

Research Article



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수출딸기 중 Cyenopyrafen과 Cyflumetofen의 잔류소실 특성평가 및 잔류농약 모니터링

김영진, 김종환, 권영상, 송종욱, 서종수*
가

Residual Characteristics and Monitoring of Cyenopyrafen and Cyflumetofen in Strawberries for Export

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Abstract

BACKGROUND: Many farmers who cultivate the strawberries for export have used agricultural chemicals which MRL (Maximum Residue Limits) of main export target countries or simultaneous multi-residue analysis in Korea have not been established. Among them, the cyenopyrafen and cyflumetofen were selected and applied to this study to determine the PHI (pre-harvest interval) which is appropriate to the PLS (Positive List System) criterion (0.01 mg/kg) and to investigate the residual amounts in the samples. In addition, Fifty pesticides were monitored to check up whether it is suitable or not for main export target countries.

METHODS AND RESULTS: Cyenopyrafen and cyflumetofen were sprayed out to the strawberries. Samples for residual analyses were taken for maximum 60 days. After sampling, they were extracted by the QuEChERS method and analyzed using the LC-MS/MS. Cyenopyrafen and cyflumetofen were detected in a range of 0.0106 ~2.6517 mg/kg and of 0.0005~1.4480 mg/kg, respectively. From this results, they were found to be suitable for PLS

concentration after 30 or 45 days after spray. In addition, they were detected in most samples that were selected at random. Their concentrations were higher than the PLS criterion in the maximum twenty samples.

Twelve of pesticides unsuitable for main export target countries have been detected in the monitoring of simultaneous multi-residue analysis. The result indicates they are unsuitable for export since they excesses over PLS criterion.

CONCLUSION: The monitoring result showed it is necessary to establish the pesticide standards of safe use suitable for the PLS criterion. In addition, it is considered continues management and inspection are needed to solve problems caused by unsuitable pesticides in export strawberries.

Key words: Cyenopyrafen, Cyflumetofen, Export strawberries, Monitoring, Residual pesticides

서론

(*Fragaria x ananassa* Duch.) 2015

6,403 ha, 194,513 , 1 2

10%

(Korean Statistical Information Service

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(KOSIS), 2015).
 (Lee et al., 1998; Kim et al., 2010).
 78.4%
 가 가
 (Korea Agro-Fisheries & Food Trade Corporation (KATI), 2017).

가 가
 (Kim et al., 2010). 1968
 가
 (Kim et al., 2008). , 2016 '320
 가

(MRL)
 (PLS) '320
 cyenopyrafen cyflumetofen

재료 및 방법

시약 및 표준품

cyenopyrafen (99.8%) cyflumetofen (97.7%)
 Sigma-Aldrich (Buchs, Switzerland)

(Table 2) LGC Standard, Sigma-Aldrich, Wako pure Chemical, HPC Standard GmbH

HPLC acetonitrile, methanol, water Burdick & Jackson (Korea), formic acid (98%) Junsei Chemical (Tokyo, Japan), ammonium formate

(99.995%) Sigma-Aldrich (Steinheim, Germany)
 QuEChERS QuEChERS extract kit (magnesium sulfate, sodium chloride, sodium citrate dibasic sesquihydrate, sodium citrate tribasic dihydrate) QuEChERS dispersive SPE 2 mL primary secondary amine(PSA), octadecylsilane end-capped, magnesium sulfate) phenomenex (Torrance, USA)

검량선 작성 및 분석정량한계(Method Limit of Quantification, MLOQ)

cyenopyrafen 10.02 mg cyflumetofen 10.24 mg
 acetonitrile 10 mL 1,000 mg/L stock solution
 , acetonitrile 10.0, 20.0, 50.0, 100.0 200.0 µg/L working solution
 . working solution 50 µL 200 µL water 750 µL
 0.5, 1.0, 2.5, 5.0 10.0 µg/L matrix matched calibration
 (Minimum detectable amount, MDA) signal/noise가 3

$$: 0.05 \mu\text{g/L} \times 1.0 \mu\text{L} = 0.00005 \text{ ng}$$

$$\text{MLOQ} : 0.00005 \text{ ng} \times \frac{1 \text{ mL}}{1 \mu\text{L}} \times \frac{10 \text{ mL}}{0.2 \text{ mL}} \times \frac{1}{10 \text{ g}} = 0.25 \text{ ng/g}$$

회수율 시험

()
 50 mL 10 g
 cyenopyrafen, cyflumetofen
 5 µg/L 0.1 mL 0.5 mL
 가 0.5 2.5 ng/g 3
 acetonitrile 10 mL 2
 , 4 g anhydrous magnesium sulfate, 1 g sodium chloride, 1 g sodium citrate, 0.5 g disodium citrate sesquihydrate 가 2
 4,500 rpm 6
 0.2 µm syringe filter (Whatman, PTFE)
 200 µL water 750 µL acetonitrile
 50 µL . Cyenopyrafen
 cyflumetofen LC-MS/MS

Table 1

약제살포 및 cyenopyrafen과 cyflumetofen의 잔류소실

Cyenopyrafen cyflumetofen 가
 가(
 156)
 cyenopyrafen (; , ; 2

Table 1. LC-MS/MS analytical method for the cyenopyrafen and cyflumetofen

Instrument	: Agilent (6460) Triple Quad LC/MS with Agilent 1260 series HPLC			
Column	: Agilent Poroshell 120 EC-C18, 2.1×100 mm, I.d., 2.7 μm			
Mobile phase A	: 5 mM ammonium formate & 0.1% formic acid in water			
Mobile phase B	: 5 mM ammonium formate & 0.1% formic acid in methanol			
Flow rate	: Mobile phase A : Mobile phase A=2:8, (v/v) : 0.3 mL/min			
Injection volume	: 1 μL			
Column temperature	: 40°C			
Ionization mode	: ESI positive			
Gas temperature	: 325°C			
Gas Flow	: 6 mL/min			
Nebulizer gas pressure	: 35 psi			
Ionspray voltage	: +4000 V			
MS/MS ion (MRM ion)				
Compounds	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	
			Quantitative ion (collision energy)	Qualitative ion (collision energy)
Cyenopyrafen	4.216	394.25	310.2 (24 V)	254.2 (32 V)
Cyflumetofen	2.241	448.18	173.1 (20 V)	145.1 (60 V)

Table 2. List of pesticides selected for monitoring pesticides in strawberries using LC-MS/MS and GC-MS/MS

No.	Pesticide	No.	Pesticide	No.	Pesticide
1.	Acetamiprid	19.	Flubendiamide	37.	Spinetoram
2.	Azoxystrobin	20.	Fludioxonil	38.	Spiromesifen
3.	Bifenazate	21.	Flufenoxuron	39.	Sulfoxaflor
4.	Bitertanol	22.	Fluopyram	40.	Tebuconazole
5.	Boscalid	23.	Fluquinconazole	41.	Teflubenzuron
6.	Buprofezin	24.	Fosthiazate	42.	Tetraconazole
7.	Carbendazim	25.	Imidacloprid	43.	Thiacloprid
8.	Chlorantraniliprole	26.	Iprobenfos/IBP	44.	Thiamethoxam
9.	Cyprodinil	27.	Isoprothiolane	45.	Tricyclazole
10.	Diazinon	28.	Kresoxim-methyl	46.	Trifloxystrobin
11.	Difenoconazole	29.	Lufenuron	47.	Triflumizole
12.	Diflubenzuron	30.	Methoxyfenozide	48.	Chlorothalonil*
13.	Dimethomorph	31.	Metrafenone	49.	Indoxacarb*
14.	Dinotefuran	32.	Novaluron	50.	Procymidone*
15.	Fenarimol	33.	Prochloraz	51.	Pyridalyl*
16.	Fenhexamid	34.	Pymetrozine	52.	Spinosad*
17.	Ferimzone	35.	Pyraclostrobin	-	-
18.	Fonicamid	36.	Pyrimethanil	-	-

* Pesticides were analyzed by GC-MS/MS

, 3), cyflumetofen(; , , 2,000 ,
; 2 , 3) , , . Cyenopyrafen

Table 3. Analytical conditions of LC-MS/MS for monitoring pesticides in strawberries

Instrument	: Agilent (6460) Triple Quad LC/MS with Agilent 1260 series HPLC			
Column	: Agilent Poroshell 120 EC-C18, 2.1×100 mm, I.d., 2.7 μm			
Mobile phase A	: 5 mM ammonium formate & 0.1% formic acid in water			
Mobile phase B	: 5 mM ammonium formate & 0.1% formic acid in methanol			
Gradient program	Time (min)	A (%)	B (%)	Flow (mL/min)
	Initial	85	15	0.3
	1	85	15	
	1.5	40	60	
	10	10	90	
	15	10	90	
	20	2	98	
	20.1	85	15	
25	85	15		
Injection volume	: 1 μL			
Column temperature	: 40°C			
Ionization mode	: ESI positive			
Gas temperature	: 325°C			
Gas Flow	: 6 mL/min			
Nebulizer gas pressure	: 35 psi			
Ionspray voltage	: +4000 V			
Scan type	: Dynamic MRM mode			

Table 4. Analytical conditions of GC-MS/MS for monitoring pesticides in strawberries

Instrument	: Bruker, SCION TQ			
Column	: BR-5ms, FS 30 m, 0.25 mm ID, 0.25 μm			
Injector temp.	: 260°C			
Injection volume	: 1 μL, split ratio 50:1			
Oven	: 90°C(3 min) → 20°C/min → 120°C → 8°C/min → 300°C(3 min)			
Carrier gas	: Helium (99.999%) at 1.5 mL/min			
Ion mode	: Electron ionization (EI), 70 eV			
Scan type	: MRM			
Manifold	: 40°C			
Transfer-line temp.	: 280°C			
Source temp.	: 200°C			

3 0 0, 3, 5, 7, 14, 30, 2016 2 2017 2 가 (2 kg)
 45 , cyflumetofen '320
 0, 3, 5, 7, 14, 30, 45, 60 1 ' (2015~2016)
 kg . 52 (Table 2)
 LC-MS/MS
 (*Tetranychus urticae*)
 cyenopyrafen cyflumetofen .
 잔류농약 모니터링 320 (Anastassiades
 가 20 *et al.*, 2003; Kim *et al.*, 2016).

Table 5. Recovery results for cyenopyrafen and cyflumetofen in strawberry at two-spiked levels

Pesticides	Fortification levels (µg/L)	Replicate	Recovery (%)	Average±SD ^{a)} (%) (RSD) ^{b)}
Cyenopyrafen	0.5	1	109.0	104.4±4.0 (3.8)
		2	102.1	
		3	102.1	
	2.5	1	96.4	97.7±1.1 (1.1)
		2	98.3	
		3	98.4	
Cyflumetofen	0.5	1	91.1	89.1±3.0 (3.4)
		2	90.6	
		3	85.6	
	2.5	1	87.6	90.8±2.8 (3.1)
		2	92.6	
		3	92.3	

^{a)} Standard deviation

^{b)} Relative Standard Deviation=(standard deviation/average)×100

200 µL water 750 µL, acetonitrile 50 µL
 LC-MS/MS GC-MS/MS
 1 mL 25 mg PSA, 150 mg magnesium sulfate (MgSO₄) 25 mg C18EC (octadecylsilane, end-capped)가 2 mL dispersive SPE tube
 2 12,000 rpm 2
 200 µL acetonitrile 800 µL
 LC-MS/MS GC-MS/MS

Table 3, 4

결 과

Cyenopyrafen과 cyflumetofen의 분석법 확립 및 회수율 시험

Cyenopyrafen cyflumetofen (Instrument detection limit, IDL, S/N ≥3.0) 0.05 µg/L 0.25 ng/g
 PLS 0.01 µg/g
 PLS

cyenopyrafen cyflumetofen
 $y=1992.0x-70.26$
 $(R^2=0.9998)$ $y=206.5x-1.7$ $(R^2=0.9995)$
 cyenopyrafen cyflumetofen

10 3 Table 5 (Relative Standard Deviation, RSD) cyenopyrafen 1.1~3.8%, cyflumetofen 3.1~3.4% CODEX 가 (CAC/GL 40, 1993)

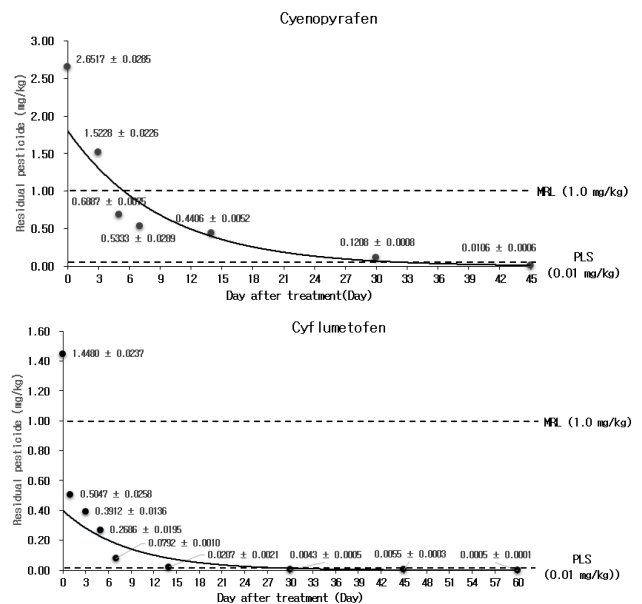


Fig. 1. Residual level and dissipation pattern of cyenopyrafen and cyflumetofen during experimental period in strawberries

Cyenopyrafen과 cyflumetofen의 잔류 소실

Cyenopyrafen cyflumetofen 가
 Cyenopyrafen 45 2.6517±0.0285 mg/kg
 cyflumetofen 1.4480±0.0237 mg/kg (MRL; Maximum Residue List, : 1.0 mg/kg)

Table 6. Dissipation regression equations and biological half-lives of cyenopyrafen and cyflumetofen in strawberries

Compounds	Dissipation regression equation	Biological half-life (days)
Cyenopyrafen	$y=1820.09e^{0.1081x}$ ($R^2=0.9552$)	6.4
Cyflumetofen	$y=344.98e^{-0.097x}$ ($R^2=0.8064$)	7.1

Table 7. Detection of cyenopyrafen and cyflumetofen in strawberry collected from the export farmland

Compounds	Year	Number of the export farm detected	Residue (mg/kg)	Detection rate(%)	Number of the export farm exceeding PLS
Cyenopyrafne	2016	20	0.0003 ~ 0.4400	100	11
	2017	20	0.0007 ~ 0.2500	100	10
Cyflumetofen	2016	5	0.0024 ~ 0.2400	25	2
	2017	14	0.0006 ~ 0.6700	70	8

45 mg/kg cyenopyrafen 0.0106~2.6517 5 가 20 가 , cyenopyrafen 2016 0.0003~0.4400 mg/kg (MRL) , MRL

Cyflumetofen 60 mg/kg 0.0005~1.4480 1 가 11 가 PLS 0.01 mg/kg 2017 20 0.0007 mg/kg 0.2500 mg/kg 가 10 (Fig. 1), PLS 가 10

Cyenopyrafen cyflumetofen 가 . Cyflumetofen 2016 20 가 5 가 $C_t=C_0e^{-kt}$ (C_t : , C_0 : , k: , t:) 0.0024 mg/kg 0.2400 mg/kg , PLS 0.01 0.693/k (Chang *et al.*, 2011). , cyenopyrafen cyflumetofen 가 2 가 . 6.4 7.1 2017 20 가 14 가 0.00062 mg/kg PLS (Table 6). 0.6700 mg/kg PLS (Table 7). cyenopyrafen 가 8 가

cyflumetofen MRL(1.0 mg/kg) 가 Fenhexamid(MRL; 2.0 mg/kg), Diflubenzuron(MRL; 2.0 mg/kg) 가 (PLS) 30 (Ministry of Food and Drug Safety (MFDS), 2017). (cyenopyrafen) 45 (cyflumetofen) PLS cyenopyrafen cyflumetofen 가 가 가 가 (Kim *et al.* 2017), , cyenopyranfen cyflumetofen 2015~2016 가 52 '320 ' 0.25~150 ng/kg acetamid 39 수출딸기 재배농가의 농약 다성분 분석 모니터링 결과 2016~2017 가 20 가 0.0006~0.282 mg/kg , cyenopyranfen cyflumetofen azoxystrobin 36

Table 8. Summary of the residual pesticide-monitoring

Pesticide	No. of pesticide detected in samples	Residual concentration (mg/kg)	MRLs (mg/kg)					
			Korea	Taiwan	Singapore	Indonesia	Japan	Hong Kong
Acetamiprid	39	0.0006~0.282	1.0	1.0	0.5	0.5	3.0	3.0
Azoxystrobin	36	0.0003~0.295	1.0	2.0	10.0	10.0	10.0	10.0
Kresoxim-methyl	34	0.0003~0.344	1.0	3.0	0.01	1.0	5.0	5.0
Thiacloprid	33	0.0004~0.207	2.0	0.01	1.0	1.0	5.0	1.0
Difenoconazole	32	0.0003~0.062	0.5	1.0	0.01	0.5	2.0	5.0
Chlorantraniliprole	24	0.0004~0.0071	1.0	0.3	1.0	1.0	1.0	1.0
Pyraclostrobin	18	0.0004~0.0664	1.0	0.5	1.5	1.5	2.0	0.5
Fludioxonil	16	0.0002~0.0585	2.0	2.0	3.0	3.0	5.0	3.0
Boscalid	13	0.0003~0.138	5.0	3.0	3.0	3.0	15.0	3.0
Tricyclazole	13	0.0006~0.0079	0.05	0.01	0.01	0.05	0.02	0.01
Flubendiamide	12	0.0002~0.0026	1.0	1.0	0.01	1.0	2.0	2.0
Procymidone	12	0.0104~0.433	10.0	5.0	0.01	10.0	10.0	10.0
Buprofezin	12	0.0002~0.0009	3.0	0.01	3.0	3.0	3.0	3.0
Triflumizole	9	0.0002~0.130	2.0	1.0	0.01	2.0	2.0	2.0
Prochloraz	8	0.0035~0.010	0.5	0.01	0.01	0.5	1.0	0.01
Methoxyfenozide	5	0.0005~0.0019	0.7	2.0	2.0	2.0	2.0	2.0
Imidacloprid	5	0.0008~0.0031	0.3	1.0	0.5	0.5	0.5	0.5
Pyrimethanil	3	0.0208~0.265	2.0	3.0	0.01	3.0	10.0	3.0
Tetraconazole	3	0.0001~0.0003	1.0	0.5	0.01	1.0	2.0	0.01
Dimethomorph	2	0.0003~0.0015	2.0	2.0	0.5	2.0	0.05	0.05
Flonicamid	2	0.147~0.286	1.0	0.01	0.01	1.0	2.0	0.01
Dinotefuran	2	0.0005~0.0019	2.0	1.5	0.01	2.0	2.0	0.01
Sulfoxaflor	2	0.0003~0.065	0.5	0.5	0.5	0.5	0.01	0.01
Fluopyram	2	0.0035	3.0	0.4	0.4	3.0	5.0	0.01
Spinetoram	2	0.0004	0.2	1.0	0.01	0.2	2.0	0.01
Ferimzone	2	0.0004	0.05	0.01	0.01	0.05	0.01	0.01
Fosthiazate	2	0.0013~0.0014	0.05	0.01	0.01	0.05	0.05	0.01
Pyridalyl	1	0.015	2.0	0.01	0.01	2.0	5.0	0.01
Metrafenone	1	0.0014	5.0	0.01	0.6	5.0	0.6	0.01
Tebuconazole	1	0.0125	0.5	0.01	0.01	0.5	0.01	0.01
Isoprothiolane	1	0.0002	0.01	0.01	0.01	0.01	0.01	0.01

0.0003~0.2950 mg/kg, 가

kresoxim-methyl 34 0.0003~0.3440 mg/kg 가

40

31

MRL

(Table 8). 12

가

MRL

PLS

가

(Table 9).

(Rural Development Administration (RDA), 2016).

2016 2017
 40 가
 , cyenopyrafen 21 가, cyflumetofen 10 가
 PLS
 52
 2016 2017 40 가
 , 12
 가 가
 ,
 가 가
 가

Notes

The author declare no conflict of interest.

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