APPLICATION NOTE 65684

Multi-pesticide residues analyses of QuEChERS extracts using an automated online µSPE clean-up coupled to LC-MS/MS

Authors: Long Sun[1], Qilei Guo[1], Cristina C. Jacob[2], Claudia P.B. Martins[2], Richard Fussell[3]; [1]Thermo Fisher Scientific, Customer Solution Center, Beijing, China; [2]Thermo Fisher Scientific, San Jose, CA, USA; [3]Thermo Fisher Scientific, Hemel Hempstead, UK

Keywords: Pesticide residues analysis, LC-MS/MS, QuEChERS, online µSPE, clean-up, automation

Goal

To demonstrate the feasibility of an automated online sample clean-up solution coupled to LC-MS/MS for rapid and robust quantitation of multi-pesticide residues in food matrices.

Introduction

Pesticides are widely used to control pests worldwide, so crops, feed, and food products are routinely tested for the presence of pesticide residues and to check for compliance with permitted Maximum Residue Levels (MRLs).[1,2] Given the globalization of the food supply, the large number of different pesticides used, and the many samples to be analyzed, robust, accurate, reproducible, and cost-effective multiresidue methods allowing the reliable analysis of hundreds of pesticides in a single experiment and in many different sample types are required.

The QuEChERS (quick, easy, cheap, effective, rugged, and safe) approach is commonly used for the analysis of multi-pesticide residues, because of the substantial productivity gains that can be achieved.[3-5] The QuEChERS approach usually involves extraction with acetonitrile in the presence of a mixture of salts followed by centrifugation. An aliquot of the supernatant is cleaned up by manual dispersive-solid phase extraction (d-SPE) in an attempt to remove unwanted matrix compounds, such as pigments, sugars, organic acids, excess water, and other components.

Undoubtedly, the QuEChERS approach is faster, more cost effective, more environmentally friendly and more generic than previous methods, which used higher volumes of solvent and more tedious clean-up procedures. Although SPE in the dispersive mode is simple and less time consuming than gel permeation chromatography or SPE in the cartridge format, it is less effective, so more co-extractives remain in the final extract. These matrix co-extractives can cause ionization suppression and faster contamination of the LC-MS/MS detection system. Automation of the SPE step using a robotic autosampler and miniaturized SPE cartridges not only increases the effectiveness of the clean-up (compared to d-SPE) but also improves productivity by reducing the amount of analyst time required.[6]

Therefore, this application note describes the online automation of the SPE process for LC-amenable pesticides, based on the use of µSPE cartridges. The µSPE cartridges are compatible with the Thermo Scientific™ TriPlus™ RSH™ multi-purpose autosampler, which was coupled to a Thermo Scientific™ Vanquish™ Horizon UHPLC system interfaced with a Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer. Grape, rice, and tea extracts were selected as matrices for evaluation of the automated µSPE-LC-MS/MS method.

Experimental

Sample preparation

Samples and extraction

Samples of grape, rice, and tea for use as blank test materials were obtained from Chinese local markets. Blank food samples (500 g) were homogenized using a laboratory blender and/or ground using a pestle and mortar. Homogenized sub-samples (10 g) were then weighed into 50 mL centrifuge tubes and extracted using either the citrate buffered, or acetate buffered, versions of the QuEChERS methods.[3-5] Dry commodities (rice and tea) were rehydrated with water and left to soak for 30 mins to help desorb the pesticides from the matrix. After the addition of acetonitrile (10 mL), the mixture was vortex-mixed for 1 min and then the appropriate salt mixture was added. The extracts were shaken for 10 min and then centrifuged at 5,000 xg for 5 min. Aliquots of the supernatant were retained for evaluation of d-SPE and automated µSPE clean-up. Table 1 summarizes the QuEChERS extraction method details for the different food matrices. For the purpose of recovery experiments, aliquots of the blank samples were spiked before extraction.

Table 1. QuEChERS acetonitrile extraction method details

Method details	Grape samples	Rice samples	Tea samples
Sample amount	10 g	5 g	2 g
Soak prior extraction	Not applicable	10 mL of water	10 mL of water
Acetonitrile volume	10 mL	15 mL containing 1% acetic acid	15 mL containing 1% acetic acid
QuEChERS salt mixture	4 g anhydrous magnesium sulfate, 1 g sodium chloride, 1 g sodium citrate tribasic dihydrate, 0.5 g disodium citrate sesquihydrate (P/N 60105-216)	6 g anhydrous magnesium sulfate, 1.5 g anhydrous sodium acetate (P/N 60105-210)	

Automated µSPE and dispersive SPE

Automated µSPE clean-up was performed using the robotic Thermo Scientific™ TriPlus™ RSH autosampler system (based on a PAL3-RTC autosampler from CTC Analytics). The configuration of the system modules required to perform the automated µSPE clean-up is shown in Figure 1. Thermo Scientific™ Xcalibur™ 4.2 software was used for system control. The miniaturized SPE cartridges containing 30 mg of Z-Sep/C18/CarbonX (QuEChERS blend for LC, (P/N 60101-30LC) were used for all extracts. The µSPE cartridges are sealed by a septum, which allows the syringe to push sample extracts or solvents through the sorbent bed. Essentially, the syringe replaces the vacuum system of the classical SPE methodology working at defined flow rates (Figure 2). Procedurally, QuEChERS extracts were transferred into 2 mL autosampler vials and placed into a 54-position tray (sample tray). The corresponding number of collection vials [500 µL, fused insert snap-top (P/N C4011-LV1) sealed with star-slit snap-it caps (P/N C4011-59)] were placed into a second 54-position tray (eluate tray). Uncleaned extracts were loaded onto a preconditioned µSPE cartridge and the pesticides eluted as shown in Figure 2. The cartridges were eluted with a mixture of acetonitrile and 100 mM ammonium formate in methanol (1:1, v/v), for optimum recovery of most the pesticides of interest.[6] The automated µSPE clean-up requires several steps, cartridge conditioning, loading of sample extract and elution of analytes which take a total of 10 minutes as detailed in Table 2.

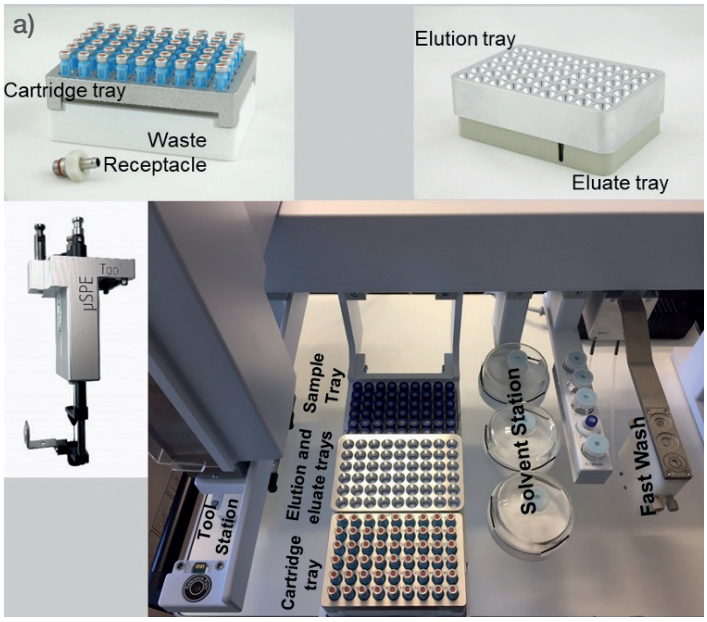

Figure 1. TriPlus RSH with µSPE capabilities system: a) TriPlus RSH modules required to perform the µSPE clean-up procedure and b) coupled to LC-MS/MS

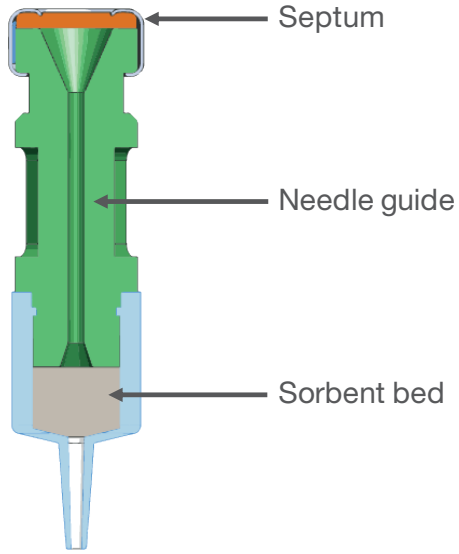

Figure 2. Automated µSPE cartridge

Table 2. Steps for automated online µSPE clean-up method with LC injection

1. Clean	Prep syringe with elution solvent
2. Condition	µSPE with 150 µL elution solvent
3. Move	µSPE cartridge to elution tray
4. Load	150 µL QuEChERS extract onto µSPE cartridge
5. Clean	The prep syringe
6. Elute	µSPE cartridge with 150 µL elution solvent
7. Move	Used µSPE cartridge to cartridge tray
8. Change	**To LC/MS injection tool**
9. Inject	**To LC-MS/MS**
10. Change	**To prep syringe for next sample**
11. Proceed	With prep-ahead for next extract sample upon Ready Signal

For the purpose of comparison, dispersive SPE was performed using two different blends of sorbents. Grape extracts (1 mL) were transferred to 2 mL centrifuge tubes containing 150 mg $MgSO_4$ and 25 mg PSA (P/N 60105-219). Rice and tea extracts (1 mL) were transferred into 2 mL centrifuge tubes containing 150 mg $MgSO_4$, 50 mg PSA, and 50 mg C18 (P/N 60105-204). Samples were then mixed for 1 min followed by centrifugation for 5 min. The supernatant was manually transferred into a 2 mL autosampler vial and analyzed by LC-MS/MS.

Preparation of matrix-matched standards

QuEChERS extracts of blank grape, rice, and tea were prepared and cleaned up through both automated µSPE and d-SPE. The µSPE and d-SPE final extracts were then spiked with a mixture of 195 pesticides (including homologues and metabolites) at different concentration levels (range 0.5–100 µg/kg) to prepare the matrix-matched calibration standards.

LC-MS/MS analysis

The LC-MS/MS system comprised a Thermo Scientific™ Vanquish™ Horizon Binary UHPLC system interfaced with a Thermo Scientific™ TSQ Fortis™ triple quadrupole mass spectrometer equipped with a H-ESI ionization probe. Chromatographic separation was carried out on a Thermo Scientific™ Accucore™ AQ column (2.1 x 100 mm, 2.6 µm, P/N 17326-102130) at a constant temperature of 25 ˚C, using a gradient elution of 2 mM ammonium formate in water containing 2% methanol and 0.1% formic acid (mobile phase A) and 2 mM ammonium formate in methanol containing 2% water and 0.1% formic acid (mobile phase B). Table 3 shows the gradient conditions. The injection volumes of 1 µL and 2 µL were used for d-SPE and µSPE cleaned extracts, respectively.

Table 3. LC gradient conditions

Time (min)	%B	Flow rate (mL/min)
0	2	0.3
2	40	0.3
11	100	0.3
11.5	100	0.5
13	100	0.5
13.1	2	0.3
15	2	0.3

The mass spectrometer was operated in both positive and negative ionization modes, with the optimized parameters shown in Table 4.

Table 4. MS parameter settings

Parameter	Setting
Spray voltage	3.5 kV, positive ionization mode 2.5 kV, negative ionization mode
Sheath gas	40 arb
Auxiliary gas	8 arb
Sweep gas	1 arb
Ion transfer tube temperature	300 ˚C
Vaporizer temperature	350 ˚C
Cycle time for scheduled SRM transitions	0.4 s
Q1 resolution	0.7 Da
Q3 resolution	1.2 Da
CID gas	2 mTorr

SRM transitions were optimized for 195 pesticides (including homologues and metabolites). The SRM transitions are detailed in Appendix Table A.

Data processing

The acquired data were processed using Thermo Scientific™ TraceFinder™ 4.1 software, and Thermo Scientific™ Freestyle™ 1.5 software was used for qualitative purposes.

Results and discussion

Extracts of three representative sample types, grape (high water), rice (cereal/dry commodity), and black tea (difficult matrix), were selected to evaluate the online µSPE-LC-MS/MS method described herein. The EU SANTE/12682/2019 guidelines[7] were used to establish method performance criteria, including linearity, accuracy (recovery), precision, reproducibility, and limit of quantitation (LOQ). Recovery and reproducibility of the method was verified at 10, 50, and 100 µg/kg. Method effectiveness was checked by comparison with the conventional d-SPE QuEChERS clean-up procedure.

The selected 195 pesticides (parent pesticides, isomers, and metabolites) were from the LC-amenable monitoring pesticide list of Chinese National Food Safety Standard GB 2763-2019[1]. An overlay of SRM ion chromatograms for all pesticides analyzed in this method is shown in Figure 3. Despite the short chromatographic run time (15 minutes), good separation and detection of the pesticide compounds was achieved using the scheduled-SRM mode.

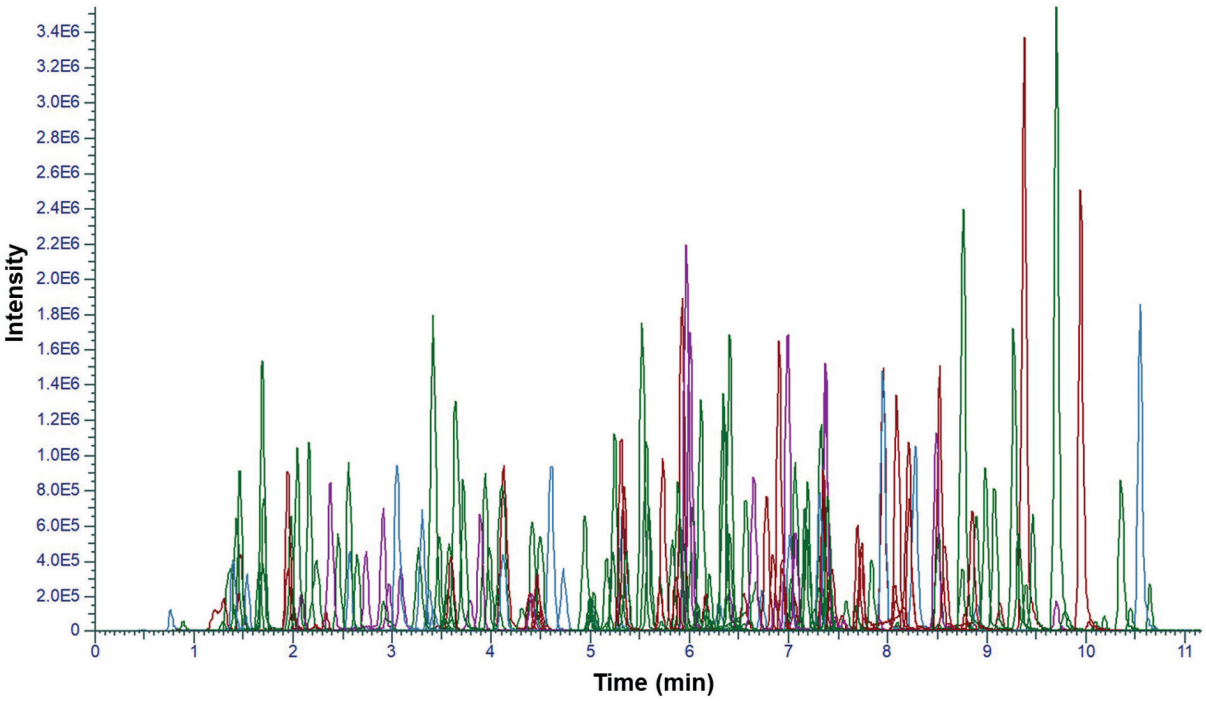

Figure 3. Overlaid chromatograms of all 195 pesticide compounds included in this method

µSPE clean-up effectiveness and matrix effects

Matrix co-extractives can contaminate the analytical column and the ion source, and also cause ion suppression, while ionized matrix components not monitored in the SRM chromatograms, but present in the background, can affect accuracy and sensitivity. LC-HRAM MS data were acquired in full scan for blank grape, rice, and tea extracts, and the total ion chromatograms (TIC) of both d-SPE and µSPE clean-up procedures were compared. Matrix effects were also evaluated by comparing the responses of pesticide standards prepared in solvent (neat solution) and in the different sample matrices.

Although both have similar LC-HRAM MS profiles (Figure 4a), the automated µSPE clean-up procedure showed higher effectiveness in removing pigments of grape sample matrix when compared with the conventional d-SPE clean-up as shown in Figure 4b, which is due mainly to carbonX sorbent. For the analysis of tea, µSPE removed more co-extractive peaks compared to dSPE as shown in the LC-HRAM MS total ion chromatograms in Figure 5.

Grape and tea sample matrix effects were less than 20% for 90% of the compounds in both automated and manual clean-up procedures. Nonetheless, matrix-matched calibrations were used in this study for quantitation of all analytes to reduce variations in the analytical results.

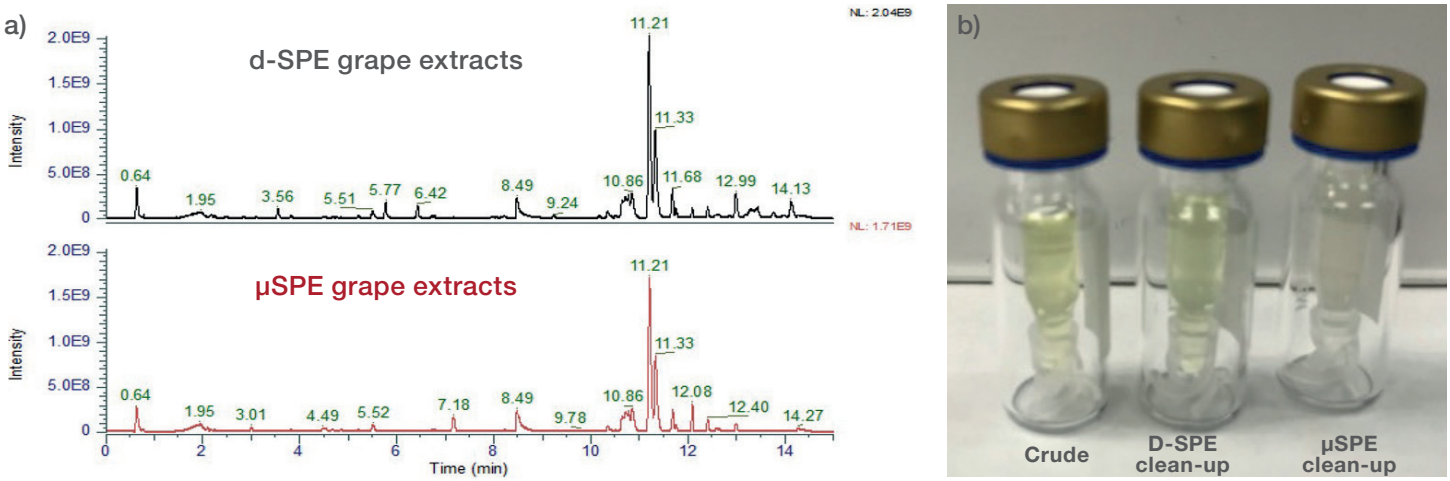

Figure 4. Blank grape extracts: a) HRAM MS full scan chromatograms after d-SPE and µSPE clean-up, b) grape extracts without clean-up, after µSPE clean-up, and after d-SPE clean-up

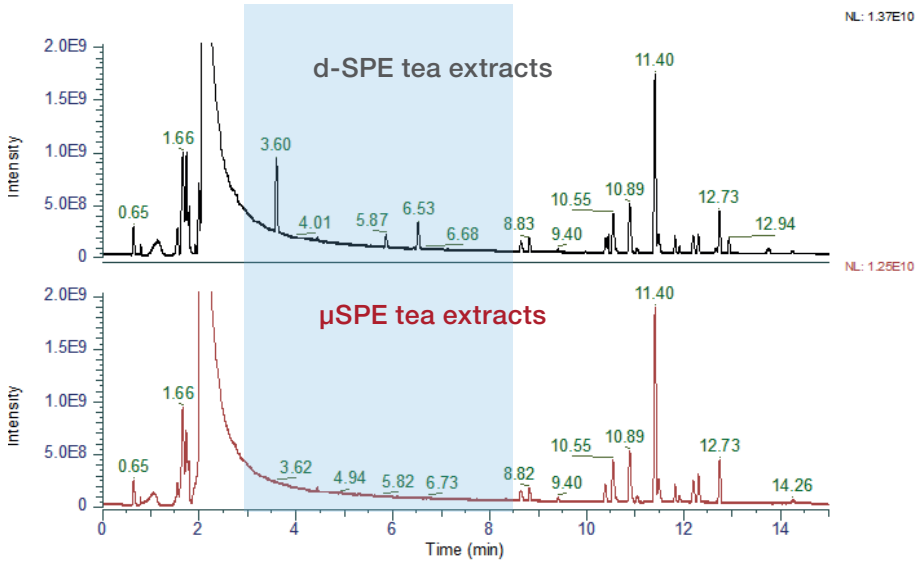

Figure 5. HRAM MS full scan chromatograms of unspiked tea extracts after d-SPE and µSPE clean-up

Improved removal of rice sample matrix components was achieved for samples cleaned up through an automated µSPE procedure where all monitored pesticide compounds showed matrix effects lower than 20% (Figure 6a). A more substantial removal of rice matrix co-extractives was also observed in the LC-HRAM MS chromatograms of blank µSPE extracts (Figure 6b), indicating higher effectiveness of µSPE clean-up when compared with d-SPE clean-up.

Linearity

Matrix-matched standards were prepared in grape, rice, and tea d-SPE and µSPE extracts. Excellent linearity was achieved using matrix-matched external calibration over the range 0.5–100 µg/kg, with correlation coefficients greater than 0.99 and respective back-extracted calculations within 20% for most of the compounds in the three different food extracts. Representative calibration curves for fluvalinate, haloxyfop, hexythiazox, and thiobencarb in rice extracts are shown in Figure 7.

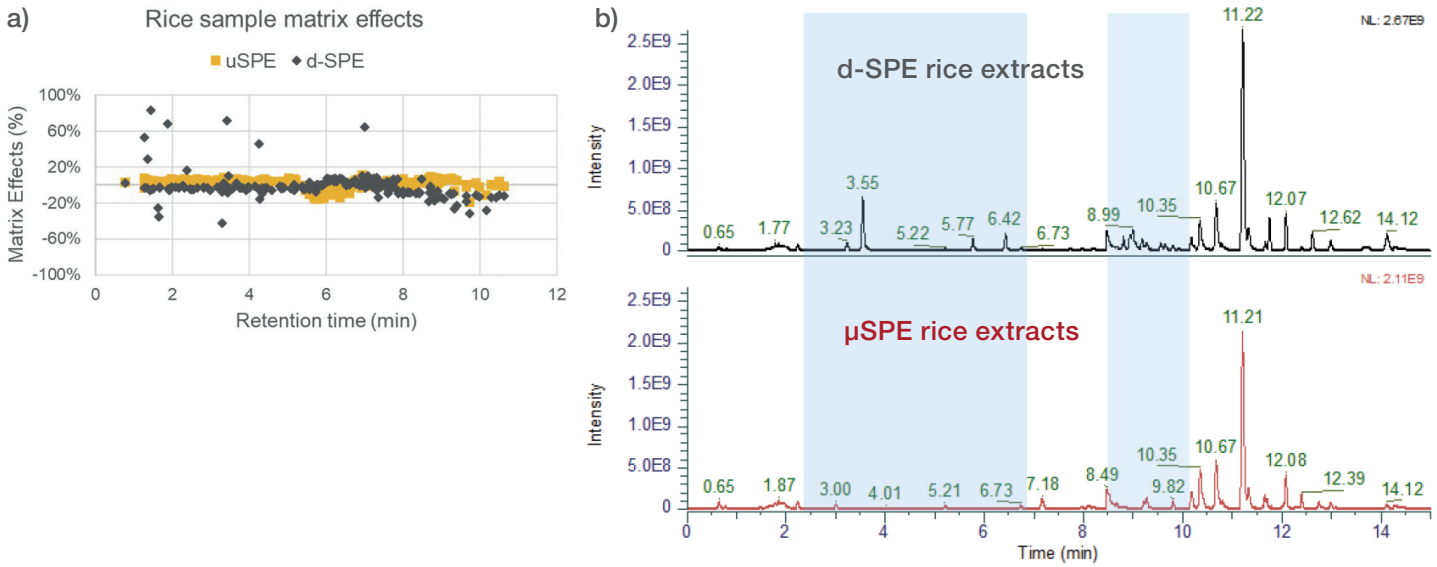

Figure 6. Removal of rice sample matrix components: a) matrix effects of 195 pesticides plotted vs. retention time in LC-MS/MS after d-SPE clean-up and after µSPE clean-up; b) total ion chromatograms in full scan LC-HRAM MS of blank rice and tea extracts after d-SPE and µSPE clean-up

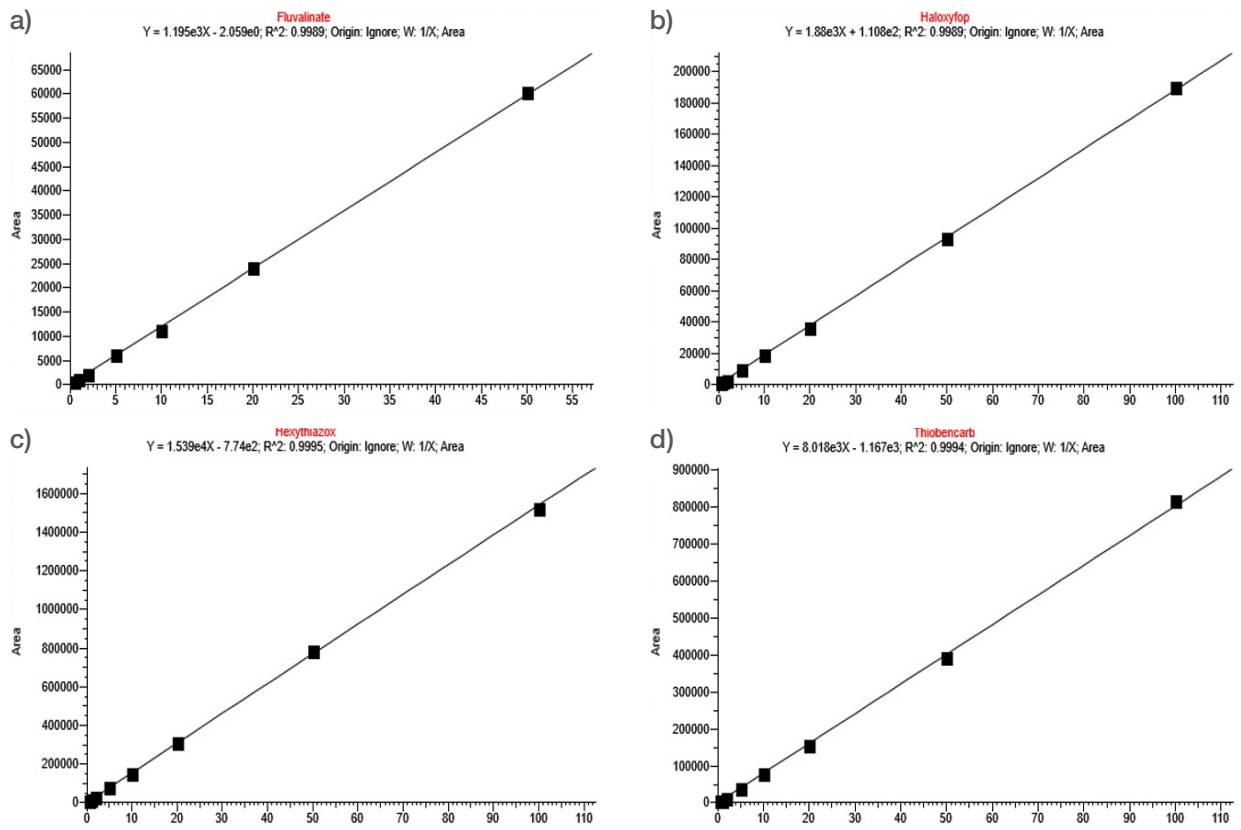

Figure 7. Representative calibration curves for a) fluvalinate, b) haloxyfop, c) hexythiazox, and d) thiobencarb in rice µSPE extracts over the range 0.5–100 µg/kg

µSPE method performance

The recoveries of 195 pesticides (including isomers and metabolites) were evaluated by spiking the analytes onto five replicate sub-samples of each of grape, rice, and tea matrices at three concentration levels of 10, 50, and 100 µg/kg, respectively. Grape samples were extracted with acetonitrile and citrate-based QuEChERS, while rice and black tea samples were extracted with acidified acetonitrile (1% acetic acid) and acetate-based QuEChERS. One aliquot of spiked QuEChERS extracts (1 mL) followed an automated and online µSPE clean-up procedure while a second aliquot (1 mL) followed the manual d-SPE clean-up method prior LC-MS/MS.

Recoveries within 70–120% with corresponding %RSDs below 20% are required for satisfactory method validation according to the EU SANTE 12682/2019 document.[7] In this method, the recoveries were calculated using matrix-matched calibration standards. Recoveries within 70–120% were achieved for 98% of the target pesticides in grape, 98% in tea, and 96% in rice extracts (Figure 8), indicating excellent reproducibility of the miniaturized SPE cartridges.

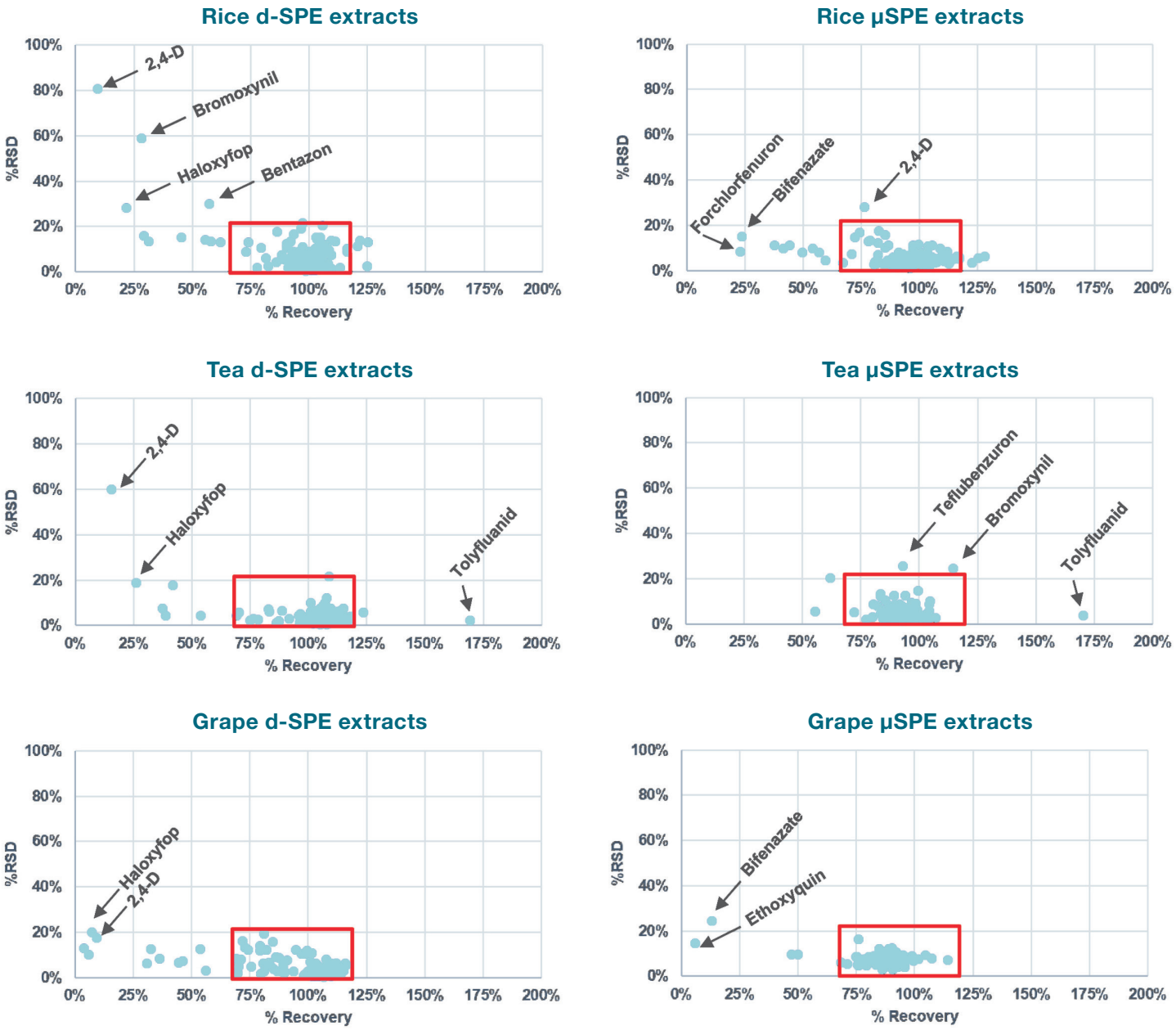

Figure 8. % Recovery vs. %RSD in grape, rice, and tea extracts at 100 µg/kg (N=5). The red boxes represent recoveries within 70–120% with %RSD <20%.

The µSPE clean-up method afforded LOQs at 10 µg/kg for 80% of the monitored pesticides in tea extracts (d-SPE 78%), 91% in rice extracts (d-SPE 80%), and 94% in grape extracts (d-SPE 94%). Table 4 summarizes the % spike recoveries for the matrix extracts at 10 µg/kg.

Table 4 (part 1). LC-MS/MS % spike recoveries in different extracts at 10 µg/kg using both automated µSPE and manual d-SPE. % Recoveries <70% and >120% and/or %RSDs >20% are highlighted bold type.

Compound	% Recovery (%RSD) at 10 µg/kg (N=5)					
	Grape		Tea		Rice	
	d-SPE	µSPE	d-SPE	µSPE	d-SPE	µSPE
2,4-D*	**30(4)**	95(18)	**1(0)**	**61(84)**	**1(0)**	**53(61)**
Abamectin-b1a	102(4)	85(6)	**87(28)**	**91(38)**	**109(27)**	94(11)
Acephate	99(3)	97(1)	88(6)	95(6)	104(3)	87(4)
Acetamiprid	103(3)	95(5)	95(11)	83(16)	107(2)	89(4)
Acetochlor	114(9)	86(9)	121(14)	100(18)	99(8)	83(18)
Alachlor	120(13)	92(6)	101(12)	91(13)	108(11)	84(5)
Aldicarb	103(1)	92(5)	101(5)	84(10)	104(3)	93(4)
Aldicarbsulfone	111(6)	90(7)	**110(21)**	**65(28)**	100(7)	93(9)
Aldicarb-sulfoxide	101(2)	99(6)	107(5)	105(10)	102(5)	90(7)
Ametryn	103(1)	95(5)	92(4)	78(6)	107(3)	88(4)
Anilofos	95(5)	93(1)	91(7)	94(8)	106(7)	85(6)
Atrazine	104(1)	92(7)	104(7)	97(5)	111(3)	88(5)
Azinphos	115(3)	80(6)	108(5)	76(19)	102(5)	68(13)
Azoxystrobin	104(2)	73(19)	101(2)	96(6)	108(3)	109(6)
Benalaxyl	96(6)	96(4)	105(6)	87(5)	97(11)	94(6)
Bensulfuron methyl	**49(9)**	74(6)	68(9)	89(6)	101(6)	**59(7)**
Bentazon	**82(21)**	78(9)	**59(42)**	**90(59)**	**59(68)**	114(17)
Benzoximate	101(4)	99(5)	99(9)	91(6)	116(16)	90(7)
Bifenazate	**39(135)**	**16(38)**	106(3)	59(10)	**156(21)**	**25(15)**
Bifenthrin	103(3)	90(5)	**52(62)**	**42(29)**	101(8)	86(8)
Bitertanol	100(8)	82(7)	**92(27)**	85(19)	**89(42)**	94(15)
Boscalid	112(5)	**50(53)**	102(10)	86(14)	105(3)	103(6)
Bromoxynil	**56(30)**	**102(24)**	**11(204)**	**132(46)**	**23(21)**	**73(67)**
Buprofezin	102(2)	96(7)	82(14)	81(18)	**130(21)**	91(3)
Butachlor	112(8)	91(6)	**97(32)**	**84(34)**	113(9)	**88(22)**
Cadusafos	100(2)	93(5)	99(7)	85(10)	105(19)	89(1)
Carbaryl	105(2)	90(5)	104(5)	94(9)	107(4)	89(1)
Carbendazim	102(2)	85(3)	**27(22)**	**48(22)**	99(4)	75(4)
Carbofuran	103(2)	92(6)	90(6)	70(11)	103(3)	84(5)
Chlorantraniliprole	114(8)	**44(48)**	92(11)	109(15)	109(11)	**62(24)**
Chlorfluazuron	104(4)	80(9)	**55(15)**	89(14)	**143(25)**	85(10)
Chlormequat	100(3)	95(3)	**61(8)**	88(8)	76(7)	92(3)

Table 4 (part 2). LC-MS/MS % spike recoveries in different extracts at 10 µg/kg using both automated µSPE and manual d-SPE. % Recoveries <70% and >120% and/or %RSDs >20% are highlighted bold type.

Compound	% Recovery (%RSD) at 10 µg/kg (N=5)					
	Grape		Tea		Rice	
	d-SPE	µSPE	d-SPE	µSPE	d-SPE	µSPE
Chlorotoluron	101(5)	98(4)	91(8)	96(10)	102(8)	85(10)
Chlorpyrifos	105(4)	87(7)	**102(29)**	**96(48)**	**146(67)**	86(11)
Chlorpyrifos-methyl	106(14)	119(9)	**116(34)**	**92(22)**	**177(21)**	**95(23)**
Clomazone	106(2)	93(6)	103(3)	90(1)	107(4)	49(7)
Clothianidin	113(3)	94(7)	116(10)	**84(25)**	106(7)	106(6)
Coumaphos	96(8)	98(13)	**75(21)**	82(10)	**115(21)**	90(13)
Cyanazine	107(2)	84(4)	105(7)	96(6)	108(4)	95(5)
Cyazofamid	**135(29)**	120(5)	105(7)	104(9)	109(3)	85(10)
Cymoxanil	100(4)	98(7)	111(11)	85(14)	105(6)	88(8)
Cyprodinil	120(7)	89(6)	**62(23)**	92(20)	110(3)	83(8)
Cyromazine	96(5)	89(12)	**44(167)**	100(16)	102(6)	87(5)
Deltamethrin	104(6)	89(8)	**93(40)**	**94(23)**	**140(28)**	**75(30)**
Demeton	96(3)	92(5)	102(8)	80(6)	112(4)	56(10)
Desmedipham	105(6)	84(7)	**163(10)**	**185(4)**	128(10)	**52(23)**
Diazinon	101(7)	94(5)	99(6)	83(6)	106(8)	88(4)
Dichlorvos	110(3)	81(8)	**32(41)**	**55(25)**	90(10)	79(5)
Diethofencarb	104(1)	82(9)	99(6)	93(6)	107(2)	73(3)
Difenonazole	102(5)	84(8)	94(11)	81(17)	**131(27)**	95(5)
Diflubenzuron	80(19)	97(7)	**78(22)**	83(14)	116(9)	104(11)
Dimethenamid	102(0)	92(6)	100(4)	87(11)	103(2)	102(7)
Dimethoate	104(2)	94(6)	108(7)	87(7)	106(4)	87(4)
Dimethomorph	**80(55)**	**34(77)**	102(6)	92(13)	108(3)	96(9)
Diniconazole	103(6)	89(13)	86(12)	91(10)	**114(26)**	99(5)
Diuron	105(3)	94(5)	95(9)	104(9)	104(11)	**61(23)**
Edifenphos	100(4)	107(5)	107(5)	92(3)	103(6)	98(7)
Epoxiconazole	114(8)	91(5)	89(3)	77(15)	112(4)	87(4)
Ethion	98(3)	97(3)	108(6)	82(6)	**144(32)**	83(5)
Ethiprole	100(2)	86(6)	100(12)	100(9)	113(2)	108(6)
Ethirimol	98(10)	90(9)	66(9)	87(6)	88(7)	86(5)
Ethoprophos	**127(13)**	92(3)	93(6)	89(12)	102(7)	90(5)
Ethoxyquin	**65(26)**	**16(8)**	**97(22)**	67(16)	99(8)	**44(18)**
Etofenprox	100(1)	92(6)	93(3)	91(7)	103(3)	83(2)
Etoxazole	101(1)	93(6)	96(2)	94(6)	117(13)	85(1)
Fenamiphos	102(6)	93(6)	94(6)	91(6)	107(4)	84(4)
Fenamiphos sulfone	101(2)	99(6)	101(7)	93(9)	105(6)	87(6)
Fenamiphos sulfoxide	98(3)	96(4)	91(9)	86(9)	96(6)	83(10)
Fenarimol	120(12)	88(11)	**96(44)**	113(8)	109(13)	96(13)

Table 4 (part 3). LC-MS/MS % spike recoveries in different extracts at 10 µg/kg using both automated µSPE and manual d-SPE. % Recoveries <70% and >120% and/or %RSDs >20% are highlighted bold type.

Compound	% Recovery (%RSD) at 10 µg/kg (N=5)					
	Grape		Tea		Rice	
	d-SPE	µSPE	d-SPE	µSPE	d-SPE	µSPE
Fenazaquin	104(2)	87(4)	**62(8)**	90(9)	94(4)	82(4)
Fenbuconazole	104(12)	101(8)	108(14)	102(19)	126(13)	102(11)
Fenhexamid	93(7)	81(9)	101(10)	**79(23)**	102(8)	96(10)
Fenobucarb	104(2)	89(5)	109(7)	97(5)	106(2)	74(8)
Fenoxanil	95(8)	93(7)	107(6)	95(15)	107(3)	83(3)
Fenpropathrin	102(8)	86(12)	**48(55)**	**65(70)**	**149(41)**	89(5)
Fenpyroximat	105(1)	89(6)	86(3)	90(5)	115(18)	87(4)
Fenthion	**123(11)**	89(9)	103(13)	81(18)	**86(24)**	99(18)
Fenthion-sulfone	106(3)	99(6)	95(9)	104(7)	106(6)	91(4)
Fenthion-sulfoxide	101(3)	96(2)	103(6)	93(7)	108(2)	90(6)
Florasulam	**59(8)**	89(5)	82(5)	94(10)	75(13)	92(4)
Fluazifop-P-butyl	102(3)	93(7)	102(2)	94(6)	**147(27)**	89(2)
Fluazinam	94(6)	94(5)	**97(26)**	111(16)	**111(21)**	108(16)
Flubendiamide	96(11)	72(18)	**105(25)**	**81(25)**	**137(22)**	**95(27)**
Flufenoxuron	106(3)	91(9)	103(11)	81(7)	**145(31)**	94(4)
Flumetsulam	**32(8)**	89(4)	77(8)	94(2)	69(9)	91(8)
Fluopicolide	105(2)	94(4)	108(6)	85(11)	103(4)	101(10)
Fluquinconazole	116(4)	86(2)	110(11)	82(20)	**126(7)**	88(10)
Flusilazole	101(8)	91(7)	91(5)	92(14)	103(5)	78(9)
Flutolanil	106(2)	90(6)	106(7)	93(3)	109(5)	104(3)
Flutriafol	110(2)	82(7)	92(17)	86(20)	110(10)	89(16)
Fluvalinate	108(6)	86(9)	**97(23)**	**89(28)**	**129(8)**	89(9)
Fonofos	106(10)	93(9)	95(14)	100(8)	98(8)	81(14)
Forchlorfenuron	102(2)	**34(6)**	**40(5)**	85(5)	104(2)	**33(7)**
Fosthiazate	105(2)	93(6)	106(3)	97(7)	113(3)	84(7)
Haloxyfop	**3(85)**	94(3)	**57(39)**	**56(46)**	**56(26)**	**95(22)**
Haloxyfop-methyl	103(3)	89(5)	105(3)	93(7)	116(17)	94(3)
Hexaconazole	98(5)	82(8)	**84(23)**	89(16)	109(14)	95(14)
Hexaflumuron	**116(27)**	**83(24)**	**79(60)**	**90(21)**	**128(19)**	**99(26)**
Hexazinone	104(2)	91(4)	90(6)	97(9)	106(7)	87(4)
Hexythiazox	100(4)	87(8)	106(6)	91(13)	**145(37)**	88(7)
Imazalil	102(7)	91(9)	98(19)	88(16)	83(15)	**85(21)**
Imazaquin	**3(65)**	70(10)	**30(17)**	100(18)	**21(21)**	89(9)
Imazethapyr	**12(14)**	73(3)	**35(14)**	94(11)	45(8)	89(5)
Imibenconazole	97(7)	84(6)	70(7)	84(14)	**135(23)**	85(10)
Imidacloprid	108(2)	80(7)	112(17)	**75(24)**	104(5)	98(2)
Indoxacarb	106(9)	87(10)	87(18)	97(12)	**129(23)**	102(8)

Table 4 (part 4). LC-MS/MS % spike recoveries in different extracts at 10 µg/kg using both automated µSPE and manual d-SPE. % Recoveries <70% and >120% and/or %RSDs >20% are highlighted bold type.

Compound	% Recovery (%RSD) at 10 µg/kg (N=5)					
	Grape		Tea		Rice	
	d-SPE	µSPE	d-SPE	µSPE	d-SPE	µSPE
Isazofos	109(9)	99(15)	**125(20)**	**114(26)**	110(10)	93(16)
Isofenphos-methyl	102(5)	93(5)	105(6)	85(8)	107(6)	90(8)
Isoprocarb	105(4)	93(6)	105(10)	93(7)	108(8)	86(5)
Isoprothiolane	105(2)	94(7)	100(5)	89(6)	110(5)	92(6)
Isoproturon	103(3)	91(7)	103(6)	84(18)	111(4)	91(10)
Kresoxim-methyl	89(16)	**56(8)**	115(16)	**97(29)**	114(6)	102(9)
Linuron	108(6)	92(8)	88(14)	99(9)	108(5)	**104(22)**
Malaoxon	105(3)	94(4)	112(6)	99(7)	106(3)	87(2)
Malathion	109(5)	93(5)	111(12)	88(11)	107(6)	101(7)
Mandipropamid	102(4)	97(3)	109(5)	91(7)	102(6)	97(8)
Metalaxyl	104(3)	93(4)	109(9)	86(11)	102(3)	90(3)
Mefenacet	114(3)	91(4)	96(5)	91(8)	108(4)	90(3)
Mepronil	107(1)	93(4)	100(7)	90(4)	109(1)	100(5)
Metazachlor	96(15)	87(15)	**82(37)**	88(12)	**93(25)**	96(18)
Methamidophos	103(2)	96(3)	115(6)	110(8)	102(5)	93(6)
Methidathion	104(4)	92(8)	100(8)	76(9)	112(7)	**54(23)**
Methiocarb	99(4)	76(6)	95(5)	80(12)	108(3)	87(7)
Methomyl	109(5)	103(5)	**71(30)**	**67(30)**	107(12)	91(10)
Methoxyfenozide	105(1)	92(6)	101(7)	95(4)	107(4)	96(3)
Metolachlor	121(5)	91(4)	103(15)	**81(23)**	117(8)	89(10)
Metribuzin	107(4)	92(7)	104(16)	75(6)	119(5)	95(4)
Metsulfuron-methyl	**45(10)**	**60(9)**	**60(3)**	84(9)	58(9)	84(11)
Molinate	104(5)	94(4)	110(8)	80(14)	111(8)	95(10)
Monocrotophos	98(4)	97(4)	113(5)	100(4)	103(5)	90(5)
Myclobutanil	107(7)	106(7)	104(19)	94(12)	112(9)	100(5)
Omethoate	104(3)	96(3)	102(6)	95(12)	108(6)	90(5)
Oxadiazon	102(6)	96(4)	100(6)	89(10)	**197(37)**	86(8)
Oxadixyl	107(4)	90(3)	104(6)	96(6)	112(6)	89(9)
Oxamyl	104(3)	95(3)	109(6)	98(8)	112(6)	92(9)
Paclobutrazol	103(3)	91(9)	96(13)	79(20)	106(5)	102(8)
Paraoxon-ethyl	110(4)	99(6)	104(8)	86(13)	109(5)	87(4)
Paraoxon-methyl	101(3)	94(4)	95(7)	95(8)	99(5)	80(7)
Penconazole	117(7)	91(8)	106(13)	**98(26)**	93(16)	88(13)
Permethrin	101(7)	97(4)	**77(30)**	**84(31)**	111(10)	78(10)
Phenmedipham	105(6)	91(5)	**140(8)**	**123(5)**	**127(4)**	**46(17)**
Phenthoate	105(7)	89(8)	96(9)	76(14)	119(5)	91(7)
Phorate	111(13)	100(13)	109(18)	**120(25)**	**112(22)**	**58(25)**

Table 4 (part 5). LC-MS/MS % spike recoveries in different extracts at 10 µg/kg using both automated µSPE and manual d-SPE. % Recoveries <70% and >120% and/or %RSDs >20% are highlighted bold type.

Compound	% Recovery (%RSD) at 10 µg/kg (N=5)					
	Grape		Tea		Rice	
	d-SPE	µSPE	d-SPE	µSPE	d-SPE	µSPE
Phorate sulfone	103(4)	88(6)	101(11)	96(14)	117(8)	87(7)
Phosalone	100(5)	91(4)	101(12)	90(15)	**125(17)**	96(5)
Phosmet	105(4)	100(6)	98(5)	86(5)	106(3)	76(12)
Phosphamidon	104(1)	94(6)	96(5)	80(8)	104(6)	93(6)
Phoxim	102(6)	98(7)	105(11)	**82(21)**	110(8)	96(9)
Piperonyl butoxide	103(1)	93(5)	94(7)	95(7)	**127(19)**	87(3)
Pirimicarb	101(2)	89(6)	96(6)	90(8)	106(3)	90(2)
Pirimiphos-methyl	98(5)	97(4)	108(3)	80(17)	107(6)	90(4)
Pretilachlor	104(2)	98(4)	99(8)	90(9)	**128(25)**	89(3)
Prochloraz	95(9)	91(4)	79(10)	95(20)	113(7)	88(9)
Profenofos	108(4)	91(4)	95(6)	94(7)	**142(26)**	95(7)
Propamocarb	94(5)	92(4)	**48(10)**	91(8)	**56(8)**	87(5)
Propanil	99(7)	94(11)	**131(29)**	**87(46)**	105(9)	101(12)
Propargite	100(1)	94(6)	96(4)	90(5)	**138(16)**	86(6)
Propiconazol	101(7)	96(3)	**87(51)**	**72(40)**	112(18)	99(17)
Pymetrozine	95(4)	74(4)	**16(18)**	75(17)	97(6)	81(10)
Pyraclostrobin	87(11)	**55(38)**	87(14)	**72(24)**	120(7)	86(4)
Pyridaben	93(15)	94(5)	87(5)	**69(23)**	**122(18)**	85(2)
Pyrimethanil	111(11)	91(16)	76(4)	85(17)	105(6)	**59(11)**
Pyriproxyfen	100(2)	94(5)	100(4)	86(7)	**126(17)**	88(3)
Quinalphos	98(8)	89(5)	100(14)	69(18)	106(9)	94(10)
Quinoxyfen	102(3)	91(5)	**60(9)**	96(10)	119(14)	78(7)
Quizalofop-ethyl	106(2)	90(5)	84(6)	91(7)	**142(24)**	86(6)
Rimsulfuron	39(5)	76(5)	**51(17)**	87(5)	72(12)	73(4)
Rotenone	104(7)	91(5)	108(6)	93(11)	116(8)	85(6)
Sethoxydim	77(7)	108(8)	94(10)	76(15)	**140(22)**	99(6)
Simazine	103(11)	86(10)	**67(43)**	**142(33)**	93(13)	95(15)
Simetryn	105(2)	98(6)	87(5)	86(9)	114(3)	93(4)
Sulfotep	102(10)	95(7)	111(7)	88(12)	102(5)	80(10)
Tebuconazole	94(14)	95(10)	**104(29)**	**106(25)**	**126(8)**	108(7)
Tebufenozide	96(3)	88(3)	102(6)	100(14)	105(4)	86(3)
Teflubenzuron	**65(65)**	**122(25)**	**106(72)**	**117(23)**	**122(24)**	**55(207)**
Terbuthylazine	105(2)	91(4)	103(5)	89(4)	104(3)	113(3)
Thiabendazole	101(3)	71(4)	35(11)	86(7)	103(5)	**63(5)**
Thiacloprid	102(2)	93(3)	99(3)	87(7)	105(2)	88(4)
Thiamethoxam	104(2)	88(11)	105(13)	94(10)	105(2)	94(6)
Thidiazuron	93(2)	**23(6)**	**48(10)**	93(18)	95(6)	**41(17)**

Table 4 (part 6). LC-MS/MS % spike recoveries in different extracts at 10 µg/kg using both automated µSPE and manual d-SPE. % Recoveries <70% and >120% and/or %RSDs >20% are highlighted bold type.

Compound	% Recovery (%RSD) at 10 µg/kg (N=5)					
	Grape		Tea		Rice	
	d-SPE	µSPE	d-SPE	µSPE	d-SPE	µSPE
Thiobencarb	97(3)	92(8)	94(8)	85(9)	126(18)	100(3)
Thiodicarb	100(5)	101(5)	103(9)	**56(22)**	115(7)	92(11)
Thiophanate-methyl	100(3)	84(7)	**172(5)**	76(16)	105(11)	97(4)
Tolclofos-methyl	87(15)	102(14)	**153(49)**	**62(39)**	**144(30)**	**126(20)**
Tolfenpyrad	104(2)	88(5)	**26(87)**	**118(43)**	**152(25)**	88(8)
Tolylfluanid	**42(18)**	**164(4)**	**NA****	**NA****	**171(7)**	**125(14)**
Triadimefon	110(5)	105(6)	111(13)	96(20)	105(6)	103(13)
Triadimenol	**124(8)**	96(1)	**106(23)**	96(8)	**110(24)**	93(4)
Triazophos	115(11)	94(5)	102(4)	95(9)	107(3)	88(1)
Trichlorphon	100(3)	94(6)	136(14)	89(17)	106(8)	104(7)
Tricyclazole	101(1)	92(2)	**46(7)**	91(10)	102(3)	84(3)
Trifloxystrobin	90(8)	**55(38)**	109(7)	87(10)	130(18)	91(3)
Triflumizole	96(4)	89(7)	92(8)	94(11)	**126(33)**	90(5)
Vamidothion	103(2)	93(5)	101(3)	95(6)	106(2)	94(3)
Zoxamide	109(7)	87(8)	105(4)	98(8)	104(6)	89(6)

*The 2,4-D poor recovery observed in d-SPE extracts is due PSA in the d-SPE mixture blend.
**NA – Not analyzed because of the instability of tolylfluanid in tea.

µSPE method robustness

Figure 9 shows the overall response of fenpyroximate for 200 consecutive injections of the 50 ppb QC in black tea µSPE extracts. The data shows that the response was within the expected ±20% range for at least 200 consecutive injections without maintenance.

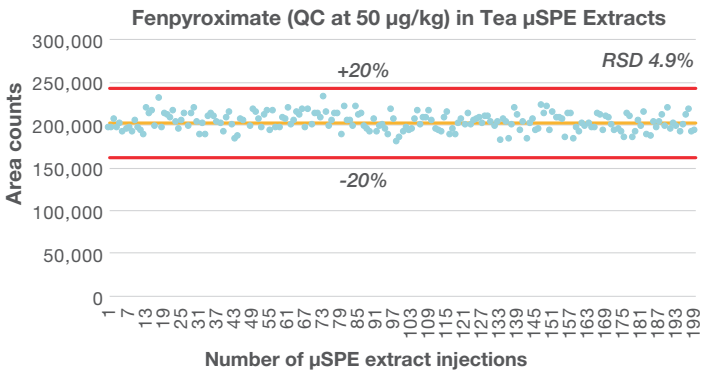

Figure 9. Fenpyroximate QC monitored in tea µSPE extracts for 200 consecutive injections (µSPE-LC-MS/MS) with 4.9% RSD. Red lines represent ±20% of fenpyroximate response at 50 µg/kg.

Conclusions

The fully automated and online µSPE clean-up procedure with LC-MS/MS described in this application note is a reliable, accurate, reproducible, and robust solution for the multi-residue pesticide analysis in representative samples of different matrix complexity (grape, rice, and tea).

- The TSQ Fortis MS is a powerful platform that offers several advantages towards developing robust, reproducible, fast and sensitive methodologies for the multi-pesticide residue analysis as demonstrated is this application note.
- The automated µSPE clean-up afforded spike recoveries within 70–120% with corresponding %RSDs below 20% for 98% of the target pesticides in grape, 98% in tea, and 96% in rice extracts.
- The automated µSPE showed reduced matrix effects when compared with d-SPE.
- Analyte responses in complex matrices (black tea) were stable for at least 200 consecutive injections without maintenance.

- With the prep ahead function the µSPE procedure for the subsequent sample is performed in parallel to the LC-MS/MS run, therefore LC-MS/MS run times are not affected.
- The sample throughput is maximized.
- The risk of human error is minimized.
- The efficiency of routine testing laboratories is greatly improved by replacing the need for a manual clean-up procedure with fully automated and unified operations.

Acknowledgements

We would like to thank Hans-Joachim Hübschmann, Benson Zhu, Tom Flug, Brian Peat, and Jonathan Beck from CTC Analytics for their extraordinary support with the TriPlus RSH autosampler with integrated µSPE capabilities.

References

1. EU Pesticides Database. https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=homepage&language=EN
2. Chinese National Food Safety standard GB 2763-2019. Maximum residue limits for pesticides in food. https://www.sdtdata.com/fx/fmoa/tsLibCard/173701.html
3. Anastassiades, M. et al. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *J. Chromatogr. A.* **2003.** *1015,* 163-184.
4. AOAC Official Method 2007.01, Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate, 2007.
5. Chinese National Food Safety Standard GB 23200.113-2018. Determination of 208 pesticides and metabolites residues in foods of plant origin-Gas chromatography-tandem mass spectrometry method. https://www.sdtdata.com/fx/fmoa/tsLibCard/169182.html
6. Morris, B.D. and Schriner, R.B. Development of an automated column solid-phase extraction cleanup of QuEChERS extracts, using Zirconia-Based sorbent, for pesticide residue analyses by LC-MS/MS. *J. Agricultural and Food Chemistry,* **2015,** *63,* 5107-5119.
7. SANTE guidelines. https://www.eurl-pesticides.eu/userfiles/file/EurlALL/AqcGuidance_SANTE_2019_12682.pdf

Appendix

Table A (part 1). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
2,4-D	Target Peak	218.962	160.9	10.25		Negative	4.41
2,4-D	Confirming	220.959	162.9	10.25	67.99	Negative	4.41
Abamectin-b1a	Target Peak	890.526	305.1	24.11		Positive	9.99
Abamectin-b1a	Confirming	890.526	567.2	12.83	74.56	Positive	9.99
Acephate	Target Peak	184.019	143.0	10.25		Positive	1.34
Acephate	Confirming	184.019	124.8	18.39	10.79	Positive	1.34
Acetamiprid	Target Peak	223.075	126.0	21.83		Positive	2.17
Acetamiprid	Confirming	223.075	90.0	33.60	23.75	Positive	2.17
Acetochlor	Target Peak	270.126	224.0	10.43		Positive	6.48
Acetochlor	Confirming	270.126	148.0	18.18	41.73	Positive	6.48
Alachlor	Target Peak	270.126	238.1	10.25		Positive	6.55
Alachlor	Confirming	270.126	162.1	20.52	39.45	Positive	6.55
Aldicarb	Target Peak	208.111	116.0	6.81		Positive	2.65
Aldicarb	Confirming	208.111	89.1	14.98	34.26	Positive	2.65
Aldicarb-sulfoxide	Target Peak	224.056	132.1	10.05		Positive	1.46
Aldicarb-sulfoxide	Confirming	224.056	89.1	17.47	53.74	Positive	1.46
Aldicarbsulfone	Target Peak	223.075	86.0	16.00		Positive	1.50
Aldicarbsulfone	Confirming	223.075	148.0	12.00	92.96	Positive	1.50
Ametryn	Target Peak	228.128	186.0	19.20		Positive	4.00
Ametryn	Confirming	228.128	96.0	25.93	14.43	Positive	4.00
Anilofos	Target Peak	368.031	198.9	13.99		Positive	7.22
Anilofos	Confirming	368.031	124.9	31.08	77.62	Positive	7.22
Atrazine	Target Peak	216.101	174.0	17.94		Positive	4.35
Atrazine	Confirming	216.101	104.0	28.35	19.82	Positive	4.35

Table A (part 2). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Azinphos-methyl	Target Peak	318.013	132.0	14.45		Positive	5.17
Azinphos-methyl	Confirming	318.013	124.9	18.85	24.20	Positive	5.17
Azoxystrobin	Target Peak	404.124	372.1	14.60		Positive	5.39
Azoxystrobin	Confirming	404.124	344.1	25.12	23.60	Positive	5.39
Benalaxyl	Target Peak	326.088	148.1	20.63		Positive	7.26
Benalaxyl	Confirming	326.088	294.1	10.10	64.44	Positive	7.26
Bensulfuron methyl	Target Peak	411.097	149.1	20.00		Positive	5.17
Bensulfuron methyl	Confirming	411.097	182.0	19.00	59.15	Positive	5.17
Bentazon	Target Peak	239.050	132.0	25.98		Negative	3.34
Bentazon	Confirming	239.050	197.0	19.71	84.53	Negative	3.34
Benzoximate	Target Peak	364.095	199.0	10.25		Positive	7.64
Benzoximate	Confirming	364.095	105.0	24.21	16.16	Positive	7.64
Bifenazate	Target Peak	301.155	198.0	10.25		Positive	6.23
Bifenazate	Confirming	301.155	170.1	19.61	67.06	Positive	6.23
Bifenthrin	Target Peak	440.159	181.1	12.54		Positive	10.62
Bifenthrin	Confirming	440.159	166.0	39.88	39.16	Positive	10.62
Bitertanol	Target Peak	338.186	269.1	10.25		Positive	7.61
Bitertanol	Confirming	338.186	69.9	10.25	46.81	Positive	7.61
Boscalid	Target Peak	343.039	307.0	19.86		Positive	5.70
Boscalid	Confirming	343.039	271.1	32.65	37.96	Positive	5.70
Bromoxynil	Target Peak	275.849	80.8	30.88		Negative	4.28
Bromoxynil	Confirming	275.849	78.8	30.93	81.54	Negative	4.28
Buprofezin	Target Peak	306.163	201.0	12.17		Positive	8.19
Buprofezin	Confirming	306.163	56.8	22.54	21.58	Positive	8.19
Butachlor	Target Peak	312.172	238.1	12.17		Positive	8.71
Butachlor	Confirming	312.172	162.1	21.78	22.15	Positive	8.71
Cadusafos	Target Peak	271.045	158.9	13.42		Positive	7.86
Cadusafos	Confirming	271.045	130.9	21.85	72.88	Positive	7.86
Carbaryl	Target Peak	202.086	145.0	10.25		Positive	3.80
Carbaryl	Confirming	202.086	127.0	28.91	47.21	Positive	3.80
Carbendazim	Target Peak	192.077	159.9	19.06		Positive	1.66
Carbendazim	Confirming	192.077	131.9	30.81	21.75	Positive	1.66
Carbofuran	Target Peak	222.112	165.1	11.82		Positive	3.29
Carbofuran	Confirming	222.112	123.0	21.63	82.53	Positive	3.29
Chlorantraniliprole	Target Peak	481.978	283.9	12.22		Positive	4.90
Chlorantraniliprole	Confirming	481.978	450.8	18.24	96.10	Positive	4.90
Chlorfluazuron	Target Peak	541.967	384.9	20.37		Positive	9.66
Chlorfluazuron	Confirming	541.967	158.0	19.61	29.86	Positive	9.66
Chlormequat	Target Peak	122.073	57.8	26.18		Positive	0.77

Table A (part 3). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Chlormequat	Confirming	122.073	62.8	21.12	38.16	Positive	0.77
Chlorotoluron	Target Peak	213.079	71.9	18.90		Positive	4.33
Chlorotoluron	Confirming	213.079	140.0	24.71	17.93	Positive	4.33
Chlorpyrifos	Target Peak	349.934	197.8	20.82		Positive	9.06
Chlorpyrifos	Confirming	349.934	321.8	12.22	53.74	Positive	9.06
Chlorpyrifos-methyl	Target Peak	321.902	124.9	19.11		Positive	8.00
Chlorpyrifos-methyl	Confirming	321.902	289.8	14.60	91.12	Positive	8.00
Clomazone	Target Peak	240.079	125.0	21.83		Positive	5.11
Clomazone	Confirming	240.079	89.0	47.11	17.66	Positive	5.11
Clothianidin	Target Peak	250.016	169.0	13.29		Positive	1.94
Clothianidin	Confirming	250.016	131.9	17.48	82.28	Positive	1.94
Coumaphos	Target Peak	363.022	306.8	17.63		Positive	7.47
Coumaphos	Confirming	363.022	334.9	16.32	69.85	Positive	7.47
Cyanazine	Target Peak	241.096	214.1	17.28		Positive	2.98
Cyanazine	Confirming	241.096	103.9	29.01	13.21	Positive	2.98
Cyazofamid	Target Peak	325.052	108.0	13.94		Positive	6.61
Cyazofamid	Confirming	325.052	261.1	10.25	31.13	Positive	6.61
Cymoxanil	Target Peak	199.083	128.0	7.70		Positive	2.27
Cymoxanil	Confirming	199.083	110.9	17.68	34.32	Positive	2.27
Cyprodinil	Target Peak	226.134	93.1	34.32		Positive	6.42
Cyprodinil	Confirming	226.134	108.0	25.89	58.00	Positive	6.42
Cyromazine	Target Peak	167.104	67.9	17.89		Positive	1.28
Cyromazine	Confirming	167.104	125.5	32.96	79.95	Positive	1.28
Deltamethrin	Target Peak	522.912	505.8	8.96		Positive	9.74
Deltamethrin	Confirming	522.912	280.8	15.45	84.54	Positive	9.74
Demeton	Target Peak	259.022	89.1	8.16		Positive	5.08
Demeton	Confirming	259.022	61.0	31.75	21.38	Positive	5.08
Desmedipham	Target Peak	301.118	182.0	10.23		Positive	4.85
Desmedipham	Confirming	301.118	108.0	35.21	29.01	Positive	4.85
Diazinon	Target Peak	305.108	169.1	19.70		Positive	7.27
Diazinon	Confirming	305.108	153.1	19.87	51.86	Positive	7.27
Dichlorvos	Target Peak	220.953	108.9	16.63		Positive	3.30
Dichlorvos	Confirming	220.953	144.9	12.20	12.29	Positive	3.30
Diethofencarb	Target Peak	268.154	226.1	10.25		Positive	5.18
Diethofencarb	Confirming	268.154	124.0	31.84	52.51	Positive	5.18
Difenonazole	Target Peak	406.072	251.0	25.78		Positive	7.98
Difenonazole	Confirming	406.072	337.0	17.38	24.95	Positive	7.98
Diflubenzuron	Target Peak	311.039	158.0	14.45		Positive	6.92
Diflubenzuron	Confirming	311.039	141.0	32.45	84.99	Positive	6.92

Table A (part 4). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Dimethenamid	Target Peak	276.082	244.0	14.55		Positive	5.43
Dimethenamid	Confirming	276.082	111.0	32.04	9.56	Positive	5.43
Dimethoate	Target Peak	230.007	198.8	10.25		Positive	2.10
Dimethoate	Confirming	230.007	124.9	21.68	59.54	Positive	2.10
Dimethomorph	Target Peak	388.131	301.0	20.97		Positive	5.90
Dimethomorph	Confirming	388.131	165.0	31.59	41.79	Positive	5.90
Diniconazole	Target Peak	326.082	69.9	26.28		Positive	7.81
Diniconazole	Confirming	326.082	159.0	32.15	12.57	Positive	7.81
Diuron	Target Peak	233.024	72.0	18.44		Positive	4.87
Diuron	Confirming	233.024	159.9	26.79	12.27	Positive	4.87
Edifenphos	Target Peak	310.982	283.0	12.54		Positive	7.24
Edifenphos	Confirming	310.982	111.0	21.22	56.29	Positive	7.24
Epoxiconazole	Target Peak	330.080	121.0	20.97		Positive	6.65
Epoxiconazole	Confirming	330.080	101.0	44.03	45.15	Positive	6.65
Ethion	Target Peak	384.958	198.9	8.83		Positive	8.82
Ethion	Confirming	384.958	142.9	24.12	55.11	Positive	8.82
Ethiprole	Target Peak	396.990	350.9	20.97		Positive	5.46
Ethiprole	Confirming	396.990	254.9	35.23	66.10	Positive	5.46
Ethirimol	Target Peak	210.160	140.1	22.79		Positive	2.39
Ethirimol	Confirming	210.160	98.0	27.44	72.54	Positive	2.39
Ethoprophos	Target Peak	243.014	130.9	20.00		Positive	6.45
Ethoprophos	Confirming	243.014	173.0	14.14	91.79	Positive	6.45
Ethoxyquin	Target Peak	218.154	174.0	29.42		Positive	3.67
Ethoxyquin	Confirming	218.154	160.0	33.87	88.66	Positive	3.67
Etofenprox	Target Peak	394.237	177.2	13.09		Positive	10.51
Etofenprox	Confirming	394.237	359.2	9.89	87.43	Positive	10.51
Etoxazole	Target Peak	360.177	141.0	30.53		Positive	9.31
Etoxazole	Confirming	360.177	304.0	18.24	36.30	Positive	9.31
Fenamiphos	Target Peak	304.113	217.0	23.04		Positive	6.78
Fenamiphos	Confirming	304.113	234.0	17.00	37.94	Positive	6.78
Fenamiphos sulfone	Target Peak	336.053	266.0	18.90		Positive	3.58
Fenamiphos sulfone	Confirming	336.053	308.0	14.06	79.12	Positive	3.58
Fenamiphos sulfoxide	Target Peak	320.058	232.9	23.41		Positive	3.44
Fenamiphos sulfoxide	Confirming	320.058	292.1	14.65	74.28	Positive	3.44
Fenarimol	Target Peak	331.039	268.0	22.94		Positive	6.36
Fenarimol	Confirming	331.039	139.0	35.53	33.20	Positive	6.36
Fenazaquin	Target Peak	307.180	161.1	17.79		Positive	10.30
Fenazaquin	Confirming	307.180	56.8	23.20	78.56	Positive	10.30
Fenbuconazole	Target Peak	337.121	125.0	29.72		Positive	6.75

Table A (part 5). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Fenbuconazole	Confirming	337.121	69.9	20.72	55.19	Positive	6.75
Fenhexamid	Target Peak	302.071	97.0	23.15		Positive	6.18
Fenhexamid	Confirming	302.071	143.0	32.25	13.03	Positive	6.18
Fenobucarb	Target Peak	208.133	95.0	14.80		Positive	5.21
Fenobucarb	Confirming	208.133	152.0	10.25	39.39	Positive	5.21
Fenoxanil	Target Peak	329.082	302.0	10.25		Positive	6.73
Fenoxanil	Confirming	329.082	86.0	21.48	21.10	Positive	6.73
Fenpropathrin	Target Peak	367.152	350.1	7.40		Positive	9.40
Fenpropathrin	Confirming	367.152	125.1	15.70	94.31	Positive	9.40
Fenpyroximate	Target Peak	422.207	366.1	14.90		Positive	9.65
Fenpyroximate	Confirming	422.207	231.1	24.56	7.98	Positive	9.65
Fenthion	Target Peak	279.027	169.0	18.65		Positive	7.31
Fenthion	Confirming	279.027	247.0	13.69	139.83	Positive	7.31
Fenthion-sulfone	Target Peak	310.967	124.9	19.66		Positive	3.93
Fenthion-sulfone	Confirming	310.967	278.9	16.46	76.80	Positive	3.93
Fenthion-sulfoxide	Target Peak	295.022	280.0	19.05		Positive	3.75
Fenthion-sulfoxide	Confirming	295.022	108.9	31.79	46.98	Positive	3.75
Florasulam	Target Peak	360.037	129.0	24.21		Positive	2.49
Florasulam	Confirming	360.037	109.0	55.00	10.11	Positive	2.49
Fluazifop-P-butyl	Target Peak	384.092	282.1	19.41		Positive	8.45
Fluazifop-P-butyl	Confirming	384.092	254.0	28.67	24.74	Positive	8.45
Fluazinam	Target Peak	462.944	415.9	18.90		Negative	8.71
Fluazinam	Confirming	462.944	398.0	15.16	61.11	Negative	8.71
Flubendiamide	Target Peak	683.031	408.0	10.25		Positive	7.02
Flubendiamide	Confirming	683.031	273.9	29.47	56.89	Positive	7.02
Flufenoxuron	Target Peak	489.044	158.0	18.54		Positive	9.33
Flufenoxuron	Confirming	489.044	141.0	42.51	82.72	Positive	9.33
Flumetsulam	Target Peak	326.052	129.0	25.88		Positive	1.92
Flumetsulam	Confirming	326.052	262.1	18.85	10.48	Positive	1.92
Fluopicolide	Target Peak	382.973	172.9	24.21		Positive	5.79
Fluopicolide	Confirming	382.973	144.9	47.62	40.51	Positive	5.79
Fluquinconazole	Target Peak	376.016	348.9	18.44		Positive	6.27
Fluquinconazole	Confirming	376.016	306.9	27.11	57.25	Positive	6.27
Flusilazole	Target Peak	316.108	247.1	17.79		Positive	6.89
Flusilazole	Confirming	316.108	165.1	27.54	70.27	Positive	6.89
Flutolanil	Target Peak	324.071	242.0	24.67		Positive	5.80
Flutolanil	Confirming	324.071	262.0	17.43	98.98	Positive	5.80
Flutriafol	Target Peak	302.109	69.9	19.66		Positive	4.34
Flutriafol	Confirming	302.109	123.0	28.46	66.95	Positive	4.34

Table A (part 6). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Fluvalinate	Target Peak	503.134	181.1	24.63		Positive	10.17
Fluvalinate	Confirming	503.134	208.0	10.94	90.51	Positive	10.17
Fonofos	Target Peak	247.037	108.9	17.76		Positive	7.31
Fonofos	Confirming	247.037	137.0	10.31	97.34	Positive	7.31
Forchlorfenuron	Target Peak	248.059	128.9	17.63		Positive	4.79
Forchlorfenuron	Confirming	248.059	93.0	32.15	38.43	Positive	4.79
Fosthiazate	Target Peak	284.054	228.0	10.25		Positive	3.97
Fosthiazate	Confirming	284.054	104.0	21.83	73.50	Positive	3.97
Haloxyfop	Target Peak	362.040	316.0	17.58		Positive	7.00
Haloxyfop	Confirming	362.040	288.0	26.69	25.16	Positive	7.00
Haloxyfop-methyl	Target Peak	376.056	316.0	17.53		Positive	7.87
Haloxyfop-methyl	Confirming	376.056	91.0	31.19	25.37	Positive	7.87
Hexaconazole	Target Peak	314.082	69.9	21.33		Positive	7.43
Hexaconazole	Confirming	314.082	159.0	31.74	24.75	Positive	7.43
Hexaflumuron	Target Peak	458.974	438.9	10.25		Negative	8.33
Hexaflumuron	Confirming	458.974	175.0	34.12	13.14	Negative	8.33
Hexazinone	Target Peak	253.166	171.1	16.42		Positive	3.52
Hexazinone	Confirming	253.166	71.0	30.68	16.02	Positive	3.52
Hexythiazox	Target Peak	353.109	228.0	15.31		Positive	9.01
Hexythiazox	Confirming	353.109	168.0	25.27	56.91	Positive	9.01
Imazalil	Target Peak	297.056	159.0	24.16		Positive	4.16
Imazalil	Confirming	297.056	255.0	18.24	58.04	Positive	4.16
Imazaquin	Target Peak	312.134	267.1	21.22		Positive	3.43
Imazaquin	Confirming	312.134	199.0	28.61	89.76	Positive	3.43
Imazethapyr	Target Peak	290.149	177.0	27.29		Positive	2.87
Imazethapyr	Confirming	290.149	230.1	24.01	87.11	Positive	2.87
Imibenconazole	Target Peak	410.999	125.0	30.07		Positive	8.82
Imibenconazole	Confirming	410.999	171.0	19.25	25.61	Positive	8.82
Imidacloprid	Target Peak	256.060	209.0	16.78		Positive	1.90
Imidacloprid	Confirming	256.060	175.1	19.35	76.34	Positive	1.90
Indoxacarb	Target Peak	528.078	249.0	16.02		Positive	8.00
Indoxacarb	Confirming	528.078	293.0	13.79	94.58	Positive	8.00
Isazofos	Target Peak	314.048	120.0	10 00		Positive	6.08
Isazofos	Confirming	314.048	162.0	30.00	22.86	Positive	6.08
Isofenphos-methyl	Target Peak	332.107	230.9	13.00		Positive	6.96
Isofenphos-methyl	Confirming	332.107	273.0	5.25	55.38	Positive	6.96
Isoprocarb	Target Peak	194.118	95.0	15.46		Positive	4.28
Isoprocarb	Confirming	194.118	137.1	10.25	39.31	Positive	4.28
Isoprothiolane	Target Peak	291.072	231.0	10.25		Positive	5.88

Table A (part 7). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Isoprothiolane	Confirming	291.072	188.8	21.22	83.67	Positive	5.88
Isoproturon	Target Peak	207.149	72.0	18.44		Positive	4.59
Isoproturon	Confirming	207.149	165.1	14.25	39.35	Positive	4.59
Kresoxim-methyl	Target Peak	314.139	222.1	14.40		Positive	6.95
Kresoxim-methyl	Confirming	314.139	267.1	10.25	78.25	Positive	6.95
Linuron	Target Peak	249.019	182.0	14.94		Positive	5.57
Linuron	Confirming	249.019	159.9	17.38	97.07	Positive	5.57
Malaoxon	Target Peak	315.066	99.0	22.74		Positive	3.35
Malaoxon	Confirming	315.066	269.0	10.25	14.54	Positive	3.35
Malathion	Target Peak	330.956	127.0	11.91		Positive	5.81
Malathion	Confirming	330.956	285.0	7.15	97.72	Positive	5.81
Mandipropamid	Target Peak	412.131	328.1	15.06		Positive	5.76
Mandipropamid	Confirming	412.131	356.1	10.25	46.93	Positive	5.76
Mefenacet	Target Peak	299.085	148.0	14.55		Positive	6.21
Mefenacet	Confirming	299.085	120.0	24.97	65.02	Positive	6.21
Mepronil	Target Peak	270.149	119.0	23.90		Positive	5.84
Mepronil	Confirming	270.149	228.1	15.41	99.27	Positive	5.84
Metalaxyl	Target Peak	280.104	220.1	13.21		Positive	4.46
Metalaxyl	Confirming	280.104	248.1	9.93	48.36	Positive	4.46
Metazachlor	Target Peak	278.105	134.0	22.69		Positive	4.43
Metazachlor	Confirming	278.105	210.0	10.25	44.20	Positive	4.43
Methamidophos	Target Peak	141.962	94.0	14.30		Positive	1.27
Methamidophos	Confirming	141.962	124.9	14.30	48.09	Positive	1.27
Methidathion	Target Peak	302.969	145.0	8.16		Positive	4.85
Methidathion	Confirming	302.969	85.1	19.57	36.58	Positive	4.85
Methiocarb	Target Peak	226.090	107.0	16.22		Positive	3.85
Methiocarb	Confirming	226.090	169.0	10.25	7.77	Positive	3.85
Methomyl	Target Peak	163.054	88.0	10.25		Positive	1.63
Methomyl	Confirming	163.054	106.0	10.25	93.73	Positive	1.63
Methoxyfenozide	Target Peak	369.217	149.0	17.48		Positive	5.99
Methoxyfenozide	Confirming	369.217	313.1	10.25	75.79	Positive	5.99
Metolachlor	Target Peak	284.141	252.1	15.21		Positive	6.53
Metolachlor	Confirming	284.141	176.1	25.93	31.78	Positive	6.53
Metribuzin	Target Peak	215.096	187.1	17.51		Positive	3.27
Metribuzin	Confirming	215.096	131.0	20.71	15.95	Positive	3.27
Metsulfuron-methyl	Target Peak	382.082	167.0	16.00		Positive	3.46
Metsulfuron-methyl	Confirming	382.082	199.0	20.00	10.40	Positive	3.46
Molinate	Target Peak	188.110	126.1	12.54		Positive	6.03
Molinate	Confirming	188.110	98.1	17.30	18.23	Positive	6.03

Table A (part 8). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Monocrotophos	Target Peak	224.068	127.0	16.17		Positive	1.67
Monocrotophos	Confirming	224.068	193.0	10.25	88.10	Positive	1.67
Myclobutanil	Target Peak	289.084	70.0	18.94		Positive	6.04
Myclobutanil	Confirming	289.084	125.0	31.41	62.95	Positive	6.04
Omethoate	Target Peak	214.029	182.9	10.25		Positive	1.43
Omethoate	Confirming	214.029	124.9	21.78	96.19	Positive	1.43
Oxadiazon	Target Peak	345.027	303.0	12.03		Positive	8.68
Oxadiazon	Confirming	345.027	219.8	18.90	74.02	Positive	8.68
Oxadixyl	Target Peak	279.134	219.1	10.25		Positive	2.81
Oxadixyl	Confirming	279.134	132.0	31.79	31.39	Positive	2.81
Oxamyl	Target Peak	237.102	71.9	10.25		Positive	1.51
Oxamyl	Confirming	237.102	90.0	10.25	46.99	Positive	1.51
Paclobutrazol	Target Peak	294.137	69.9	21.43		Positive	5.74
Paclobutrazol	Confirming	294.137	125.0	37.81	20.93	Positive	5.74
Paraoxon-ethyl	Target Peak	276.026	219.9	14.22		Positive	4.33
Paraoxon-ethyl	Confirming	276.026	248.0	9.42	26.09	Positive	4.33
Paraoxon-methyl	Target Peak	265.058	236.9	14.52		Positive	2.55
Paraoxon-methyl	Confirming	265.058	218.9	21.34	29.91	Positive	2.55
Penconazole	Target Peak	284.072	159.0	30.28		Positive	7.20
Penconazole	Confirming	284.072	69.9	17.48	89.51	Positive	7.20
Permethrin	Target Peak	408.113	183.1	19.11		Positive	10.41
Permethrin	Confirming	408.113	355.1	8.24	56.46	Positive	10.41
Phenmedipham	Target Peak	301.118	136.0	19.91		Positive	5.02
Phenmedipham	Confirming	301.118	168.1	10.25	89.07	Positive	5.02
Phenthoate	Target Peak	321.038	247.0	10.25		Positive	6.96
Phenthoate	Confirming	321.038	135.0	19.61	40.21	Positive	6.96
Phorate	Target Peak	260.983	124.9	17.47		Positive	5.17
Phorate	Confirming	260.983	167.0	13.93	58.74	Positive	5.17
Phorate sulfone	Target Peak	293.009	171.1	10.14		Positive	4.26
Phorate sulfone	Confirming	293.009	143.1	0.00	35.25	Positive	4.26
Phosalone	Target Peak	367.994	182.0	13.72		Positive	7.63
Phosalone	Confirming	367.994	321.9	8.41	34.83	Positive	7.63
Phosmet	Target Peak	317.952	160.0	12.33		Positive	5.22
Phosmet	Confirming	317.952	133.0	35.12	20.35	Positive	5.22
Phosphamidon	Target Peak	300.038	127.0	21.34		Positive	2.81
Phosphamidon	Confirming	300.038	226.9	12.83	60.72	Positive	2.81
Phoxim	Target Peak	299.061	129.0	10.25		Positive	7.58
Phoxim	Confirming	299.061	77.0	29.82	83.49	Positive	7.58
Piperonyl butoxide	Target Peak	356.193	177.1	11.32		Positive	8.69

Table A (part 9). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Piperonyl butoxide	Confirming	356.193	119.1	32.80	23.76	Positive	8.69
Pirimicarb	Target Peak	239.150	182.1	16.07		Positive	2.32
Pirimicarb	Confirming	239.150	72.0	21.07	39.25	Positive	2.32
Pirimiphos-methyl	Target Peak	306.104	164.1	22.44		Positive	7.21
Pirimiphos-methyl	Confirming	306.104	108.0	30.58	79.95	Positive	7.21
Pretilachlor	Target Peak	312.122	252.1	15.15		Positive	8.12
Pretilachlor	Confirming	312.122	176.1	27.28	22.16	Positive	8.12
Prochloraz	Target Peak	376.038	307.9	11.97		Positive	7.32
Prochloraz	Confirming	376.038	265.9	17.28	12.63	Positive	7.32
Profenofos	Target Peak	374.942	304.8	18.49		Positive	8.43
Profenofos	Confirming	374.942	346.8	13.13	50.22	Positive	8.43
Propamocarb	Target Peak	189.159	102.0	17.33		Positive	1.44
Propamocarb	Confirming	189.159	144.1	13.39	32.87	Positive	1.44
Propanil	Target Peak	218.013	162.0	18.00		Positive	5.57
Propanil	Confirming	218.013	127.0	20.00	81.07	Positive	5.57
Propargite	Target Peak	368.102	231.2	9.47		Positive	9.21
Propargite	Confirming	368.102	175.1	14.73	51.80	Positive	9.21
Propiconazol	Target Peak	342.077	158.9	28.04		Positive	7.36
Propiconazol	Confirming	342.077	204.9	17.13	13.57	Positive	7.36
Pymetrozine	Target Peak	218.104	105.0	20.47		Positive	1.37
Pymetrozine	Confirming	218.104	78.0	39.38	9.29	Positive	1.37
Pymetrozine	Confirming	218.104	79.0	40.49	0.00	Positive	1.37
Pyraclostrobin	Target Peak	388.106	194.0	12.12		Positive	7.59
Pyraclostrobin	Confirming	388.106	163.0	23.96	58.46	Positive	7.59
Pyridaben	Target Peak	365.108	309.1	11.49		Positive	9.90
Pyridaben	Confirming	365.108	147.1	24.04	77.38	Positive	9.90
Pyrimethanil	Target Peak	200.118	107.0	24.92		Positive	4.89
Pyrimethanil	Confirming	200.118	168.0	30.63	43.91	Positive	4.89
Pyriproxyfen	Target Peak	322.106	96.0	15.78		Positive	8.91
Pyriproxyfen	Confirming	322.106	227.1	13.93	37.34	Positive	8.91
Quinalphos	Target Peak	299.011	163.0	20.16		Positive	7.08
Quinalphos	Confirming	299.011	119.0	40.55	78.3	Positive	7.08
Quinoxyfen	Target Peak	308.004	196.9	32.85		Positive	9.25
Quinoxyfen	Confirming	308.004	162.0	44.74	77.29	Positive	9.25
Quizalofop-ethyl	Target Peak	373.095	299.0	18.60		Positive	8.41
Quizalofop-ethyl	Confirming	373.095	271.0	25.52	14.99	Positive	8.41
Rimsulfuron	Target Peak	432.064	182.0	21.00		Positive	3.98
Rimsulfuron	Confirming	432.064	325.0	16.00	82.52	Positive	3.98
Rotenone	Target Peak	395.149	213.0	23.15		Positive	6.82

Table A (part 10). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Rotenone	Confirming	395.149	192.0	23.96	62.84	Positive	6.82
Sethoxydim	Target Peak	328.194	178.0	19.20		Positive	8.49
Sethoxydim	Confirming	328.194	282.1	11.82	92.52	Positive	8.49
Simazine	Target Peak	202.085	124.1	17.76		Positive	3.42
Simazine	Confirming	202.085	103.9	24.59	69.88	Positive	3.42
Simetryn	Target Peak	214.112	124.0	19.56		Positive	3.17
Simetryn	Confirming	214.112	96.0	23.80	56.68	Positive	3.17
Sulfotep	Target Peak	323.030	171.0	14.50		Positive	7.05
Sulfotep	Confirming	323.030	114.8	29.31	70.86	Positive	7.05
Tebuconazole	Target Peak	308.152	69.9	23.04		Positive	7.15
Tebuconazole	Confirming	308.152	125.0	37.46	21.50	Positive	7.15
Tebufenozide	Target Peak	353.222	133.0	19.66		Positive	6.88
Tebufenozide	Confirming	353.222	297.1	10.25	86.38	Positive	6.88
Teflubenzuron	Target Peak	378.967	338.9	10.23		Negative	8.93
Teflubenzuron	Confirming	378.967	358.9	7.00	27.37	Negative	8.93
Terbuthylazine	Target Peak	230.117	174.0	17.18		Positive	5.60
Terbuthylazine	Confirming	230.117	132.0	25.32	9.65	Positive	5.60
Thiabendazole	Target Peak	202.043	175.0	25.02		Positive	1.89
Thiabendazole	Confirming	202.043	131.0	32.80	71.31	Positive	1.89
Thiacloprid	Target Peak	253.031	126.0	21.33		Positive	2.47
Thiacloprid	Confirming	253.031	99.0	41.30	12.79	Positive	2.47
Thiamethoxam	Target Peak	292.027	211.0	10.25		Positive	1.67
Thiamethoxam	Confirming	292.027	131.9	22.59	33.32	Positive	1.67
Thidiazuron	Target Peak	221.049	102.0	15.56		Positive	3.46
Thidiazuron	Confirming	221.049	127.9	16.27	19.74	Positive	3.46
Thiobencarb	Target Peak	258.071	124.9	20.16		Positive	7.74
Thiobencarb	Confirming	258.071	89.0	48.78	17.64	Positive	7.74
Thiodicarb	Target Peak	355.018	88.1	14.69		Positive	4.26
Thiodicarb	Confirming	355.018	107.9	14.18	55.08	Positive	4.26
Thiophanate-methyl	Target Peak	343.053	151.0	20.87		Positive	3.18
Thiophanate-methyl	Confirming	343.053	311.0	10.25	29.65	Positive	3.18
Tolclofos-methyl	Target Peak	300.961	125.0	10.00		Positive	7.76
Tolclofos-methyl	Confirming	300.961	175.0	12.50	95.23	Positive	7.76
Tolfenpyrad	Target Peak	384.147	197.0	25.83		Positive	8.77
Tolfenpyrad	Confirming	384.147	154.1	42.41	28.22	Positive	8.77
Tolylfluanid	Target Peak	363.962	237.9	13.42		Positive	7.27
Tolylfluanid	Confirming	363.962	137.0	28.17	25.68	Positive	7.27
Triadimefon	Target Peak	294.100	197.0	15.56		Positive	5.95
Triadimefon	Confirming	294.100	141.0	22.34	15.79	Positive	5.95

Table A (part 11). Detailed SRM transitions

Compound name	Workflow	Precursor *m/z*	Product *m/z*	Collision energy	Target ratio	Peak polarity	Retention time (min)
Triadimenol	Target Peak	296.116	70.1	55.00		Positive	6.10
Triadimenol	Confirming	296.116	227.0	0.00	7.90	Positive	6.10
Triazophos	Target Peak	314.072	162.1	18.65		Positive	6.27
Triazophos	Confirming	314.072	119.0	33.61	25.86	Positive	6.27
Trichlorphon	Target Peak	256.930	108.9	17.84		Positive	2.03
Trichlorphon	Confirming	256.930	220.9	10.25	60.83	Positive	2.03
Tricyclazole	Target Peak	190.043	163.0	22.24		Positive	2.93
Tricyclazole	Confirming	190.043	136.0	28.46	92.61	Positive	2.93
Trifloxystrobin	Target Peak	409.137	186.0	17.69		Positive	8.00
Trifloxystrobin	Confirming	409.137	145.0	43.22	52.59	Positive	8.00
Triflumizole	Target Peak	346.093	278.0	10.25		Positive	8.12
Triflumizole	Confirming	346.093	73.0	16.47	6.16	Positive	8.12
Vamidothion	Target Peak	288.049	146.0	12.48		Positive	1.98
Vamidothion	Confirming	288.049	118.0	22.84	34.34	Positive	1.98
Zoxamide	Target Peak	336.032	186.9	22.79		Positive	7.29
Zoxamide	Confirming	336.032	159.0	39.73	46.33	Positive	7.29