Simple and Rapid Method for Pyrethroid Residues Analysis by Test Kit

Udomluck Unjitwatana (consultant)
Agricultural Production
Research and Development , DOA. + Private sector (Thailand)

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Introduction

From 2003-2014 , vegetables exported from Thailand and imported from the other countries are always found some pyrethroids residues contaminated. Sometimes they have been found more than MRLs values but only a few samples.

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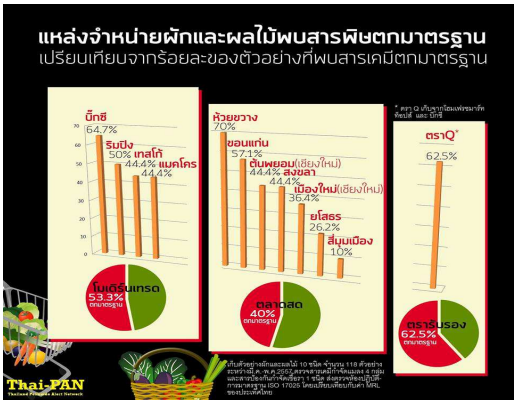

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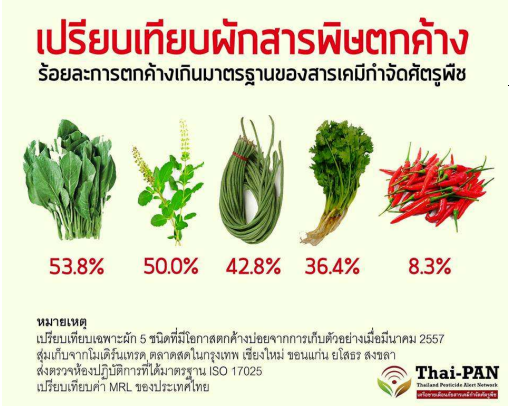

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Introduction

Since 2004-2014 Cypermethrin residues have been often found in exported and imported vegetables. Most of them sometimes had been detected over MRLs .Cypermethrin was always found in almost every sample. So we have to find out the quickest method to check the product residues before selling to the market.

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Cypermethrin Toxicity

LD_{50} = insecticide concentration that caused half of animals in experiments died 50%.

LD_{50} (oral) rats 187-326 mg/kg

LD_{50} (dermal) rats >1,600 mg/kg

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Acceptable daily intake (ADI)

ADI : Insecticide concentration that intake to the human body continuously for 1 year and no toxicity happened.

ADI Cypermethrin (human body) 0.05 mg/kg/day

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Cypermethrin & Chlorpyrifos toxicity on birds and bees

Animal test	LD_{50} (mg/kg)	
	cypermethrin	chlorpyrifos
Bird	nontoxic	highly toxic
Mallard ducks	4,640	112
Bobwhite quail	< 20,000	108
Bees	nontoxic	highly toxic

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Cypermethrin & Chlorpyrifos toxicity on fish

Animal test	LC_{50} ppb. (µg/l)	
	cypermethrin	chlorpyrifos
Small fish, invertebrate aquatic organism	0.2 (24 hrs.)	highly toxic
Rainbow trout	8.2 (96 hrs.)	98 (96 hrs.)
Blue gill sunfish	1.8 (96 hrs.)	331(96 hrs.)

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Metabolism in rats

Cypermethrin Degradation will be happened suddenly by hydroxylation & cleavage at cyclopropane ring , >99% excreted at few hour, 1% accumulated in fat tissue.

Half life 18 days(cis), 3.4 days (trans) isomer.

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Metabolism in human body

Cypermethrin : After cypermethrin intake into human body, it can be reacted in many process in human body and excreted the metabolites by urine in 48 hours.

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Persistence of residues in soil

Cypermethrin : Persist moderately in soils. Degradation grows very fast in less organic matter & aerobic soils. Insoluble in water, adsorbed to soils and penetrated into soils, no leaching to ground water.

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Degradation in soils & water

Cypermethrin: In basidic soils , degrade very fast.
Half life > 100 days. In sunlight , half life > 50 days.
Degrade in water by adsorbing to sediment and aquatic plants .

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Cypermethrin bioaccumulation

Cypermethrin: After fish intake cypermethrin that adsorbed with sediment and aquatic plants, bioaccumulation will be happened 1,200 times (rainbow trout) more than in water.

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Residue in Vegetables

Cypermethrin: Residues remain on plant surface for 14-19 days. Ester cleavage take place in plants. The phenoxybenzyl and cyclopropyl moieties are readily converted into glucoside conjugates.

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In the process of vegetables exportation, have to be inspected the pesticide residues in the agricultural products. Certifications from the exported country are very important. The products have to be checked for pesticide residue first before leaving to the market.

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DOA and ACFS work together to improve the commercial products

DOA work in the field, recommend farmer how to use the pesticide, and harvest after the residue safe before going to the market. The barcode is necessary for the product. The symbol of the barcode will tell about name of farmer, kind of crop, planting location , pesticide used etc. The product can be checked back to the origin if the problem occurred. ACFS use test kit check for pesticide residue that referred on the barcode to approve below than MRLs in the market.

Test kit is the simple and rapid method for screening them in farm before going to GC or HPLC. It is very cheap and convenient to carry with you to work in the farm.

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Cypermethrin has been always found in nearly almost samples for vegetables in the market since 2003 - 2014. Dept. of Agriculture tried to find out the test kit to detect cypermethrin residues for many years, in order to save money, simple and rapid method and convenient to carry to work outsides.

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2 Innovation Patents

1. The patent no. 3098 (cypermethrin) had been got from the Dept. of Intellectual property. Ministry of Commerce on Faboury, 20 2007.
2. The patent no. 5069 (mixed pyrethroids) had been got from the Dept. of Intellectual property. Ministry of Commerce on September, 2 2009.

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Get a reward from DOA

Cypermethrin (2009)

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Cypermethrin

This innovation also received the admirable reward from the Thai National Research Council in 2009

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Get a reward from NRCT(2009)

Cypermethrin (2009)
Admiral level reward

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Get a reward from NRCT (2011)

Mixed Pyrethroids (2011)
Good level reward

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Reward from The NRCT

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Basic Theory of TLC

Phases to separate compounds :

- stationary phase: Silica or Alumina
- mobile phase : 2 or 3 kinds of solvents mixed together.

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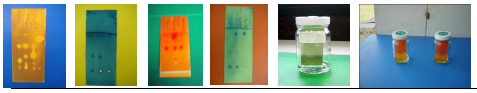

Stationary phase was produced by mixing alumina or silica with chromogenic agent that could detect the insecticide. Mobile phase was 2 or 3 solvents mixed together which could separate each insecticide. This method can be saved time, money and manpower.

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Pyrethroids

Pyrethroid structures are composed of cyclopropane ring that can be detected by TLC. The suitable stationary and mobile phases have to be find out first and the propropiate ratio of 2-3 kinds of solvents are fixed for mobile phase.

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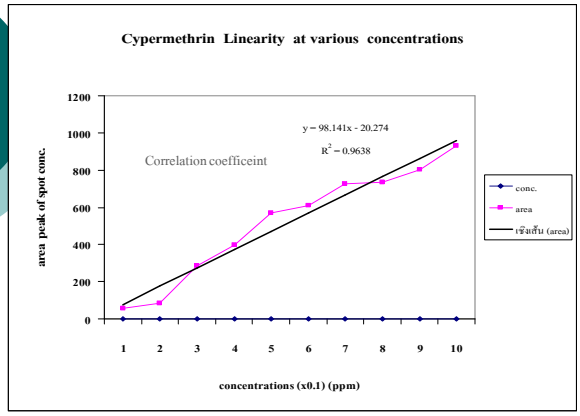

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% Recovery of cypermethrin

%Recovery at 0.2 ppm. = 83.10%
%Recovery at 0.4 ppm. = 85.30%
%Recovery at 0.6 ppm. = 85.80%
%Recovery at 0.8 ppm. = 84.20%
%Recovery at 1.0 ppm. = 80.40%

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SD, mean, % RSD, HR., Predicted Horwitz values(cypermethrin)

N = 10

%RSD = SD x 100 / mean

HR. (Horrat) = %RSD experiment/ Predicted Horwitz RSD Should be less than 2

Predicted Horwitz RSD=$0.66 \times 2^{(1-0.5 \log C)}$
c = ppm.

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Cypermethrin precision Value

(Horrat should < 2)

conc.	0.3 ppm.	0.4 ppm.	0.6 ppm.	0.8 ppm.	1.0 ppm.
SD	9.2437	12.8513	14.6286	21.1158	20.7128
mean	280.337	390.906	625.294	726.824	945.972
n	10	10	10	10	10
%RSD	3.2974	3.2876	2.3395	2.9052	3.2498
Horrat*	0.2605	0.2712	0.2051	0.2660	0.3077
Predicted Horwitz	12.6580	12.1216	11.4040	10.9207	10.5600

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Pyrethroids Test Kit Analysis

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Prepare Samples

Slice Fresh vegetables into small pieces(0.5x 0.5 cm.)



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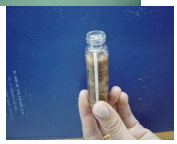
Extraction



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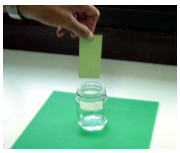
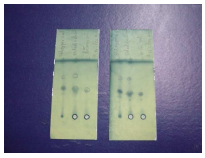
Process of Determination (Pyrethroids)

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Organic Farming has been promoted to use in producing vegetables since 2005 .

Everywhere in the world needs clean foods. In Thailand , government had also promoted farmers to make **biofertilizers** by themselves. Biofertilizers collected from the markets, sometimes had been found **pyrethroids contaminated.** So before using biofertilizer in organic farm , you should **check for pyrethroids residue first.** The quickest way, test kit can be used.

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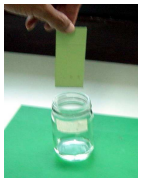
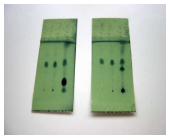
Determination in Biofertilizer (pyrethroids)



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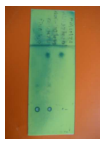
Evaluation (Pyrethroids)


Cyhalothrin

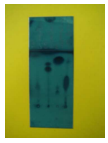
1.7cm.


Deltamethrin

4.1 cm.


Permethrin

3.1, 3.7 cm.


Mixed pyrethroids

Cyhalothrin,

permethrin,

Deltamethrin,

cypermethrin

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Thank You for Your Kind Attention

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