, mg/kg), and maximum residue limit (MRL, mg/kg) of etoxazole.

Pesticide	R^2	LOD	LOQ	MRL*
Etoxazole	0.999	0.007	0.02	0.3

* MRL values determined by The Korea Food and Drug Administration (KFDA, 2012)

Table 3. Spiked levels, recovery, and precision (intra-day and inter-day repeatability) of etoxazole in red pepper samples

Compound	Spiked levels (mg/kg, n=3)	Mean recovery (%)	Intra-day repeatability, RSD (%)	Inter-day repeatability, RSD (%)
Etoxazole	0.2	79.1	1.8	4.9
	1.0	74.4	2.9	2.8

Chromatograms

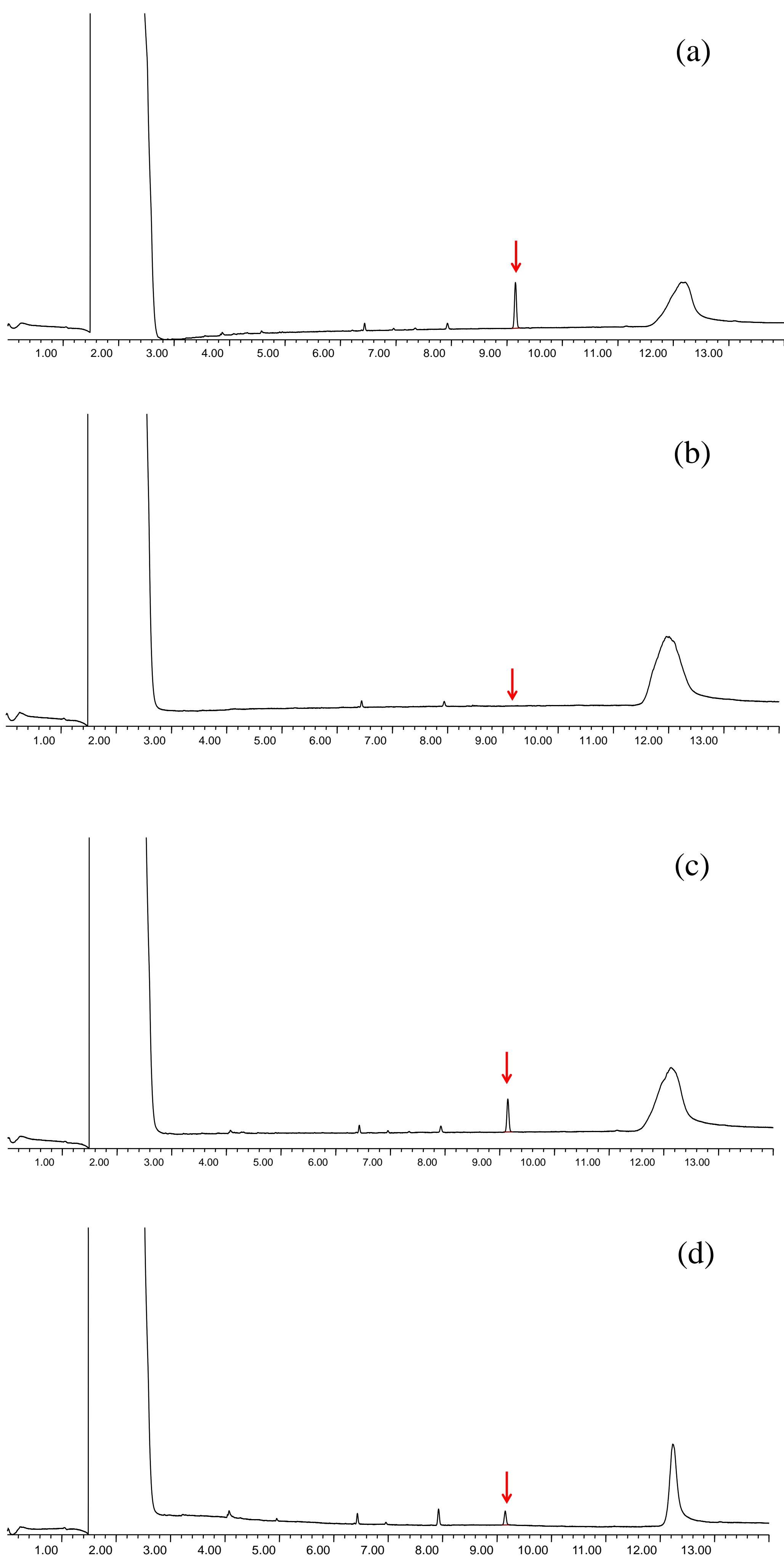


Fig. 2. Chromatograms of etoxazole analyzed by GC-NPD. (a) Standard etoxazole at 0.3 mg/L, (b) untreated red pepper sample, (c) fortified red pepper sample at 0.3 mg/kg, and (d) field incurred sample.

Residues

Table 4. Residue (mg/kg) of etoxazole (with half life and percent of dissipation) in red pepper at various time intervals following application.

Treatment	Day after application	Residue	Dissipation of etoxazole (%)
Untreated	-	ND	-
	0	0.16	
	1	0.15	12.51
	2	0.14	21.76
Single dose (plot A)	3	0.12	22.66
	5	0.11	23.68
	7	0.07	32.88
	9	0.09	37.29
	10	0.08	37.34
	Half life = 9.6 day		
Double dose (plot B)	7-0	0.26	
	8-1	0.24	10.85
	9-2	0.23	14.86
	10-3	0.19	28.60
	12-5	0.16	33.80
	14-7	0.16	36.27
	16-9	0.15	31.19
	17-10	0.15	45.76
	Half life = 12.2day		

Dissipation pattern

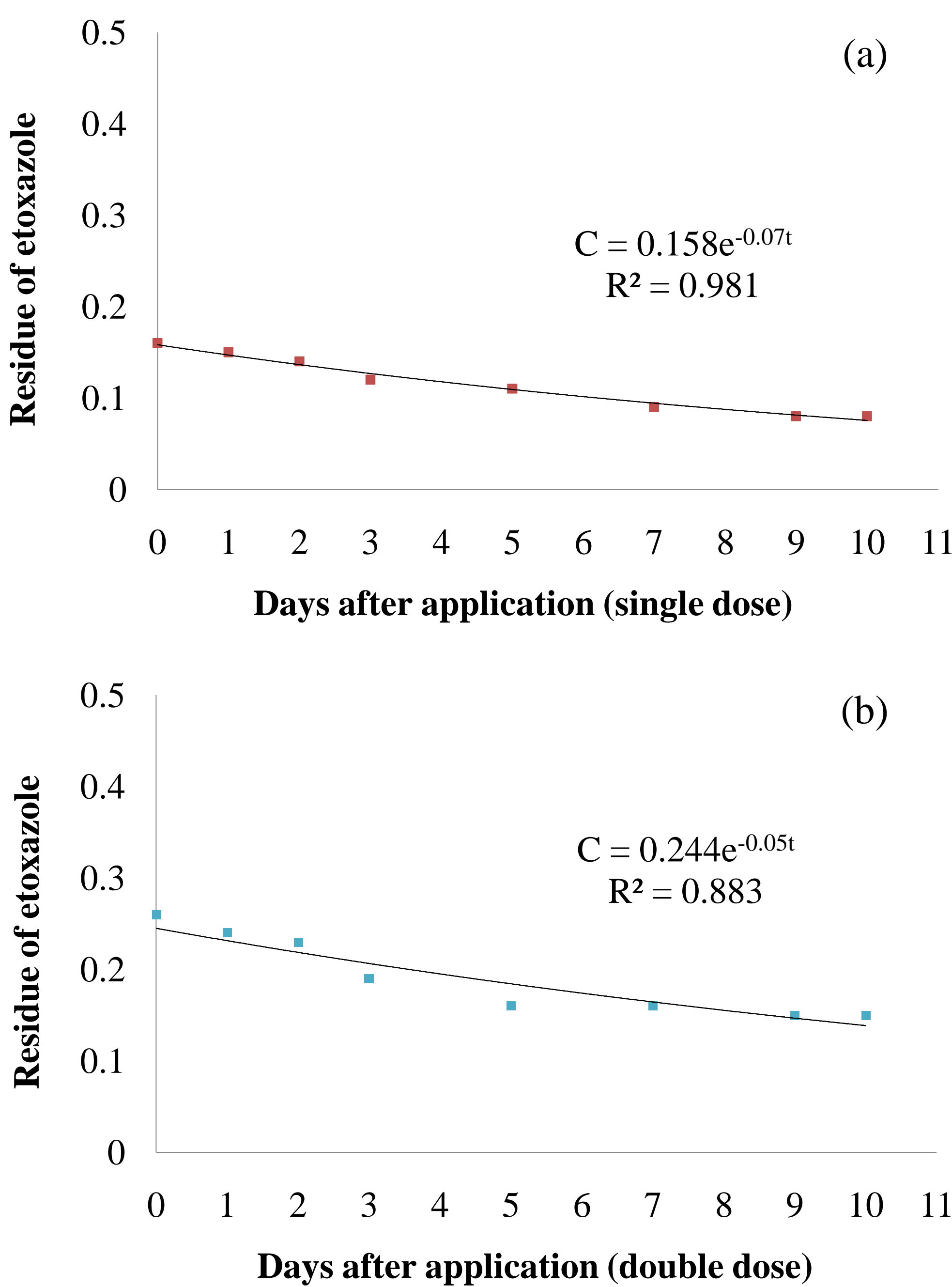


Fig. 3. Degradation of etoxazole in red pepper following single (a) and double doses (b) of application.

Conclusions

Satisfactory validation parameters such as linearity, recovery and precision were obtained. The recoveries were obtained in the range of 74.4% and 79.1%. After treatments, all etoxazole residues on red pepper samples were below the MRL (0.3 mg/kg, KFDA). These results showed that it is safe to use etoxazole formulation (10% SC) on red pepper under the recommended dosage. The results would be useful for the safe use of etoxazole and to prevent any health problem to consumers.