

SUPPLEMENTARY MATERIAL

**Comparison of Recovery Efficiency and Matrix Effect Reduction in Pesticide Residue Analysis:
QuEChERS with d-SPE, SPE, and FaPEX in Apples and Korean Cabbage**

Hyosub Lee,^{*a} Yuran Cho,^a Geonhee Jung,^a Hyanghee Kim,^a Wontae Jeong^a

^aNational Institute of Agricultural Sciences, 166 Nongsaengmyeong-ro, Iseo-myeon, Wanju-gun, Jeollabuk-do,
55365, Korea

*Corresponding author. Fax: +82 63 238 3238

Email address: lhs8255@korea.kr

Table S1. Comparison of recovery rates in apples and Korean cabbages according to the purification methods in QuEChERS and d-SPE

Group	QuChERS and d-SPE clean up					
	PSA		PSA+C18		PSA+GCB	
	Apple	Korean cabbage	Apple	Korean cabbage	Apple	Korean cabbage
I	1%	6%	1%	6%	0%	5%
II	9%	3%	9%	3%	5%	5%
III	89%	85%	89%	88%	92%	87%
IV	1%	5%	2%	3%	2%	2%
V	0%	0%	0%	0%	1%	0%

Table S2. Comparison of recovery rates in apples and Korean cabbages according to the purification methods in QuEChERS and SPE

Group	QuChERS and SPE clean up							
	PSA		PSA+C18		PSA+GCB		Lipid filtr	
	Apple	Korean cabbage	Apple	Korean cabbage	Apple	Korean cabbage	Apple	Korean cabbage
I	0%	1%	2%	4%	2%	2%	2%	6%
II	9%	8%	12%	11%	16%	9%	7%	5%
III	84%	83%	83%	85%	79%	86%	89%	87%
IV	6%	9%	2%	0%	2%	3%	2%	2%
V	0%	0%	2%	0%	1%	0%	0%	0%

Table S3. Comparison of recovery rates in apples and Korean cabbages according to the purification methods in FaPEX

Group	FaPEX					
	Amine		Amine+C18		Amine+GCB	
	Apple	Korean cabbage	Apple	Korean cabbage	Apple	Korean cabbage
I	9%	5%	5%	5%	20%	5%
II	88%	31%	87%	21%	79%	85%
III	3%	63%	8%	70%	2%	9%
IV	1%	2%	1%	4%	0%	0%
V	0%	0%	0%	0%	0%	0%

Table S4. Validation of 128 pesticides recovery and RSD in apple and korean cabbage at two different concentration and clean-up methods with LC-MS/MS

Compounds	Recovery (RSD, %)							
	Apple				Korean cabbage			
	QuChERS and SPE		FaPEX(Amine+C18)		QuChERS and SPE		FaPEX(Amine+C18)	
	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg
Acephate	93(0)	101(1)	81(1)	102(1)	89(2)	91(2)	117(20)	78(5)
Acetamiprid	98(2)	103(1)	87(1)	81(1)	105(2)	101(2)	94(3)	80(8)
Acrinathrin	113(18)	103(2)	103(2)	78(1)	103(9)	104(3)	96(2)	80(6)
Alachlor	91(5)	101(2)	91(4)	82(2)	117(8)	105(4)	92(2)	78(8)
Ametoctradin	97(2)	103(1)	75(2)	74(2)	102(1)	100(2)	88(3)	78(7)
Azoxystrobin	100(0)	104(1)	87(1)	79(1)	107(2)	104(2)	94(3)	79(8)
Benthiavdicarb isopropyl	103(4)	104(1)	84(1)	79(1)	105(4)	101(2)	92(4)	79(8)
Bifenthrin	97(1)	104(2)	82(1)	77(1)	102(3)	103(3)	91(2)	79(7)
Boscalid	99(3)	103(1)	87(1)	77(1)	106(4)	102(3)	92(2)	78(9)
Bromuconazole	87(4)	99(2)	78(3)	77(2)	85(4)	80(2)	74(9)	75(11)
Buprofezine	98(1)	104(1)	84(3)	76(1)	105(2)	100(3)	90(2)	79(7)
Cadusafos	97(1)	104(1)	86(2)	79(1)	106(2)	103(3)	92(3)	79(7)
Carbofuran	111(1)	103(2)	86(2)	79(2)	104(2)	103(3)	91(4)	79(8)
Carpropamid	99(1)	104(1)	86(1)	80(1)	105(3)	103(3)	90(5)	80(8)
Chlorfluazuron	100(4)	103(1)	88(8)	79(2)	96(2)	103(4)	100(3)	82(8)
Chlorpyrifos	104(2)	102(2)	84(2)	78(1)	111(4)	102(2)	96(1)	78(8)
Chromafenozide	99(2)	104(2)	87(2)	80(2)	110(2)	104(2)	92(3)	78(6)
Clethodim	82(5)	80(2)	88(1)	78(1)	41(27)	42(4)	63(17)	79(22)
Clomazone	100(1)	104(10)	86(1)	80(1)	106(2)	103(2)	92(3)	79(8)
Clothianidin	109(2)	101(2)	86(3)	79(2)	111(2)	102(3)	95(3)	80(8)
Cyflufenamid	101(9)	102(3)	89(7)	80(4)	99(15)	106(1)	105(3)	76(8)
Cyproconazole	101(3)	104(1)	81(0)	77(2)	104(4)	102(2)	87(4)	79(8)
Cyprodinil	104(3)	103(1)	84(5)	78(1)	105(2)	101(2)	89(3)	79(8)
Diazinon	102(2)	103(1)	85(1)	79(1)	103(3)	103(3)	92(3)	79(7)
Diethofencarb	108(17)	102(2)	91(11)	84(3)	96(9)	97(5)	99(6)	83(7)
Difenoconazole	96(2)	109(2)	86(21)	79(2)	99(1)	107(4)	108(2)	78(4)

Compounds	Recovery (RSD, %)							
	Apple				Korean cabbage			
	QuChERS and SPE		FaPEX(Amine+C18)		QuChERS and SPE		FaPEX(Amine+C18)	
	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg
Dimethametryn	101(1)	103(2)	85(0)	78(1)	104(1)	102(2)	91(2)	79(8)
Dimethenamid	101(1)	103(1)	86(1)	80(1)	104(3)	102(3)	92(3)	79(7)
Dimethomorph_E	73(16)	76(3)	74(8)	69(2)	119(2)	100(2)	71(2)	80(8)
Dimethomorph_Z	118(3)	127(1)	94(2)	87(1)	116(1)	107(3)	114(7)	79(7)
Diniconazole	98(3)	102(1)	85(0)	78(1)	105(2)	101(2)	90(0)	77(8)
Dinotefuran	96(1)	104(1)	86(1)	88(1)	91(1)	97(2)	107(7)	80(7)
Epoxiconazole	99(2)	104(1)	89(2)	82(1)	107(2)	103(2)	100(5)	77(7)
Ethoprophos	102(1)	105(1)	87(1)	81(1)	105(2)	104(3)	91(3)	79(7)
Etoxazole	98(2)	102(1)	85(1)	79(1)	105(2)	102(3)	92(2)	78(7)
Famoxadone	95(16)	100(3)	85(10)	78(1)	105(6)	102(1)	91(6)	79(8)
Fenazaquin	98(2)	104(1)	82(1)	76(2)	102(2)	101(2)	90(1)	78(7)
Fenbuconazole	105(5)	103(2)	86(1)	82(0)	105(5)	102(2)	92(3)	78(7)
Fenhexamid	115(12)	104(2)	73(13)	73(2)	125(2)	105(4)	90(10)	78(8)
Fenitrothion	101(13)	105(5)	102(9)	83(1)	100(8)	103(6)	102(10)	81(7)
Fenobucarb	101(1)	104(1)	87(1)	79(1)	106(1)	103(2)	93(3)	79(8)
Fenoxanil	98(1)	95(12)	89(2)	80(1)	109(2)	104(3)	95(5)	77(7)
Fenpropathrin	99(1)	103(0)	86(2)	78(1)	109(2)	106(2)	99(10)	77(9)
Fenpyroximate	98(5)	101(1)	84(1)	78(1)	107(1)	104(3)	95(3)	79(8)
Fenthion	99(5)	101(3)	81(0)	78(2)	104(3)	99(2)	92(6)	78(7)
Fentrazamide	105(5)	105(2)	94(4)	75(3)	101(4)	102(3)	90(6)	83(6)
Ferimzone	81(2)	82(5)	56(0)	48(5)	90(2)	84(7)	82(1)	75(7)
Flubendiamide	102(1)	105(2)	88(1)	78(2)	112(3)	107(2)	93(2)	78(7)
Fludioxonil	95(4)	99(1)	88(2)	81(1)	83(12)	84(2)	81(8)	76(9)
Flufenoxuron	98(2)	103(1)	89(1)	82(1)	106(1)	103(3)	93(0)	77(7)
Fluopicolide	103(1)	104(2)	88(1)	79(1)	107(1)	104(2)	92(4)	79(8)
Fluopyram	98(3)	106(1)	85(2)	81(1)	106(4)	105(3)	94(4)	78(7)
Flupyradifuron	101(2)	101(3)	87(1)	80(1)	105(2)	103(3)	94(3)	80(8)
Fluquinconazole	99(2)	103(1)	85(5)	80(1)	110(4)	104(4)	92(3)	79(7)

Compounds	Recovery (RSD, %)							
	Apple				Korean cabbage			
	QuChERS and SPE		FaPEX(Amine+C18)		QuChERS and SPE		FaPEX(Amine+C18)	
	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg
Flutolanil	100(0)	104(1)	87(1)	80(1)	109(2)	103(2)	94(4)	78(7)
Flutriafol	99(1)	103(1)	79(2)	75(1)	105(3)	101(1)	91(3)	79(8)
Fluxapyroxad	100(1)	104(1)	87(1)	79(1)	110(0)	103(2)	91(3)	79(7)
Fosthiazate	101(1)	104(1)	87(1)	80(1)	107(3)	103(3)	94(3)	79(8)
Hexaconazole	102(3)	103(2)	81(5)	76(2)	106(3)	100(2)	86(4)	80(8)
Hexythiazox	98(2)	103(2)	84(2)	75(2)	106(1)	100(2)	93(2)	78(9)
Imicyafos	100(1)	103(1)	87(1)	79(1)	105(2)	102(2)	94(3)	79(7)
Imidacloprid	101(1)	96(3)	89(1)	78(3)	113(2)	105(3)	93(5)	80(10)
Indoxacarb	102(2)	102(0)	90(2)	78(1)	105(9)	106(4)	88(3)	79(7)
Ipconazole	98(1)	103(1)	86(1)	78(1)	104(1)	102(2)	90(2)	79(8)
Iprobenfos	102(2)	104(1)	87(1)	81(1)	107(2)	104(2)	92(3)	80(8)
Iprovalicarb	101(3)	109(1)	85(1)	78(1)	104(3)	97(21)	76(17)	80(8)
Isazofos	101(2)	105(2)	86(1)	80(1)	108(0)	105(2)	94(4)	79(7)
Isoprocarb/MIPC	101(1)	103(1)	87(0)	79(1)	106(1)	103(2)	94(3)	79(8)
Isoprothiolane	98(1)	104(1)	87(1)	79(1)	106(1)	103(3)	92(2)	79(8)
Isopyrazam	101(2)	102(4)	87(3)	79(1)	109(5)	103(1)	101(6)	79(7)
Kresoxim-methyl	101(2)	104(2)	86(1)	81(1)	108(1)	105(3)	92(3)	80(7)
Linuron	101(1)	103(1)	86(1)	81(1)	104(2)	102(2)	92(3)	80(8)
Lufenuron	99(2)	103(1)	86(1)	82(1)	105(1)	102(2)	93(3)	79(8)
Mandipropamid	99(0)	103(2)	87(3)	79(1)	106(2)	104(2)	88(2)	79(7)
Metalaxyl	99(2)	104(1)	86(1)	78(1)	106(2)	102(2)	93(3)	79(8)
Metamifop	98(0)	105(2)	84(4)	76(1)	106(3)	103(3)	94(2)	78(8)
Metconazole	97(1)	102(1)	80(2)	76(1)	104(1)	99(2)	88(2)	78(8)
Mefenoxam	99(1)	104(1)	87(2)	79(1)	106(2)	102(2)	93(3)	79(7)
Methidathion	104(2)	103(2)	90(1)	80(1)	109(2)	103(2)	95(3)	78(8)
Methoxyfenozide	88(5)	101(5)	90(2)	80(1)	104(2)	103(3)	90(6)	80(7)
Metrafenone	96(0)	103(0)	87(1)	75(1)	105(1)	103(3)	90(3)	79(8)
Molinate	104(8)	103(2)	87(6)	77(2)	97(1)	104(4)	88(4)	80(7)

Compounds	Recovery (RSD, %)							
	Apple				Korean cabbage			
	QuChERS and SPE		FaPEX(Amine+C18)		QuChERS and SPE		FaPEX(Amine+C18)	
	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg
Myclobutanil	98(4)	104(1)	85(1)	79(0)	113(5)	104(3)	90(2)	79(8)
Napropamid	99(2)	103(1)	86(1)	79(1)	108(3)	102(3)	92(4)	79(7)
Novaluron	99(3)	106(2)	85(1)	73(1)	110(5)	104(3)	98(4)	79(8)
Nuarimol	99(1)	102(2)	81(1)	78(2)	110(3)	103(2)	91(2)	79(6)
Oxadiazon	101(1)	104(1)	88(1)	78(0)	106(3)	104(3)	88(3)	79(8)
Oxadixyl	108(2)	103(1)	88(2)	80(1)	107(12)	99(10)	76(17)	78(8)
Paclobutrazol	101(2)	104(0)	89(1)	78(1)	105(3)	102(2)	90(1)	79(8)
Penconazole	97(2)	105(2)	85(1)	79(1)	103(3)	104(2)	92(2)	79(7)
Pencycuron	94(1)	98(1)	79(1)	124(1)	92(1)	92(3)	84(2)	89(7)
Pendimethalin	95(1)	103(0)	87(2)	77(0)	108(4)	103(3)	94(4)	79(8)
Pentoxazone	103(9)	101(6)	96(5)	76(0)	ND	98(9)	99(8)	82(6)
Phenthoate	99(1)	105(1)	88(1)	81(1)	107(1)	105(2)	94(4)	79(7)
Phorate	96(10)	102(1)	92(2)	78(2)	91(3)	95(4)	88(8)	77(9)
Phosphamidon	78(4)	101(2)	85(1)	78(1)	104(1)	86(1)	98(3)	80(7)
Picoxystrobin	101(1)	104(1)	85(0)	81(1)	106(1)	104(3)	93(4)	79(8)
Fluxorbutol	99(1)	104(1)	86(1)	78(1)	106(2)	104(3)	91(2)	80(7)
Probenazole	93(2)	92(2)	54(1)	54(1)	92(2)	86(3)	63(2)	51(11)
Prochloraz	86(3)	100(1)	79(3)	78(1)	85(4)	83(2)	75(7)	77(11)
Propamocarb	89(1)	98(1)	19(1)	0(-)	90(1)	89(1)	22(23)	74(8)
Propaquizafop	102(2)	103(1)	84(5)	75(0)	109(3)	102(2)	96(4)	78(8)
Propiconazole	104(4)	105(2)	89(3)	79(1)	110(3)	102(2)	93(4)	79(7)
Pyraclonil	100(1)	104(1)	87(1)	79(1)	106(2)	103(3)	93(3)	79(8)
Pyraclostrobin	95(4)	103(9)	87(4)	78(0)	108(3)	103(3)	96(4)	79(7)
Pyridaben	94(1)	99(1)	84(2)	77(1)	103(1)	102(2)	85(2)	79(7)
Pyridaphenthion	97(2)	105(1)	87(1)	79(1)	109(1)	103(2)	94(5)	79(8)
Pyrifluquinazon	91(4)	93(1)	34(2)	33(7)	98(1)	92(4)	64(19)	78(8)
Pyrimethanil	98(2)	102(1)	85(4)	78(1)	102(2)	101(2)	90(2)	79(8)
Pyriproxyfen	100(2)	104(1)	85(1)	78(1)	106(2)	103(3)	91(3)	79(7)

Compounds	Recovery (RSD, %)							
	Apple				Korean cabbage			
	QuChERS and SPE		FaPEX(Amine+C18)		QuChERS and SPE		FaPEX(Amine+C18)	
	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg	0.01 mg/kd	0.1 mg/kg
Quinoclamine	102(3)	104(1)	88(1)	79(1)	108(2)	103(2)	94(3)	79(7)
Spinetoram(J)	88(3)	100(2)	29(2)	13(16)	89(1)	77(4)	50(11)	73(19)
Spinetoram(L)	81(1)	96(1)	25(3)	12(17)	86(2)	72(3)	49(12)	75(20)
Spirotetramat	94(1)	98(1)	81(0)	78(2)	101(2)	96(3)	89(2)	72(7)
Sulfoxaflor	100(0)	105(2)	87(1)	80(1)	104(2)	103(2)	93(3)	79(7)
Tebufenozide	101(1)	105(1)	87(1)	82(1)	108(2)	104(2)	95(2)	79(8)
Tebufenpyrad	99(4)	104(1)	82(2)	75(0)	110(2)	101(3)	94(4)	78(9)
Tebupirimfos	99(1)	104(1)	84(2)	77(1)	104(2)	103(2)	91(3)	79(8)
Tetraconazole	103(2)	104(2)	88(1)	82(1)	110(3)	102(3)	99(2)	77(9)
Thiacloprid	98(0)	104(1)	85(1)	81(1)	105(2)	102(2)	94(4)	79(8)
Thiamethoxam	100(2)	102(2)	85(1)	83(4)	104(1)	102(2)	91(3)	80(10)
Thifluzamide	105(2)	105(2)	88(2)	82(1)	105(3)	106(3)	96(4)	77(8)
Thiobencarb	96(1)	103(1)	85(1)	79(1)	106(2)	104(2)	90(4)	78(8)
Triadimefon	101(2)	104(1)	83(3)	78(2)	100(3)	102(3)	88(5)	78(8)
Tricyclazole	89(3)	102(2)	77(2)	75(1)	109(12)	98(2)	91(3)	78(7)
Trifloxystrobin	94(2)	102(1)	87(2)	80(1)	107(2)	104(2)	94(3)	79(8)
Triflumizole	85(1)	95(2)	75(0)	83(1)	79(7)	76(2)	77(9)	71(13)
Uniconazole	99(2)	103(2)	81(3)	76(1)	106(3)	101(2)	89(4)	78(7)