

Application Note

Introduction

Pesticide residue laboratories are required to undertake analyses of an ever increasing number of samples. The analyses typically involve use of multi-residue methods (both GC-MS and LC-MS) to test for over 500 pesticide residues. Due to its ease of use and proven robustness, the QuEChERS extraction has become the method of choice for pesticides multi-residue analyses in a wide range of matrices.

This study used laboratory spiked samples and samples previously shown to have incurred residues to validate the performance of implementing QuEChERS on a fully automated system for pesticides amenable to analysis by UHPLC-MS/MS.

Method

Sample preparation/Extraction

Three commodities (apples, lettuce, and oats) were chosen to represent a wide range of samples tested for pesticide residues. The appropriate sample weights for apples and lettuce were 10.0 g and 5.0 g for the oats. These were then transferred into a 50.0 mL centrifuge tube, and placed into the AutoMate-Q40 sample prep workstation, which then automated the QuEChERS procedure (EN15662:2008) (Figure 1) developed and defined by the European Reference Laboratory.¹

Figure 1 EN 15662:2008 QuEChERS Extraction

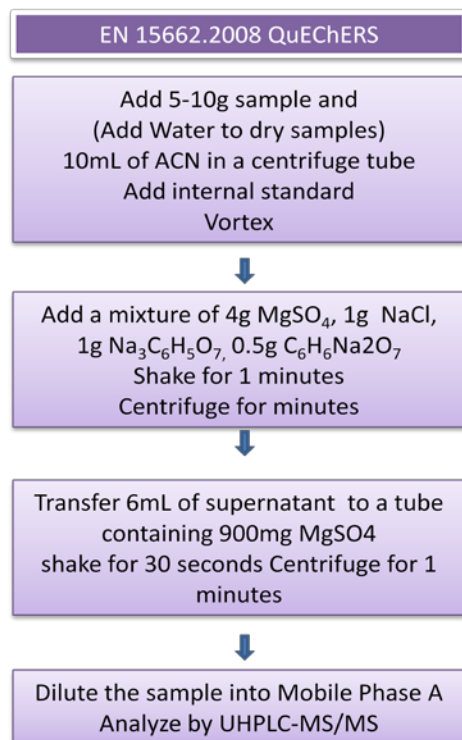


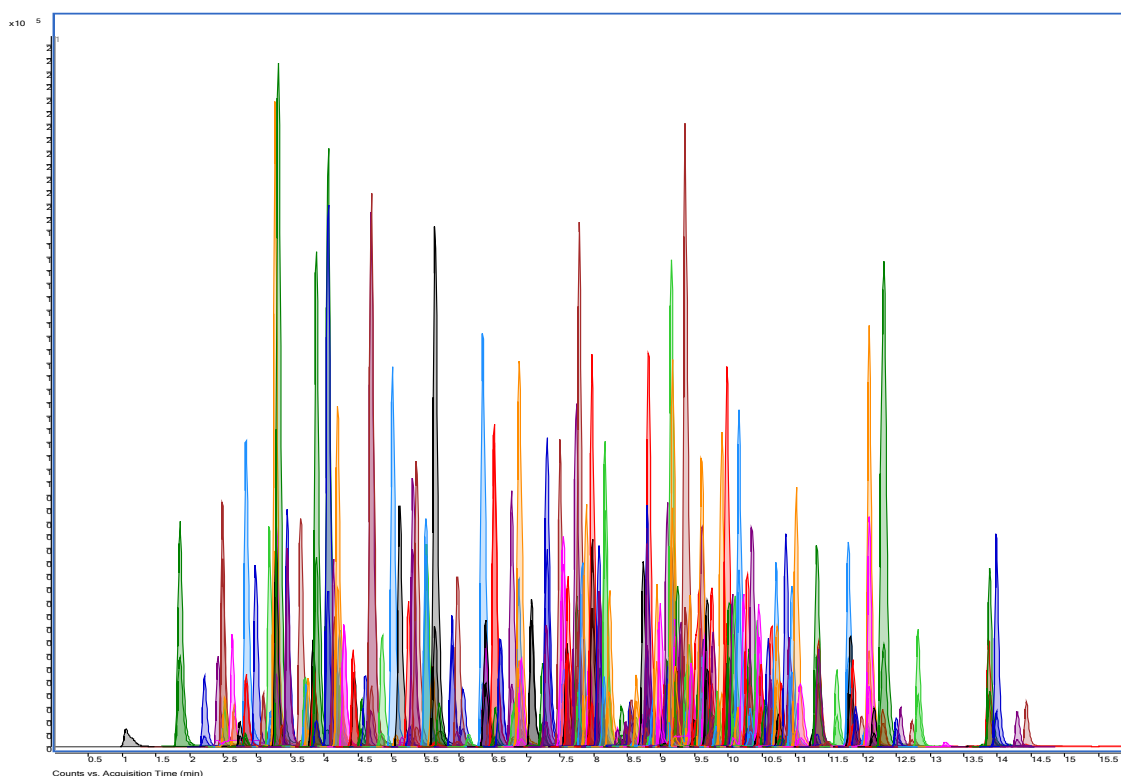
Figure 1 shows the extractions steps that are performed by the AutoMate-Q40 to extract the pesticides

residues from these commodities. For this analysis, the AutoMate-Q40 used the EN QuEChERS extraction salts: Magnesium Sulfate (MgSO₄), sodium chloride (NaCl), sodium citrate dibasic sesquihydrate (SCDS), and sodium citrate tribasic dihydrate (SCTD). Replicates (n =5) of organically produced, residue free samples were spiked with a mixture of more than 200 different pesticides at concentrations of 0.01, 0.02 and 0.05 mg/kg to validate the procedure, following the EU AQC guidelines (SANCO/12571/2013).²

UHPLC-MS/MS Analysis

An Agilent 1290 Infinity UHPLC interfaced to an Agilent 6490 triple quadrupole (UHPLC-MS/MS). For separation, an Agilent Zorbax RRHD Eclipse Plus C18 1.8 μm (150 × 2.1 mm) column separated the pesticides for detection and quantification by the MS/MS. Tables I gives UHPLC-MS/MS analysis parameters, Figure II shows the MRM chromatogram for a matrix-matched calibrant at 0.02 mg/kg.

Table I UHPLC-MS/MS Parameters	
Agilent 1290 Infinity UHPLC	
Column	Agilent Zorbax RRHD Eclipse Plus C18 1.8 μm (150 × 2.1 mm)
Column Temp	40°C
Column Flow	0.50 mL/min
Mobile Phase	Mobile Phase A: 5mM Ammonium acetate Mobile Phase B: Methanol
Injection Volume	15 μL
Agilent 6490 Triple Quadrupole	
Gas Temp	110°C
Gas Flow	20 L/min
Nebulizer Gas Flow	40 psi
Capillary Voltage	+4000/-3000 V
Sheath Gas Flow	10

Figure 2 MRM Chromatogram of 241 pesticides (calibrant at 0.02mg/kg)


Results

By automating the QuEChERS extraction, it enables a fast, easy, reliable and more reproducible extraction as compared to the manual QuEChERS extraction. The AutoMate-Q40 offers significant labor saving, while showing excellent repeatability and consistency between the samples.

This poster shows the precision and accuracy of the measurement of laboratory spiked samples of apples, lettuce and oats with 241 pesticides. The AutoMate-Q40 is able to generate these spiked samples (0.01, 0.02, and 0.05 mg/kg) by adding the appropriate volumes of the stock pesticides solution. These laboratory spiked samples were quantitated against their corresponding matrix matched calibration.

Table II shows recoveries from 25% to 134% using the AutoMate-Q40. On average, 94% of the spike recoveries fell within the recommended mean values for the Document N° SANCO/12571/2013.² This document states that the mean recoveries must fall within 70% to 120% and have a RSD <20%. The AutoMate-Q40, also, demonstrated great precision ranging from 1.0% to 18%RSD for the spiked laboratory samples.

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
2,4-D	80%	4%	77%	4%	48%*	12%	47%*	5%	50%*	3%	71%	4%	76%	4%
abamectin	120%	3%	122%	8%	108%	3%	110%	4%	109%	4%	115%	6%	115%	4%
acephate	100%	3%	103%	2%	102%	3%	99%	3%	101%	2%	105%	2%	97%	2%
acetamiprid	106%	3%	119%	1%	115%	4%	117%	2%	118%	3%	115%	3%	116%	3%
acibenzolar-S-methyl	105%	4%	105%	5%	100%	5%	103%	6%	104%	1%	118%	2%	108%	6%
acrinathrin	112%	4%	107%	3%	102%	12%	89%	4%	82%	4%	116%	4%	99%	2%
alachlor	106%	6%	105%	2%	113%	5%	112%	5%	114%	2%	118%	4%	110%	5%
aldicarb sulfone	105%	2%	109%	3%	117%	3%	110%	4%	112%	2%	115%	3%	112%	5%
aldicarb sulfoxide	101%	2%	104%	2%	108%	4%	105%	3%	106%	2%	109%	3%	105%	3%
aldicarb	104%	2%	106%	2%	116%	8%	107%	7%	111%	2%	112%	1%	110%	1%
amidosulfuron	106%	5%	117%	5%	114%	3%	112%	4%	117%	3%	107%	2%	112%	6%
asulam	93%	7%	94%	10%	68%*	4%	61%*	2%	60%*	3%	75%	1%	68%*	3%
atrazine	109%	2%	111%	2%	110%	6%	105%	4%	110%	2%	112%	4%	108%	3%
azinphos-methyl	111%	3%	115%	2%	112%	6%	106%	5%	105%	3%	125%*	6%	116%	2%
azoxystrobin	108%	4%	104%	4%	111%	2%	111%	2%	111%	4%	116%	5%	113%	4%
bendiocarb	105%	3%	110%	1%	116%	5%	114%	4%	114%	2%	115%	3%	113%	4%
benthiavalicarb-isopropyl	105%	2%	105%	2%	114%	3%	110%	4%	111%	3%	113%	2%	111%	4%
bispyribac-sodium	101%	4%	106%	4%	103%	2%	103%	5%	105%	5%	101%	3%	103%	2%
bitertanol	98%	5%	102%	8%	117%	5%	116%	6%	114%	2%	117%	6%	110%	6%
boscalid	109%	3%	111%	9%	104%	5%	104%	7%	116%	8%	106%	4%	113%	9%
bromoxynil	103%	3%	104%	3%	97%	4%	92%	5%	97%	1%	105%	5%	103%	5%
bromuconazole	106%	8%	110%	4%	112%	9%	107%	4%	108%	5%	109%	3%	105%	4%
butachlor	106%	2%	107%	3%	107%	6%	103%	2%	106%	2%	116%	3%	111%	3%
butocarboxim sulfoxide	100%	3%	99%	2%	108%	3%	102%	4%	104%	1%	111%	1%	105%	4%
butocarboxim	103%	3%	107%	3%	123%	7%	114%	4%	112%	2%	113%	3%	106%	2%
butoxycarboxim	105%	4%	107%	2%	112%	4%	109%	5%	112%	3%	112%	2%	109%	3%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
carbaryl	106%	3%	110%	2%	112%	4%	111%	3%	114%	2%	112%	3%	107%	4%
carbendazim	106%	2%	106%	2%	106%	4%	106%	4%	108%	3%	114%	3%	114%	3%
carbofuran (3-hydroxy)	105%	3%	108%	1%	113%	3%	111%	3%	114%	4%	114%	3%	113%	4%
Carbofuran	107%	2%	108%	3%	115%	4%	111%	5%	113%	3%	114%	3%	110%	4%
carboxin	104%	3%	108%	1%	110%	3%	110%	3%	111%	2%	89%	3%	81%	7%
chlorantranilprole	104%	4%	105%	2%	112%	5%	110%	3%	112%	4%	116%	4%	111%	4%
chlorfenapyr	113%	7%	110%	3%	121%*	18%	113%	4%	100%	9%	127%*	15%	121%*	5%
chlorfenvinphos	107%	3%	109%	3%	116%	4%	113%	6%	113%	5%	119%	4%	112%	3%
chloridazon	108%	3%	111%	2%	108%	3%	107%	6%	109%	1%	116%	3%	113%	5%
chlortoluron	105%	5%	111%	3%	115%	4%	113%	4%	113%	2%	117%	3%	112%	4%
chromafenozide	110%	6%	114%	2%	114%	9%	122%*	9%	123%*	5%	124%*	9%	123%*	7%
clethodim	101%	4%	107%	5%	111%	3%	109%	5%	107%	2%	97%	7%	91%	4%
clofentezine	107%	4%	95%	4%	108%	10%	111%	7%	107%	2%	118%	7%	119%	9%
clothianidin	107%	3%	114%	4%	108%	4%	109%	6%	110%	1%	115%	5%	122%*	7%
cyazofamid	109%	4%	107%	4%	113%	5%	117%	4%	121%*	2%	114%	6%	112%	4%
cycloxydim	102%	2%	99%	4%	109%	4%	104%	4%	105%	5%	86%	1%	70%	6%
cyflufenamid	103%	4%	101%	4%	113%	6%	110%	3%	115%	2%	118%	4%	114%	5%
cymoxanil	109%	3%	110%	2%	117%	3%	109%	5%	112%	3%	112%	2%	110%	3%
cyproconazole	106%	5%	111%	5%	112%	6%	108%	7%	106%	6%	116%	6%	112%	5%
cyprodinil	107%	6%	101%	4%	105%	9%	100%	3%	103%	8%	117%	3%	106%	4%
cyromazine	76%	3%	79%	3%	64%*	4%	63%*	4%	66%*	5%	94%	3%	90%	3%
demeton-S-methyl sulfone	106%	2%	109%	3%	113%	2%	111%	3%	115%	1%	113%	1%	111%	4%
demeton-S-methyl sulfoxide	104%	2%	103%	2%	110%	3%	107%	3%	109%	3%	113%	3%	111%	3%
Demeton-S-Methyl	105%	3%	106%	3%	114%	4%	110%	3%	115%	1%	112%	5%	103%	4%
desmedipham	108%	3%	109%	4%	106%	10%	106%	4%	112%	2%	111%	3%	104%	4%
Dichlorprop	95%	3%	91%	5%	70%	4%	66%*	2%	69%*	1%	85%	2%	86%	1%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
diclobutrazol	104%	4%	105%	4%	110%	4%	109%	4%	108%	4%	117%	3%	108%	4%
diethofencarb	111%	3%	108%	2%	116%	4%	116%	6%	118%	5%	114%	7%	114%	6%
difenoconazole	110%	5%	105%	4%	103%	7%	109%	4%	105%	5%	111%	4%	112%	2%
diflubenzuron	105%	4%	111%	5%	100%	6%	108%	6%	107%	2%	116%	5%	109%	7%
dimethoate	108%	4%	112%	2%	116%	5%	116%	3%	116%	2%	112%	4%	109%	3%
dimethomorph	108%	5%	106%	4%	108%	8%	115%	4%	113%	6%	110%	4%	105%	5%
dimoxystrobin	107%	3%	110%	2%	110%	9%	114%	3%	114%	4%	115%	5%	117%	10%
diniconazole	107%	3%	104%	2%	113%	4%	111%	6%	110%	3%	117%	4%	113%	3%
dinotefuran	105%	2%	115%	6%	107%	5%	108%	4%	112%	2%	111%	2%	102%	2%
disulfoton sulfone	110%	2%	109%	3%	112%	3%	114%	6%	115%	3%	114%	2%	115%	4%
disulfoton sulfoxide	106%	2%	110%	2%	113%	5%	115%	5%	116%	2%	115%	4%	114%	2%
Disulfoton	108%	3%	105%	4%	106%	4%	103%	4%	106%	2%	107%	4%	97%	6%
diuron	108%	4%	116%	3%	113%	5%	110%	3%	113%	4%	114%	6%	109%	4%
dodine	107%	5%	115%	5%	72%	13%	77%	8%	87%	8%	121%*	5%	128%*	7%
epoxiconazole	107%	4%	110%	5%	113%	7%	112%	10%	115%	1%	113%	3%	116%	4%
ethiofencarb sulfone	105%	4%	109%	3%	112%	2%	110%	4%	111%	2%	110%	4%	110%	6%
ethiofencarb sulfoxide	107%	5%	106%	3%	112%	6%	110%	5%	112%	2%	117%	3%	112%	2%
ethiofencarb	106%	1%	107%	2%	111%	4%	108%	3%	116%	2%	104%	2%	99%	4%
ethirimol	104%	3%	105%	2%	109%	8%	105%	5%	106%	2%	101%	5%	97%	5%
etofenprox	104%	2%	109%	17%	91%	4%	85%	1%	83%	2%	115%	2%	105%	3%
fenamidone	103%	2%	108%	6%	112%	6%	111%	6%	110%	4%	112%	5%	113%	3%
fenamiphos sulfone	109%	2%	107%	3%	114%	6%	114%	2%	115%	1%	111%	2%	108%	5%
fenamiphos sulfoxide	105%	4%	106%	1%	115%	5%	111%	3%	113%	3%	107%	2%	97%	2%
fenamiphos	105%	3%	108%	4%	112%	4%	112%	5%	116%	5%	119%	5%	109%	6%
fenarimol	107%	6%	117%	7%	116%	17%	108%	8%	109%	9%	112%	5%	116%	9%
fenbuconazole	104%	2%	109%	3%	113%	6%	115%	5%	115%	3%	118%	4%	113%	7%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
fenbutatin oxide	84%	2%	76%	3%	58%*	6%	53%*	1%	53%	6%	70%	6%	64%*	7%
fenhexamid	108%	2%	111%	4%	111%	13%	109%	3%	112%	5%	121%*	3%	118%	4%
fenoxycarb	111%	3%	111%	7%	108%	4%	112%	5%	112%	2%	119%	5%	122%*	3%
fenpropimorph	105%	2%	103%	2%	94%	5%	90%	4%	89%	3%	123%*	1%	118%	4%
fenpyroximate	109%	4%	112%	4%	106%	7%	101%	4%	103%	1%	124%*	2%	124%*	2%
Fensulfothion	105%	8%	111%	4%	112%	6%	114%	5%	114%	5%	112%	3%	109%	3%
Fensulfothion-Oxon	105%	2%	108%	3%	115%	4%	111%	7%	113%	2%	119%	2%	112%	3%
Fensulfothion-Oxon-Sulfone	108%	2%	109%	4%	116%	7%	115%	4%	115%	2%	115%	4%	112%	3%
Fensulfothion-Sulfone	109%	2%	107%	3%	116%	5%	112%	6%	118%	4%	114%	3%	108%	4%
fenthion sulfone	114%	7%	114%	3%	114%	3%	113%	4%	113%	2%	117%	3%	116%	4%
fenthion sulfoxide	107%	1%	110%	3%	115%	4%	112%	4%	115%	2%	114%	4%	111%	2%
Fenthion	111%	4%	106%	2%	111%	4%	109%	6%	114%	6%	113%	5%	108%	3%
Fipronil sulfone	116%	27%	105%	35%	98%	34%	95%	22%	107%	7%	136%*	9%	126%*	19%
fipronil	113%	7%	116%	4%	111%	5%	109%	5%	114%	1%	115%	1%	106%	7%
fluazifop (free acid)	98%	2%	101%	3%	79%	6%	87%	4%	90%	4%	94%	5%	93%	4%
Fluazifop-P-Butyl	109%	2%	111%	1%	106%	6%	103%	5%	107%	2%	119%	3%	117%	5%
fluazinam	110%	4%	109%	4%	112%	7%	108%	3%	107%	1%	119%	4%	113%	5%
fludioxonil	106%	4%	108%	5%	111%	6%	110%	4%	112%	3%	112%	5%	105%	7%
flufenacet	108%	4%	111%	3%	110%	10%	115%	8%	113%	6%	108%	4%	106%	4%
flufenoxuron	113%	5%	108%	4%	104%	4%	101%	2%	100%	2%	124%	2%	118%	3%
fluometuron	107%	1%	108%	3%	118%	4%	113%	2%	115%	4%	115%	1%	112%	4%
fluopicolide	115%	4%	117%	4%	118%	6%	122%*	5%	123%*	1%	115%	4%	109%	5%
fluoxastrobin	109%	6%	108%	5%	118%	8%	119%	8%	119%	6%	120%	7%	117%	5%
fluquinconazole	106%	6%	103%	7%	109%	8%	104%	7%	103%	3%	117%	6%	117%	7%
fluroxypyr	75%	6%	76%	8%	36%*	4%	34%*	3%	36%*	8%	60%*	7%	64%*	9%
flusilazole	106%	5%	108%	4%	112%	6%	115%	5%	115%	3%	112%	6%	105%	8%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
flutriafol	109%	4%	110%	3%	112%	5%	111%	5%	114%	2%	114%	3%	107%	2%
fonofos	105%	10%	104%	6%	103%	6%	100%	2%	101%	3%	111%	4%	106%	3%
formetanate-HCl	104%	4%	98%	3%	420%*	7%	394%*	3%	380%*	2%	108%	1%	95%	1%
fosthiazate	106%	1%	107%	3%	117%	3%	113%	3%	118%	2%	113%	5%	111%	4%
furathiocarb	110%	2%	107%	2%	108%	7%	104%	4%	109%	5%	114%	5%	112%	4%
Furmecyclox	88%	5%	85%	2%	100%	8%	99%	3%	99%	1%	16%*	7%	9%*	43%
halofenozide	109%	9%	112%	4%	107%	6%	111%	6%	117%	4%	111%	3%	100%	5%
halosulfuron-methyl	106%	4%	112%	1%	115%	3%	111%	5%	113%	3%	110%	6%	114%	4%
haloxyfop (free acid)	108%	10%	104%	7%	82%	5%	81%	5%	87%	4%	92%	10%	98%	4%
heptenophos	104%	3%	104%	1%	117%	4%	111%	5%	113%	5%	117%	6%	110%	2%
hexaconazole	110%	3%	104%	4%	110%	5%	109%	7%	114%	4%	121%*	7%	108%	6%
hexythiazox	106%	4%	103%	4%	93%	6%	90%	8%	96%	4%	119%	3%	121%*	7%
imazail	104%	4%	101%	3%	109%	9%	105%	3%	111%	2%	116%	7%	103%	7%
imidacloprid	109%	3%	117%	7%	110%	3%	112%	4%	118%	2%	113%	6%	117%	5%
indoxacarb	110%	6%	112%	4%	116%	7%	109%	6%	111%	3%	112%	3%	115%	4%
ioxynil	102%	2%	102%	2%	96%	2%	96%	3%	96%	0%	105%	4%	100%	3%
iprovalicarb	106%	4%	105%	3%	115%	5%	113%	6%	112%	6%	113%	4%	113%	3%
isazofos	105%	5%	103%	3%	116%	3%	113%	3%	111%	5%	114%	4%	105%	2%
isocarbofos	111%	3%	113%	3%	104%	3%	109%	4%	114%	3%	115%	4%	113%	5%
isofenphos	106%	3%	107%	2%	110%	6%	110%	2%	114%	2%	117%	4%	111%	6%
isofenphos-methyl	106%	6%	109%	3%	110%	7%	110%	4%	114%	6%	114%	6%	114%	13%
isoprocarb	108%	4%	110%	2%	114%	6%	112%	4%	112%	2%	112%	5%	112%	4%
isoprotiolane	107%	4%	99%	3%	116%	7%	108%	6%	114%	4%	118%	6%	113%	5%
isoproturon	105%	4%	111%	4%	114%	8%	112%	4%	112%	2%	114%	3%	111%	3%
isoxaben	108%	2%	110%	2%	112%	2%	112%	6%	117%	6%	112%	8%	117%	4%
isoxaflutole	90%	3%	92%	4%	104%	7%	109%	5%	113%	3%	114%	2%	112%	4%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate-Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
kresoxim-methyl	105%	5%	109%	8%	115%	8%	111%	7%	116%	4%	114%	5%	111%	4%
lenacil	108%	3%	113%	4%	111%	4%	110%	7%	106%	1%	112%	3%	108%	6%
linuron	107%	2%	108%	3%	113%	3%	110%	6%	111%	5%	114%	3%	109%	6%
lufenuron	115%	7%	120%	6%	115%	6%	109%	5%	108%	3%	131%*	5%	129%*	4%
malathion	110%	4%	108%	2%	117%	4%	117%	8%	115%	6%	111%	4%	112%	4%
mandipropamid	111%	6%	105%	4%	117%	8%	111%	8%	115%	4%	111%	11%	111%	6%
mecarbam	107%	5%	114%	5%	108%	9%	106%	5%	105%	4%	116%	7%	114%	4%
mepanipyrim	106%	3%	101%	9%	106%	4%	104%	8%	105%	2%	110%	2%	104%	3%
mepronil	113%	4%	113%	7%	111%	4%	112%	6%	110%	3%	119%	8%	115%	4%
mesosulfuron-methyl	102%	3%	106%	3%	112%	5%	107%	5%	108%	4%	107%	8%	104%	5%
metaflumizone	101%	10%	115%	8%	111%	11%	105%	7%	107%	4%	125%*	12%	128%*	6%
metalaxyl	108%	3%	108%	5%	116%	4%	116%	4%	114%	3%	112%	2%	107%	4%
metamitron	103%	2%	114%	3%	110%	3%	110%	3%	108%	4%	110%	3%	108%	3%
metconazole	105%	2%	107%	4%	112%	8%	109%	5%	111%	5%	116%	2%	113%	5%
methabenzthiazuron	105%	2%	106%	2%	108%	6%	108%	4%	108%	4%	116%	3%	111%	4%
methamidophos	97%	2%	95%	3%	99%	4%	95%	3%	97%	2%	104%	2%	101%	3%
methiocarb sulfone	103%	3%	104%	3%	111%	3%	106%	5%	110%	2%	108%	2%	104%	5%
methiocarb sulfoxide	105%	1%	107%	2%	112%	5%	109%	2%	112%	2%	111%	2%	110%	4%
methiocarb	109%	3%	112%	2%	110%	3%	112%	5%	116%	2%	115%	3%	107%	3%
methomyl	105%	3%	109%	2%	120%	4%	117%	4%	119%	2%	112%	4%	114%	2%
methoxyfenozide	108%	3%	111%	6%	114%	6%	118%	9%	119%	3%	117%	4%	112%	3%
metobromuron	108%	5%	111%	1%	111%	3%	113%	7%	114%	2%	116%	5%	114%	3%
metolachlor	110%	2%	113%	2%	110%	6%	109%	6%	110%	2%	115%	4%	111%	6%
metolcarb	105%	2%	106%	4%	113%	5%	106%	2%	110%	1%	112%	2%	108%	4%
metosulam	110%	5%	115%	2%	100%	5%	100%	3%	105%	4%	115%	4%	113%	3%
metoxuron	108%	2%	110%	2%	113%	4%	111%	3%	115%	4%	113%	2%	113%	3%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
metrafenone	107%	1%	103%	2%	110%	6%	106%	3%	109%	1%	115%	2%	115%	4%
metsulfuron-methyl	104%	6%	105%	6%	97%	3%	90%	4%	86%	4%	110%	5%	109%	6%
mevinphos	104%	1%	104%	2%	116%	3%	106%	5%	110%	5%	114%	2%	108%	7%
molinate	110%	6%	106%	4%	109%	5%	102%	8%	106%	4%	117%	4%	111%	9%
monocrotophos	104%	2%	105%	1%	112%	4%	106%	4%	109%	2%	112%	3%	107%	4%
monuron	106%	3%	109%	2%	111%	4%	111%	3%	112%	3%	115%	2%	112%	4%
myclobutanil	109%	2%	112%	3%	114%	4%	116%	5%	116%	3%	112%	4%	110%	5%
n-2,4 dmpnmf	93%	2%	89%	3%	154%*	5%	144%*	5%	150%*	4%	105%	3%	94%	4%
neoquassia	106%	6%	106%	3%	115%	1%	110%	6%	114%	5%	115%	3%	108%	5%
nitenpyram	102%	4%	102%	4%	104%	4%	103%	3%	107%	1%	104%	4%	107%	5%
nuarimol	106%	7%	115%	4%	111%	8%	116%	7%	112%	4%	119%	6%	107%	5%
ofurace	106%	1%	107%	2%	113%	2%	112%	5%	115%	3%	113%	3%	110%	3%
omethoate	102%	2%	103%	2%	109%	3%	106%	4%	107%	3%	111%	2%	106%	3%
oxadixyl	108%	2%	106%	2%	114%	5%	109%	5%	111%	2%	118%	3%	110%	4%
oxamyl	104%	4%	107%	4%	112%	5%	110%	4%	109%	2%	112%	2%	111%	2%
paclobutrazol	110%	3%	118%	4%	111%	3%	111%	6%	115%	3%	109%	12%	102%	8%
penconazole	102%	3%	106%	4%	112%	5%	110%	4%	109%	2%	114%	4%	116%	2%
pencycuron	106%	2%	108%	4%	108%	7%	105%	4%	106%	4%	116%	4%	113%	6%
phenmedipham	107%	4%	107%	5%	110%	6%	107%	3%	113%	3%	115%	2%	107%	5%
phenthoate	106%	4%	112%	5%	110%	2%	112%	5%	115%	5%	117%	5%	109%	8%
phorate sulfone	104%	6%	111%	2%	109%	3%	111%	5%	115%	4%	117%	4%	113%	2%
phorate sulfoxide	109%	2%	107%	1%	116%	3%	111%	2%	113%	3%	108%	3%	107%	4%
Phorate	109%	2%	109%	5%	101%	10%	107%	12%	103%	7%	107%	8%	104%	12%
phosphamidon	108%	2%	107%	2%	115%	4%	113%	5%	114%	2%	113%	1%	108%	5%
phoxim	113%	8%	108%	4%	104%	4%	109%	1%	110%	4%	102%	7%	102%	8%
picolinafen	107%	4%	113%	4%	110%	4%	105%	7%	110%	3%	131%*	3%	126%*	5%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate-Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
picoxystrobin	109%	4%	107%	2%	118%	5%	113%	2%	112%	5%	114%	3%	112%	4%
Piperonyl butoxide	108%	2%	110%	3%	109%	4%	108%	2%	109%	3%	114%	4%	111%	5%
pirimicarb	105%	3%	105%	4%	112%	3%	111%	6%	113%	2%	116%	4%	109%	1%
pirimicarb-desmethyl	104%	3%	108%	2%	116%	5%	111%	4%	111%	1%	111%	3%	108%	1%
prochloraz	106%	5%	101%	3%	91%	10%	92%	4%	97%	5%	118%	3%	112%	6%
profenfos	108%	1%	107%	5%	102%	8%	105%	3%	103%	2%	115%	6%	108%	2%
promecarb	107%	4%	107%	3%	114%	4%	111%	6%	113%	5%	115%	2%	112%	4%
prometryn	108%	4%	107%	7%	111%	5%	108%	4%	109%	3%	111%	5%	110%	6%
propamocarb (free base)	84%	3%	84%	4%	93%	5%	91%	4%	93%	3%	106%	3%	99%	3%
propaquizafop	98%	16%	108%	5%	111%	9%	108%	4%	110%	4%	115%	4%	113%	8%
propiconazole	110%	3%	107%	4%	112%	3%	111%	7%	118%	2%	113%	4%	111%	4%
propoxur	106%	2%	108%	4%	117%	2%	113%	3%	112%	2%	115%	4%	111%	3%
propyzamide	107%	3%	107%	4%	106%	4%	108%	4%	112%	5%	117%	5%	113%	6%
prosulfuron	106%	2%	107%	2%	108%	4%	108%	4%	113%	3%	106%	3%	100%	5%
prothioconazole-desthio	106%	3%	111%	2%	108%	9%	107%	6%	110%	1%	116%	2%	109%	1%
pymetrozine	95%	3%	106%	3%	100%	4%	99%	4%	100%	1%	108%	3%	104%	5%
pyraclostrobin	106%	3%	109%	2%	113%	7%	112%	4%	113%	7%	113%	3%	109%	5%
pyrethrin I	110%	2%	111%	4%	106%	5%	97%	6%	98%	3%	121%*	2%	116%	3%
pyrethrin II	110%	4%	107%	5%	108%	4%	112%	4%	109%	3%	118%	4%	112%	5%
pyrimethanil	105%	2%	101%	5%	107%	5%	99%	1%	99%	3%	112%	5%	106%	4%
pyriproxyfen	108%	3%	109%	6%	99%	5%	96%	3%	93%	2%	124%*	1%	119%	6%
quassia	108%	4%	106%	3%	117%	4%	115%	6%	114%	2%	115%	4%	110%	7%
quinmerac	25%*	7%	39%*	5%	23%*	6%	25%*	3%	30%*	11%	42%*	7%	47%*	7%
quinoxifen	104%	4%	104%	3%	93%	6%	87%	5%	90%	2%	130%*	2%	125%	4%
rimsulfuron	93%	5%	81%	4%	109%	4%	100%	4%	97%	4%	99%	7%	100%	9%
rotenone	100%	9%	107%	4%	113%	4%	111%	4%	118%	4%	118%	3%	114%	3%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate-Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
spinosin a	111%	4%	112%	4%	115%	4%	111%	4%	112%	2%	119%	2%	120%	2%
spinosin d	103%	3%	107%	4%	110%	6%	105%	7%	111%	2%	119%	3%	120%	2%
spiromesifen	111%	3%	114%	1%	107%	4%	104%	4%	104%	5%	127%*	7%	119%	4%
spiroxamine	109%	3%	104%	4%	101%	6%	99%	5%	102%	3%	121%*	3%	115%	4%
sulcotrione	75%	5%	89%	7%	56%*	6%	66%*	4%	77%	7%	90%	2%	90%	7%
tebuconazole	105%	4%	103%	4%	109%	6%	107%	3%	112%	2%	114%	3%	109%	4%
tebufenozide	106%	3%	108%	5%	120%	5%	113%	5%	115%	5%	115%	4%	110%	9%
tebufenpyrad	111%	3%	113%	2%	104%	5%	102%	3%	99%	3%	111%	7%	115%	2%
tebuthiuron	106%	3%	107%	3%	110%	5%	107%	4%	108%	0%	100%	3%	83%	2%
teflubenzuron	103%	12%	108%	7%	99%	6%	103%	7%	105%	2%	131%*	5%	122%	7%
terbufos sulfone	107%	2%	107%	4%	115%	6%	113%	3%	115%	4%	113%	3%	112%	6%
terbufos sulfoxide	109%	4%	110%	5%	113%	5%	113%	5%	114%	3%	120%	4%	117%	2%
Terbufos	110%	4%	109%	8%	107%	6%	100%	7%	97%	4%	116%	9%	109%	6%
tetraconazole	111%	5%	112%	4%	122%*	15%	106%	7%	104%	10%	117%	4%	111%	4%
thiabendazole	100%	5%	96%	2%	104%	5%	102%	2%	104%	3%	114%	5%	107%	6%
thiacloprid	110%	2%	116%	3%	114%	5%	115%	3%	117%	1%	116%	2%	112%	2%
thiamethoxam	109%	2%	118%	4%	115%	5%	115%	4%	122%*	2%	115%	4%	111%	5%
thiodicarb	108%	2%	106%	3%	107%	4%	103%	6%	105%	2%	110%	4%	103%	4%
thiophanate-methyl	98%	7%	90%	3%	122%*	4%	118%	4%	120%	1%	105%	2%	94%	4%
tofenpyrad	105%	4%	109%	4%	105%	4%	103%	4%	100%	2%	120%	3%	124%	2%
triadimefon	110%	4%	106%	3%	108%	5%	116%	3%	118%	1%	117%	2%	112%	5%
triadimenol	112%	3%	116%	8%	116%	3%	110%	7%	113%	4%	114%	3%	107%	4%
triasulfuron	106%	2%	110%	1%	109%	4%	107%	5%	109%	2%	109%	4%	106%	6%
triazamate (free acid)	97%	4%	95%	5%	66%*	4%	68%*	3%	74%	4%	77%	4%	88%	6%
triazophos	103%	5%	104%	5%	109%	6%	110%	7%	103%	5%	117%	5%	111%	5%
triclopyr	90%	7%	85%	8%	45%*	16%	55%*	8%	62%*	6%	101%	4%	97%	7%

Table II Laboratory Spiked Sample Results														
Compounds	Apple QuEChERS Validation on Automate-Q40				Oats QuEChERS Validation on Automate- Q40						Lettuce QuEChERS Validation Automate-Q40			
	0.01 mg/kg		0.02 mg/kg		0.01 mg/kg		0.02 mg/kg		0.05 mg/kg		0.01 mg/kg		0.02 mg/kg	
	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD	Recovery	RSD
tricyclazole	105%	2%	109%	3%	109%	2%	103%	3%	104%	2%	111%	4%	110%	4%
trifloxystrobin	110%	4%	111%	3%	112%	6%	111%	4%	110%	4%	117%	4%	115%	5%
triflumizole	104%	3%	104%	3%	107%	11%	111%	4%	112%	5%	113%	2%	108%	5%
triflumuron	110%	4%	107%	8%	113%	6%	111%	7%	114%	4%	118%	3%	121%	6%
triforine	102%	9%	103%	8%	110%	5%	109%	3%	108%	3%	121%*	5%	108%	4%
triticonazole	109%	3%	108%	2%	112%	10%	113%	5%	108%	3%	116%	2%	111%	3%
zoxamide	106%	4%	107%	3%	111%	5%	109%	5%	111%	4%	119%	8%	117%	7%

*Value was outside the recommended EU AQC guidelines (70%-120%)

Conclusion

The results of both approaches were compared. Automation of the QuEChERS extraction method was found to produce reliable results for the spiked samples, which compared favorably with those from the existing manual procedure. There was excellent agreement between results for the analysis of samples with incurred residues prepared manually and using the automated system. Automating the procedure led to improved repeatability, a reduction in the likelihood of human error and the potential for significant labor savings.

Precision and accuracy were assessed for the three commodities analyzed. Results for the automated procedure were well within the criteria set in the EU AQC guidelines: Average recoveries for the range of commodities were between 106% and 114% with good precision (ca. 4% RSD).

Acknowledgement

Special thanks to The Food and Environmental Research Agency (FERA) who took their time to evaluate the QuEChERS extraction using the AutoMate-Q40 sample prep workstation and also providing the data for this project. This project wouldn't have been possible without their support and hard work.

References

1. European Committee for Standardization/Technical Committee CEN/TC275 (2008), Foods of plant origin: Determination of pesticide residues using GC-MS and/or LC-MS/MS following Acetonitrile extraction/ partitioning and cleanup by dispersive SPE QuEChERS-method.
2. Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. (SANCO/12571/2013)