Fast Multiresidue Method for the Determination of Pesticides Residues in Crops Using Mini Solid-Phase Extraction and Large Volume Injection-Gas Chromatography

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Abstract

In recent years, the problem of pesticide residues in crops has been raised on a number of occasions and concern about the safety of food has increased. In order to respond to the increase in the number of pesticides subject to inspection according to the adoption of the Positive List system, the simultaneous analysis of more than 300 constituents is required for GC/MS (Gas Chromatography/Mass Spectrometry). However, it is difficult to greatly increase the number of samples inspected, because a pretreatment process of each sample is time consuming using current analysis techniques. Therefore, in order to accelerate the pretreatment process, we examined fast multiresidue analysis method for the determination of pesticide residue in crops, which combines reducing sample volume using a large volume GC injection method, and re-concentrating the samples by the solid phase extraction (reversed phase mode). As a result, conventional procedures, such as liquid-liquid distribution by a 1)separatory funnel, and concentration process by an evaporator etc., were able to be omitted. The pretreatment process time by one person after fractioning was 15 minutes for one sample and 60 minutes for ten samples. Moreover, measurement by the SCAN mode is employed because of the difficulty of setting the ion set etc. in SIM (Selected Ion Monitoring) mode for an increased number of pesticides to be measured.
We obtained an excellent result for examining and evaluating many kinds of agricultural products.

Experiment

SAIKA Technological method

Sample 10.0 g

Add 25 mL of acetonitrile

Homogenize

Filter

Wash with acetonitrile 10 mL

Filtrate

Add water, make up to 50mL

Adjust filtrate to 50 mL

Take 1 mL of filtrate (Equivalent of 0.2g sample)

A

Solid phase C18 30 mg (purification)

1mL Acetonitrile:Water (80:20) Wash

Outflow liquid

Dilute by adding 2mL water

B

HBS-20mg (Retention)

Outflow liquid

Dilute by adding 20% saline solution 20mL

HBS-20mg (Second Retention)

Vacuum dry:3min

C

Bound PSA 30 mg (purification)

Elute Acetone/Hexane(3/7) 1mL

Eluate

Add PEG300

Adjust eluate to 1mL with Acetone/Hexane(3:7)

GC/MS (SCAN)

25 μL injection (Large volume injection method)

GC/MS Conditions

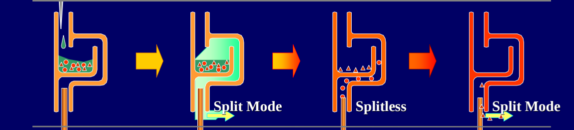
PTV Injector	LaviStoma (EMINET):Stomach-shaped insert
Injection Temp.	70°C-120°C/min-240°C(3min)-50°C/min-260°C(20min)
Solvent Purge Time	15 sec.
Auto Injector	Agilent 7683:50mL syringe
GC	Agilent 6890N
Pre-column	Deactivated silica capillary tube 0.32mm×0.3m
Column	Inert Cap 5MS 0.25 mm i.d.×30 m, df 0.25mm
Column Oven Temp.	60°C(3min)-20°C/min-160°C-7°C/min-230°C-2°C/min-235°C-10°C/min-310°C(8min)
Splitpurge Flow	50 mL/min(6min)-20mL/min
Splitless Time	4 min
MS	JMS-K9 (JEOL)
Detector Temp.	280°C
MS Method	SCAN:50-450

Large Volume Injection-Gas chromatography

we have developed new PTV injector named "LVI-S200" which has a unique "stomach" shaped insert inside as shown in Fig. 1. In this injector, sample introduced can stay as liquid in the insert. This unique shape of the insert makes it possible to carry out Large Volume Injection, Derivatization Injection or Cold Splitless Injection of sample.

LVI Method

Analysis of even heat sensitive materials such as pesticide can be performed since the samples inside of the insert can be transferred to the column at a lower temperature.



1st Stage	2nd Stage	3rd Stage	4th Stage
Injection	Concentration	Transfer	Elimination
The injector is kept at a temperature lower than the boiling point of sample solvent.	While the evaporated sample solvent is exhausted, the sample is concentrated.	Target compounds are transferred to the column at an elevated temperature.	Matrix compounds are eliminated from the insert at further elevated temperature.

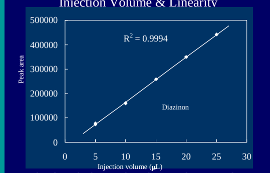


Fig. The relationship between the peak areas and injection volumes

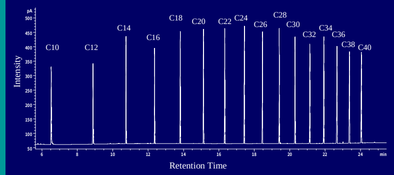


Fig. Chromatogram obtained by injecting 50 μL volume of n-alkanes in hexane

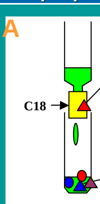
Table Peak areas and the relative standard deviations (R.S.D., n=8)

No.	1	2	3	4	5	6	7	8	RSD(%)
n-C10	185.9	186.2	183.2	187.3	187.8	184.4	186.5	185.5	0.81
n-C12	191.0	192.1	189.8	193.3	193.4	189.7	190.6	191.3	0.75
n-C14	216.3	217.4	215.0	218.6	219.1	214.8	215.2	216.1	0.76
n-C16	203.8	204.6	203.6	206.4	207.4	202.6	203.0	203.7	0.82
n-C18	228.6	229.6	228.0	230.5	231.7	226.9	227.1	229.0	0.72
n-C20	242.5	243.7	242.2	244.3	245.6	240.0	240.7	242.4	0.76
n-C22	249.6	251.0	249.3	251.1	253.0	247.1	247.5	249.2	0.78
n-C24	241.3	242.7	240.9	243.0	244.8	238.9	240.8	241.0	0.74
n-C26	231.7	233.1	231.1	233.1	234.9	229.1	229.7	231.3	0.82
n-C28	235.6	236.9	235.1	237.2	239.1	234.2	233.7	235.5	0.74
n-C30	222.4	223.6	222.0	223.9	225.7	221.4	220.6	222.5	0.72
n-C32	222.2	223.2	221.6	223.4	225.4	220.1	220.6	222.4	0.76
n-C34	233.4	234.2	232.5	234.5	236.6	231.0	231.8	233.8	0.75
n-C36	226.3	227.3	225.1	227.3	230.8	224.0	224.8	227.3	0.94
n-C38	214.6	215.0	213.3	215.1	218.7	212.4	213.3	215.9	0.91
n-C40	227.7	227.9	226.4	227.9	231.8	226.2	227.0	230.7	0.88

:Injection volume; 25 μL

Sample preparation

A



*Removal substances

Plant constituent of lower polarity

Higher fatty acid esters

Chlorophyll

Trap non-polar impurities in the solid phase C18 mini column while pesticide flow through.

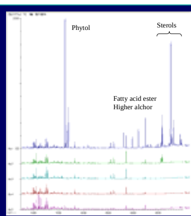
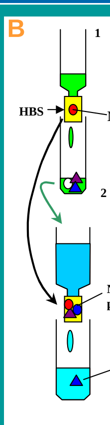


Fig. Total-ion chromatograms for sample extract before No.1 and after purification with C18 : each solvents

B



1 Dilute samples by adding small amount of water and flow through the solid phase HBS

2 Further dilute the outflow liquid by saline solution and then flow through the solid phase HBS again

*Removal substances

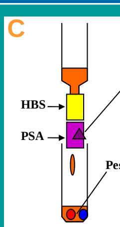
Plant constituent of high water solubility

Saccharide

Water

Trap pesticides in the solid phase HBS mini column while non-polar impurities flow through.

C



*Removal substances

Higher fatty acids

Colorants

During the elution from HBS mini column, trap ionic impurities in the solid phase PSA mini column while pesticides flow through.

B. Retention by HBS. Initially, we diluted the outflow liquid refined by HBS by adding water or saline solution, and then re-concentrated the samples in HBS. Although retention of polar pesticides was improved by raising the dilution rate, the recovery rate decreased because non-polar pesticides were adsorbed onto glass components, etc. Thus, successful retention of polar pesticides in the HBS was achieved by first retaining the non-polar pesticides by the HBS at a lower dilution rate, further diluting the outflow liquid at that time, and then flowing the diluted outflow liquid through the HBS again.

Recoveries of Pesticides Added to Agricultural Products

Sample were spiked at 0.1 μg/g of each pesticides (313 compounds).

Pestisides	Carrot REC	Apple REC	Spinach (n=5) REC	Spinach (n=5) RSD(%)
Dichlorvosr	90.4	83.5	85.7	4.3
Allidochlor	79.4	82.4	92.2	6.6
EPTC	101.0	96.9	120.2	8.1
Biphenyl	92.5	91.7	92.5	9.1
Mevinphos (1+2)	62.9	57.2	55.7	3.5
Acephate	80.9	4.9	15.0	8.1
Etridiazol	99.6	97.4	89.9	5.1
Propham	97.6	96.6	98.1	2.9
Metolcarb	91.0	88.9	91.3	2.7
Methacrifos	100.6	96.3	95.8	3.7
Chloroneb	89.3	95.4	98.3	3.2
OPP	86.7	84.3	88.9	2.6
Isoprocarb	94.0	94.0	96.9	1.8
Molinate	96.7	94.3	100.6	3.8
XMC	95.5	93.5	99.0	2.5
Tecnazene	89.7	87.3	99.5	5.3
Xylylcarb(MPMC)	99.4	96.7	103.4	2.2
Fenobcarb	96.3	95.3	100.4	1.7
Propachlor	93.4	89.8	92.5	3.2
Propoksuru	94.4	93.0	95.3	2.1
Diphenylamine	90.0	91.1	95.5	1.7
Ethoprophos	99.5	96.6	106.7	2.2
Ethalfluralin	90.2	91.6	87.6	7.7
Chloropropham	96.9	103.0	105.9	2.3
Trifluralin	89.0	91.6	86.5	5.9
Benfluralin	87.4	89.6	86.2	5.8
Salithion	95.6	98.2	94.1	3.6
Cadusafos	92.7	94.8	106.2	2.5
Promecarb	92.9	94.0	106.4	1.9
Phorate	86.6	85.4	80.5	8.3
alpha-BHC	84.1	83.5	88.3	5.3
Hexachlorobenzene	74.5	73.8	67.0	5.5
Thiometon	59.1	48.8	54.9	6.8
Desmedipham	77.6	80.8	76.7	6.7
Dicloran	87.4	86.6	84.9	4.9
Dimethoate	67.4	62.5	58.9	5.0
Furilazole	94.6	92.5	90.1	3.6
Carbofuran	97.1	97.7	102.2	2.2
Simazine	90.8	88.7	92.6	1.4
bata-BHC	86.1	87.1	91.4	1.6
Monolinuron	93.2	91.9	89.5	3.0
Swep	86.0	85.4	89.9	3.0
Atrazine	92.2	92.5	91.6	2.0
Triflumizol-metabolic	87.3	85.0	89.1	3.1
Dimethipin	18.7	20.4	26.1	4.8
Quintozen(PCNB)	84.1	83.6	78.8	3.0
clomazone	92.6	93.3	95.0	2.9
Diazinon-ox	101.4	102.4	93.1	6.0
ganma-BHC	90.1	89.3	95.9	2.2
Cyanophos	96.2	96.7	108.6	1.4
Terbufos	84.5	86.8	80.8	5.7
Fonofos	93.1	92.2	101.0	2.8
Propyzamide	86.0	90.4	97.1	2.3
Pyroquilon	79.8	76.4	83.2	2.2
Diazinon	92.1	90.8	106.8	2.1
Phosphamidon E	87.3	83.9	77.1	5.9
Pyrimethanil	89.3	89.3	89.3	1.7
Terbacil	94.4	91.4	91.0	1.8
Disulfoton	48.7	40.6	51.4	5.8
Isazophos	98.2	96.6	89.6	4.5
Tefluthrin	84.0	87.6	94.0	2.2
Etrimfos	92.4	92.4	91.1	3.5
delta-BHC	102.5	88.7	90.0	2.3
Triallate	89.4	90.9	92.4	1.9
Pirimicarb	95.8	82.9	95.8	1.6
Iprobenfos	96.7	94.5	85.7	7.4
Benoxacor	95.6	95.8	91.9	3.2
Phosphamidon Z	97.3	97.1	86.0	6.6
Benfuresate	96.4	97.5	96.6	1.6
Dichlofenthion	90.8	92.7	90.5	3.1
MEP-ox	97.9	93.0	83.3	7.9
Dimethenamid	93.8	93.0	96.1	2.0
Propanil	87.8	88.9	91.5	2.5
Terbucarb	90.5	91.2	91.1	2.1
Acetochlor	94.7	94.1	88.4	3.7
Chlorpyriphos-methyl	90.5	90.8	91.6	2.3
Bromobutide	94.9	96.3	93.2	1.9
Metribuzin	88.8	85.6	83.2	3.3
Vinclozoline	91.3	91.6	91.6	1.7
Malaoxon	94.1	95.9	101.8	4.2

Pestisides	Carrot REC	Apple REC	Spinach (n=5) REC	Spinach (n=5) RSD(%)
3-Hydroxycarbofuran	76.1	61.5	62.7	13.6
Methyl parathion	94.8	91.9	85.2	5.6
Simeconazole	93.7	92.3	87.0	6.4
Tolclofos methyl	90.7	93.0	90.1	3.4
Alachlor	91.8	89.2	89.9	2.3
Symetryne	93.7	92.1	91.7	2.0
Carbaril	108.7	92.6	91.8	6.9
Heptachlor	89.4	91.4	85.2	4.1
Metalaxyl	94.1	93.2	96.9	2.2
Ametryn	92.3	93.1	91.2	1.7
Fenchlorphos	90.2	91.0	92.2	1.7
Cinmethylin	90.2	90.5	94.1	1.3
Prometryn	92.2	93.0	90.0	1.9
Dithiopyr	88.7	93.5	94.3	1.3
Pirimiphos methyl	92.1	93.8	89.5	3.6
Terbutryn	91.6	93.3	89.3	2.2
Fenitrothion	100.8	93.2	92.2	3.5
Ethofumesate	90.7	92.5	91.9	1.7
Probenazole	83.0	72.1	81.3	3.0
Linuron	92.7	90.2	90.0	2.4
Dimethylvinphos E	91.5	91.1	94.0	1.7
Quinoclamine	88.3	82.0	71.3	2.8
Esprocarb	94.5	96.4	94.0	1.6
Malathion	102.0	102.1	89.9	3.0
Thiazopyr	88.3	86.3	86.2	1.7
Metolachlor	94.4	92.6	91.4	1.8
Chlorpyrifos	91.4	92.2	92.7	2.0
Aldrin	80.5	86.9	84.2	2.0
Thiobencarb	92.5	94.8	90.8	2.0
Dimethylvinphos-z	93.1	91.9	91.2	1.3
Clorthal dimethyl	86.5	88.5	90.9	1.3
Diethofencarb	95.3	95.2	87.7	4.1
Fenthion	82.0	81.6	81.0	3.3
Cyanazine	79.1	84.7	111.6	9.1
Parathion	101.7	94.0	101.9	4.5
Fenpropemorph	66.9	79.6	76.6	2.1
Toriadimefon	94.6	94.6	91.6	1.9
Isophenfos P=O	98.4	96.3	82.7	7.8
Tetraconazole	89.2	90.8	86.4	2.6
Isocarbofos	95.2	90.3	90.7	4.3
Phthalide	93.0	94.5	85.7	3.4
Nitrothal-isopropyl	106.3	88.5	72.9	7.0
Bromophos	94.2	91.4	92.1	1.8
Diphenamide	95.0	95.4	97.2	2.0
Fosthiazate 1	104.9	101.9	83.4	7.0
Fosthiazate 2	102.7	99.4	84.2	7.7
Pendimethalin	105.8	92.1	79.0	7.5
cis-Chlorfenvinphos	92.6	96.2	89.7	4.5
Penconazole	96.4	92.6	90.2	2.1
Heptachlor epoxide cis	90.6	92.7	89.5	1.8
Fipronil	98.4	92.4	84.9	5.0
Dimethametryn	102.9	92.1	86.4	2.4
Pyrifenox E	97.6	95.3	89.8	1.9
Isofenphos	101.4	102.4	91.5	2.8
trans-Chlorfenvinphos	86.9	88.8	89.1	1.4
Heptachlor epoxide trans	92.6	94.0	89.2	2.5
Ethychlozate	96.8	93.3	91.8	1.2
Allethrin	89.3	91.4	86.7	1.9
Thiabendazole(TBZ)	75.9	55.4	37.1	7.5
Diclocymet 1	91.5	92.7	88.8	1.5
Quinalphos	96.8	93.8	88.6	1.7
Phenthoate	102.3	95.6	83.6	4.6
Procymidone	94.0	92.9	90.6	1.5
Dimepiperate	101.8	97.4	84.4	5.2
Triadimenol	96.4	92.2	88.3	4.0
Triflumizol	89.9	85.6	70.4	7.5
Methidathion	106.8	98.0	89.0	4.2
Chlordane cis	89.9	91.2	87.7	1.7
Propaphos	83.9	73.4	77.6	4.0
Pyrifenox Z	93.2	94.3	82.2	4.0
Paclobutrazol	97.9	95.4	87.7	4.9
Tetrachlorvinphos	92.0	89.2	90.3	1.7
Butachlor	93.4	92.9	87.9	3.1
Vamidothion	90.1	98.0	102.0	4.1
Chlordane trans	88.8	89.2	86.3	1.6
Fenothiocarb	95.1	93.4	92.0	1.3
Endosulfan 1	96.0	91.6	87.9	2.0
Methoprene	100.2	100.2	112.3	4.0
Butamifos	107.2	97.8	77.6	8.0
Flutriafol	100.0	92.9	81.0	6.1

Pestisides	Carrot REC	Apple REC	Spinach (n=5) REC	Spinach (n=5) RSD(%)
Napropamid	95.8	94.0	93.2	1.1
Fenamiphos	89.2	79.8	77.8	4.9
Flutolanil	92.1	93.6	90.6	1.4
Fludioxonil	89.1	88.0	83.2	3.3
Hexaconazol	91.8	92.5	75.0	6.2
Prothiofos	96.4	90.2	84.7	3.2
Metominostrobin E	98.8	92.8	86.8	3.5
Pretilachlor	95.1	91.0	87.5	3.2
Isoprothiolane	103.6	95.0	92.0	1.9
Isoxathion-ox	101.3	81.3	90.3	1.1
Profenofos	94.3	93.0	88.7	2.3
p,p'-DDE	86.8	85.6	81.5	1.8
Uniconazole P	104.0	100.0	84.9	7.1
Dieldrin	91.4	91.4	84.3	1.4
Oxadiazone	91.9	93.8	91.1	2.3
Flamprop-methyl	94.9	93.3	90.2	1.8
Thifluzamide	46.8	47.7	89.4	1.5
Myclobutanil	96.0	92.5	86.8	2.0
Tribuphos	96.2	93.8	87.0	4.1
Iprovalicarb 1	101.5	96.7	86.2	5.1
Flusilazole	92.7	92.1	86.0	3.0
Buprofezin	91.7	92.7	87.1	2.3
Dichlobutrazol	96.7	94.9	84.0	5.0
Oxyfluorfen	103.5	94.3	79.6	6.4
Buprimate	93.5	94.0	87.8	3.0
Azaconazole	105.6	95.0	87.7	2.1
Kresoxim-methyl	228.0	92.5	89.8	1.9
Metominostrobin Z	119.0	94.4	78.8	6.4
Pyrethrins	108.0	104.2	95.1	1.7
Iprovalicarb 2	109.9	96.8	91.9	5.2
Chlorfenapyr	95.9	92.4	93.4	1.6
Cyproconazole(1+2)	101.9	93.9	84.5	6.0
Cyflufenamid	104.3	101.6	96.4	3.3
Isoxathion	123.3	110.7	114.5	1.7
Endrin	99.5	93.8	81.5	5.2
Fenoxanil	92.9	91.5	95.4	7.4
Dicofol	103.9	96.5	89.7	5.2
Chlorobenzilate	103.3	95.9	89.8	5.0
Pyriminobac-methyl E	109.4	96.4	85.3	6.4
Fensulfothion	127.2	100.4	84.7	7.2
Oxadixyl	96.7	92.9	92.4	1.6
p,p'-DDD	95.3	92.2	84.5	2.4
o,p'-DDT	94.5	89.4	73.7	3.8
Ethion	108.8	97.2	84.7	7.7
Fluacrypyrim	110.6	97.0	91.6	5.9
Mepronil	104.7	95.4	92.9	3.4
Triazophos	111.9	94.4	86.6	7.4
CNP	102.0	85.7	81.6	3.3
Benalaxyl	96.7	93.6	98.7	0.9
Carfentrazone ethyl	100.8	92.9	86.4	4.2
Norflurazon	93.7	89.6	93.2	1.3
Edifenphos	99.6	90.2	91.2	5.3
Cyanophenphos	96.2	90.3	86.4	2.7
Quinoxyfen	91.7	89.7	86.8	2.1
Endosulfan sulfate	93.7	88.8	88.2	1.6
Propiconazole 1	104.5	93.9	84.2	7.4
Lenacil	94.5	90.4	90.4	1.3
Diofenolan 1	94.4	95.7	88.9	1.6
Trifloxystrobin	79.1	74.6	95.5	6.4
p,p'-DDT	101.8	90.2	76.7	1.6
Pyriminobac-methyl Z	99.7	91.3	84.2	3.3
Propiconazole 2	94.8	89.9	76.3	2.8
Diofenolan 2	91.9	91.7	87.0	1.8
Pyraflufen-ethyl	92.5	92.7	88.1	1.8
Hexazinone	88.2	83.6	80.7	0.9
Clodinafop-propargyl	121.7	99.7	98.7	3.1
EPN Oxon	122.8	93.9	113.1	4.8
Thenylchlor	102.9	96.3	88.8	3.8
Tebuconazole	99.0	92.6	87.5	6.0
Diclofop-methyl	95.8	95.2	93.9	0.9
Propargite(BPPS)	91.0	97.4	100.8	0.8
Diflufenican	98.7	98.1	85.6	3.0
Piperonyl butoxide	100.2	97.2	89.9	5.1
Bioresmethrin	92.9	85.0	77.6	4.1
Pyributicarb	102.9	96.7	93.3	3.1
Acetamipride	79.5	73.3	61.0	5.3
Pyridafenthion	99.8	89.6	89.7	2.5
Iprodione	102.5	89.0	91.1	5.1
Carbosulfan	99.8	83.1	46.6	20.2
Phosmet	110.4	88.7	93.7	5.2

Pestisides	Carrot REC	Apple REC	Spinach REC
EPN	97.9	86.2	82.7
Bromopropylate	92.8	91.0	87.3
Piperophos	101.5	91.9	83.0
Bifenthrin	78.7	81.9	74.2
Picolinafen	90.1	91.5	84.0
Cloquintocet-methyl	88.9	88.4	80.0
Fenoxycarb	96.6	92.8	89.5
Bifenazate	74.5	71.2	80.8
p,p'-Methoxychlor	94.6	91.4	76.0
Etoxazole	90.1	89.3	90.0
Fenpropathrin	96.3	92.4	89.1
Anilofos	105.2	92.6	84.7
Bifenox	94.5	84.1	76.1
Tebufenpyrad	86.9	90.5	85.7
Clomeprop	93.2	92.8	80.5
Furametpyr	97.6	93.2	95.2
Tetradifon	93.6	92.7	92.0
Iprodione rearrangement	78.2	80.4	86.0
Furathiocarb	101.2	92.9	85.6
Phenothrin 1	89.7	89.0	88.5
Phosalone	104.7	94.6	88.3
Pentoxazone	88.7	90.9	85.9
Phenothrin 2	91.2	91.5	85.4
Mefenacet	98.6	92.9	91.4
Pyriproxyfen	96.8	95.1	94.8
Cyhalothrin 1	97.6	98.7	95.1
Mirex	44.8	56.3	43.3
Cyhalofop-butyl	96.3	96.4	95.8
Cyhalothrin 2	105.3	94.9	87.8
Lactofen	96.6	86.9	74.0
Fenarimol	92.0	88.8	88.7
Pyrazophos	100.2	93.7	82.4
Acrinathrin	106.9	94.8	99.2
Pyraclofos	91.6	87.3	86.7
Fenoxaprop-ethyl	93.7	93.0	88.7
Bitertanol	91.0	88.6	82.6
Permethrin cis	86.6	86.5	84.8
Fluquinaconazole	93.0	88.9	82.5
Coumaphos	98.7	92.0	87.8
Prochloraz	87.6	87.1	76.5
Pyridaben	94.4	92.5	87.8
Permethrin trans	88.0	86.7	85.3
Etobenzanid	94.3	92.7	29.4
Cafenstrole	99.4	91.5	91.3
Fenbuconazole	93.4	90.9	91.2
Cyfluthrin 1	105.6	101.8	98.1
Cyfluthrin 2	109.1	103.0	105.9
Cyfluthrin 3	76.5	72.7	92.3
Cyfluthrin 4	99.1	93.8	86.0
Boscalid	94.5	91.9	94.6
Cypermethrin 1	98.1	93.8	88.5
Halfenprox	79.2	80.4	70.5
Cypermethrin 2	95.3	91.8	87.4
Cypermethrin 3	99.4	92.8	91.8
Flucythrinate 1	97.9	94.4	85.0
Cypermethrin 4	98.3	96.7	98.9
Etofenprox	74.6	81.6	87.4
Flucythrinate 2	99.9	96.4	89.0
Silafluofen	43.5	57.3	52.6
Pyrimidifen	79.0	84.7	74.7
Flumioxazin	102.0	88.6	92.5
Fenvalerate1	88.2	87.3	86.8
Fluvalinate 1	94.4	86.9	86.1
Fenvalerate 2	92.3	90.0	92.5
Fluvalinate 2	92.7	85.9	86.4
Difenoconazole 1	90.5	90.4	81.2
Difenoconazole 2	90.2	89.6	87.0
Pyrazoxyfen	99.7	91.5	92.4
Deltamethrin	99.4	91.4	90.4
Flumiclorac-pentyl	95.1	94.1	92.7
Azoxystrobin	92.2	87.8	87.0
Tolfenpyrad	91.5	94.6	90.3
Imibenconazole	105.9	97.6	65.5

Reference

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