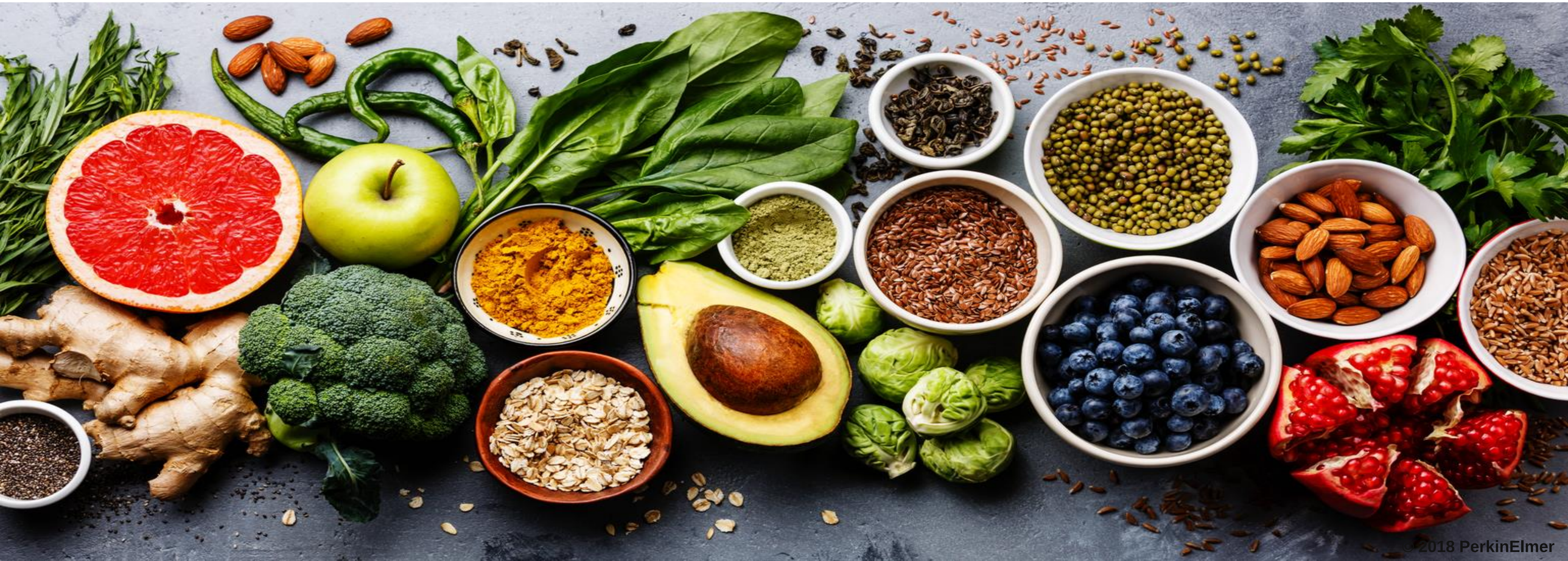
Analyse de contaminants organiques dans des matrices alimentaires complexes par la technologie QSight LC/MS/MS

Christophe CLARYSSE : SME Chromatography & Mass Spec Solutions EMEAI

CECM Atelier du 26 Mars 2021



Agenda

- Pesticide Analysis
- Overview of pesticide workflow
  - Sample to result
- QSight flow-based mass spectrometry
- Selected applications
- Conclusions

Pesticides in foods and their regulation

- Regulation (EC) 396/2005
  - maximum residue limits (MRLs) are generally set at 0.01 mg/kg (with range from 0.001 – 100 mg/kg)

- SANTE 12682/2019
  - guidance document
  - performance requirements for analytical methods

Parameter	What/how	Criterion	Cross reference to AQC document
Sensitivity/linearity	Linearity check from five levels	Deviation of back-calculated concentration from true concentration ≤± 20 %	C14-C19
Matrix effect	Comparison of response from solvent standards and matrix-matched standards	*	C21-C29
LOQ	Lowest spike level meeting the identification and method performance criteria for recovery and precision	≤ MRL	G6[8]
Specificity	Response in reagent blank and blank control samples	≤ 30 % of RL	C41
Recovery	Average recovery for each spike level tested	70-120 %	G3,G6
Precision (RSD_r)	Repeatability RSD_r for each spike level tested	≤ 20 %	G3, G6
Precision (RSD_{wR})	Within-laboratory reproducibility, derived from on-going method validation/verification	≤ 20 %	G3, G6
Robustness	Average recovery and RSD_{wR}, derived from on-going method validation/verification	See above	G6, C39-C44
Ion ratio	Check compliance with identification requirements for MS techniques	Table 3	Section D
Retention time		± 0.1 min.	D2

Challenges in multi-residue pesticide analysis in foods

European Commission

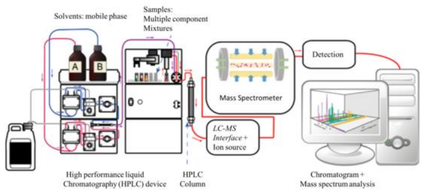
efsa
European Food Safety Authority

Changing legislation

Variety of pesticides

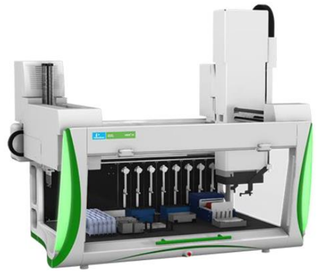
Multitude of food matrixes

Instrument performance



PerkinElmer

Analytical workflows by LC-MS/MS



QSight LC-MS/MS

Columns

Simplicity 3Q

QuEChERS Kits

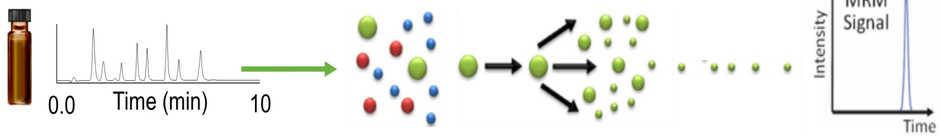
Filters

Vials

Sample preparation

LC-MS/MS

Data analysis & reporting



PerkinElmer

QuEChERS method is a simple two step procedure …Quick Easy Cheap Effective Rugged Safe – Step 1: Extraction




Step 1: Extraction

Homogenize sample and place10 g in a 50 mL tube → Add 10 mL acetonitrile and mix → Add internal standard(s) → Add prepared sample to an extraction reagent tube → Shake → Centrifuge

Extraction Kits

Method	Vol.	Qty.	MgSO4	Na Acetate	Na Citrate	Na Citrate Sesquihydrate	NaCL	Part No.
AOAC 2007.01	50 mL	50	6 g	1.5 g				N9306900
EN 15662	50 mL	50	4 g		1 g	0.5 g	1 g	N9306901
Original	50 mL	50	4 g				1 g	N9306902

QuEChERS method is a simple two step procedure …Quick Easy Cheap Effective Rugged Safe – Step 2: Clean-up

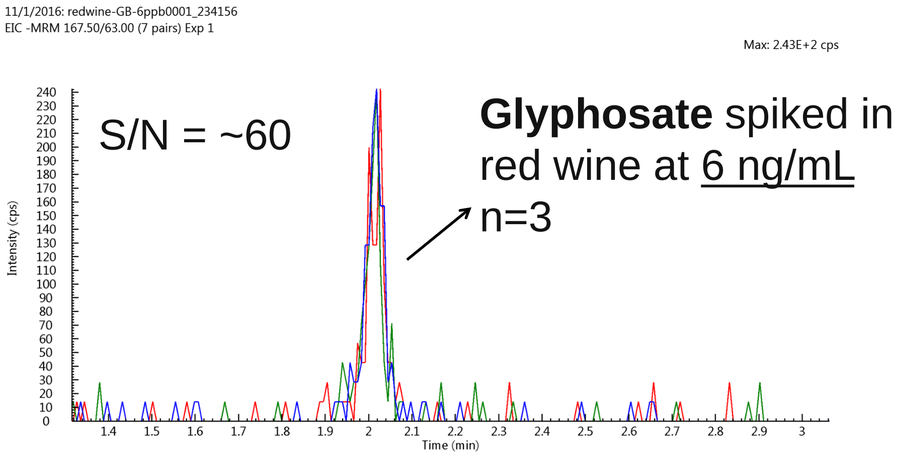
Step 2: Clean-Up

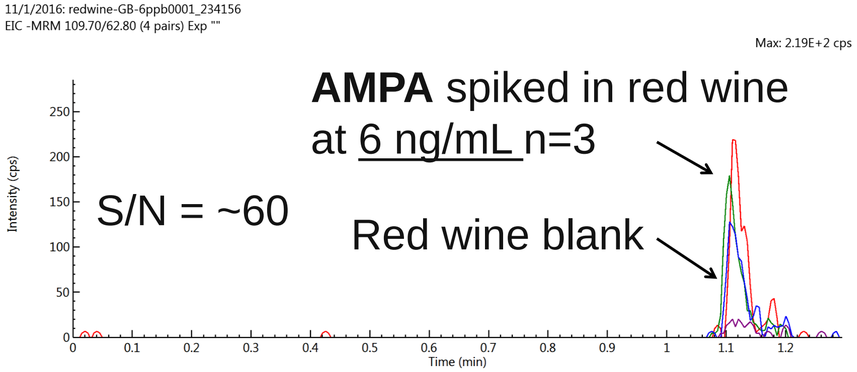
Transfer an aliquot of the supernatant to a clean-up tube → Shake → Centrifuge → Test supernatant directly by GC, GC/MS, LC, LC/MS

EN 15662 Clean-up Kits

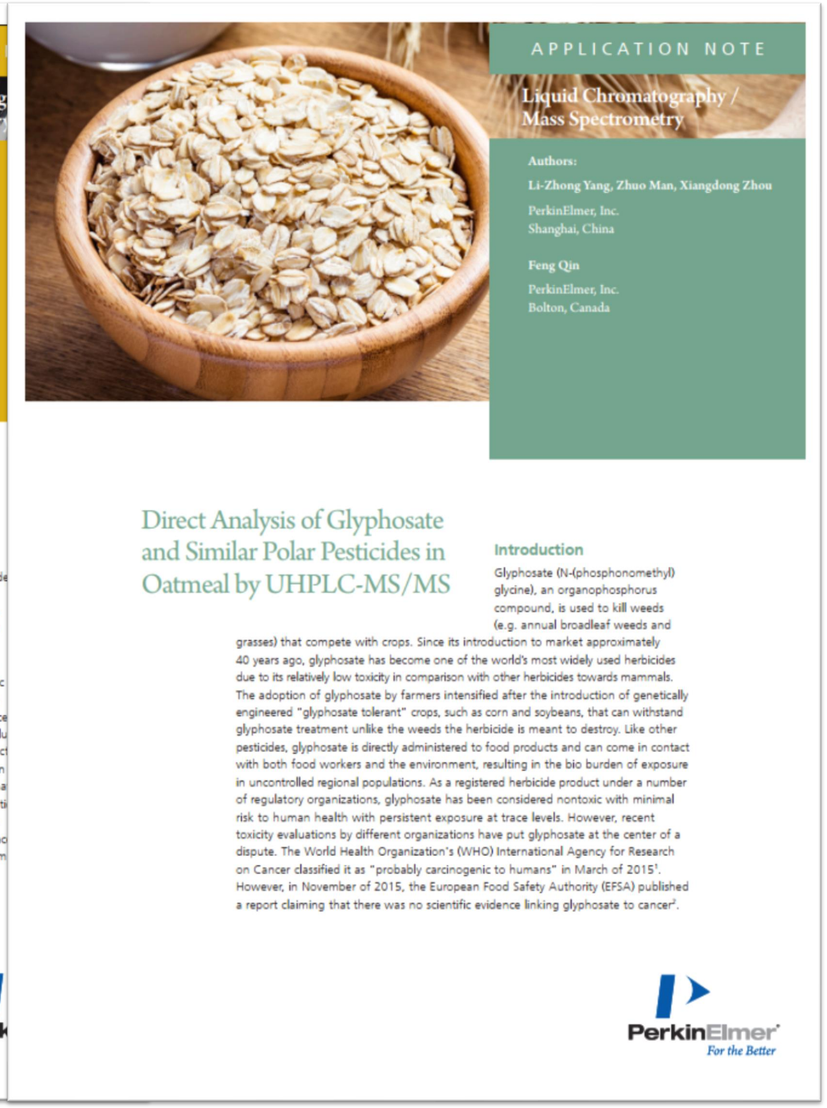
Description	Vol.	Qty.	MgSO4[1]	PSA[2]	C18[3]	PGC[4]	Part No.
Fruit & Vegetables	2 mL	100	150 mg	25 mg			N9306920
Fruit & Vegetables	15 mL	50	900 mg	150 mg			N9306921
Fruit & Vegetables with Fats and Waxes	2 mL	100	150 mg	25 mg	25 mg		N9306922
Waxed Fruit & Vegetables	15 mL	50	900 mg	150 mg	150 mg		N9306923
Pigmented Fruit & Vegetables	15 mL	50	900 mg	150 mg		15 mg	N9306924
Pigmented Fruit & Vegetables	2 mL	100	150 mg	25 mg		2.5 mg	N9306925
High Pigmented Fruit & Vegetables	2 mL	100	150 mg	25 mg		7.5 mg	N9306926
High Pigmented Fruit & Vegetables	15 mL	50	900 mg	150 mg		45 mg	N9306927

Special case: polar pesticides – Glyphosate, AMPA and others



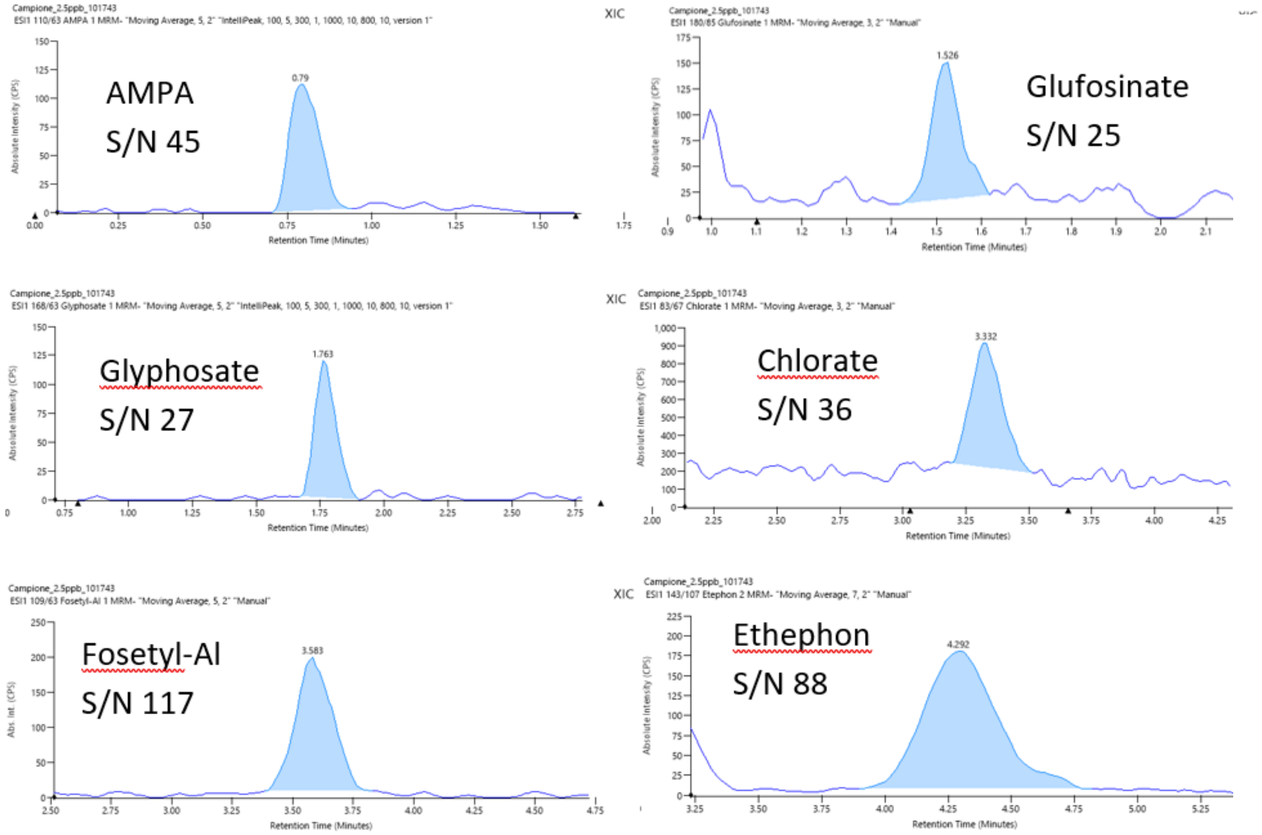


No sample preparation



Special case: polar pesticides – Glyphosate, AMPA and others

2.5 ppb in vegetable extract

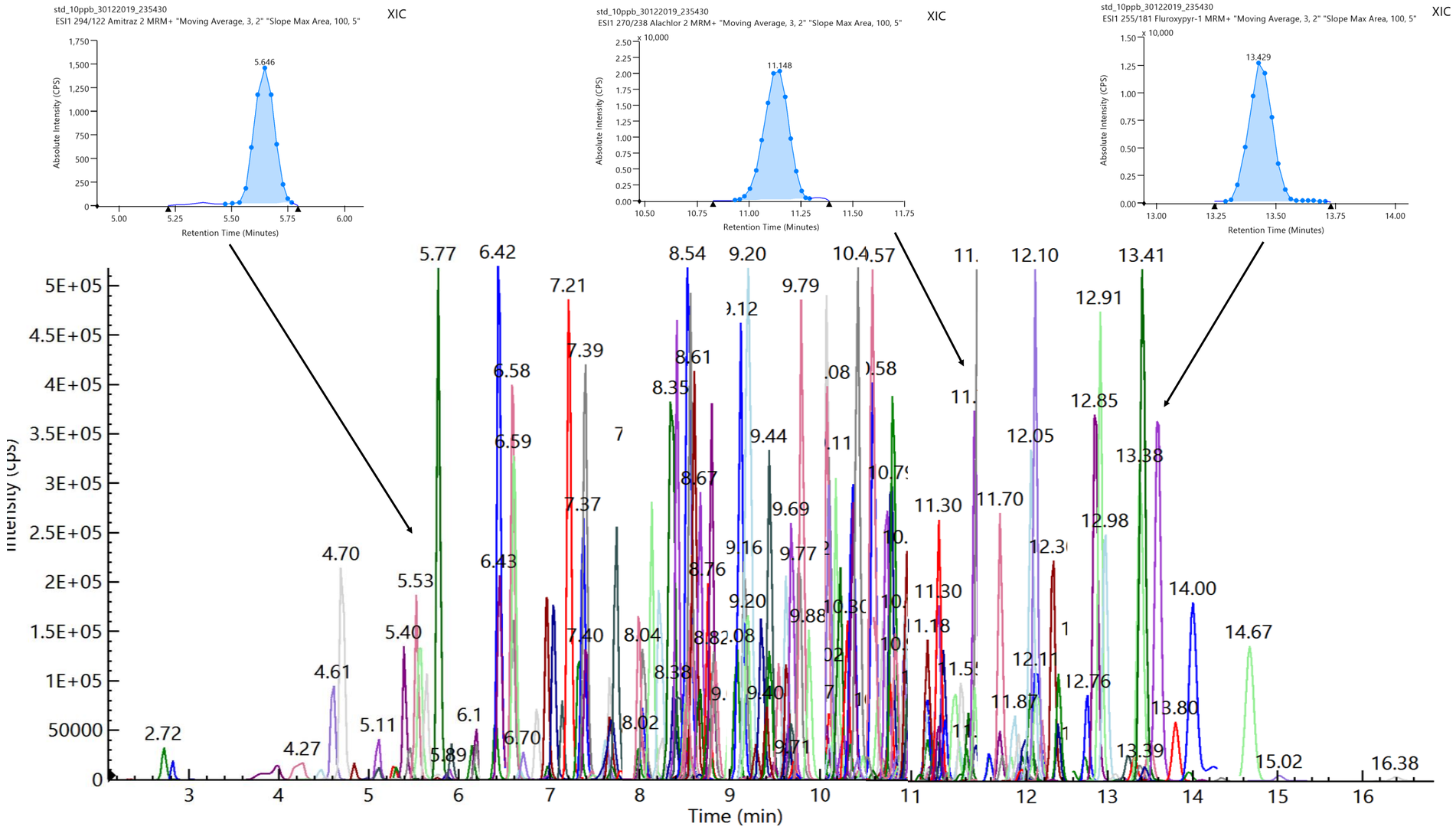


Method	Analyte	Commodity Group	Matrix	Spiking Level (mg/kg)	n	Mean Recov. %	RSD
M 1.3	AMPA	High water content + acidic	Grapes	0.02	12	110	9
	AMPA	Dry (cereals)	Barley	0.02	5	101	14
	AMPA	Dry (pulses)*	Lentil	0.1	10	95	17
	AMPA	Dry (cereals)	Wheat flour	0.1	5	119	6
	AMPA	High water content	Apple	0.02	17	100	12
	Cyanuric Acid	High water content	Cucumber	0.02	3	106	13
	Ethephon	Dry (cereals)	Barley	0.02	5	110	2
	Ethephon	Dry (cereals)	Wheat flour	0.1	5	85	6
	Ethephon	High water content	Apple	0.02	7	105	11
	Ethephon	High water content	Cucumber	0.02	3	101	11
	Ethephon	High water content + acidic	Grapes	0.01	5	104	4
	Fosetyl	High water content + acidic	Strawberry	0.1	6	94	4
	Fosetyl	Dry (cereals)	Barley	0.02	5	106	7
	Fosetyl	High water content	Apple	0.02	7	104	5
	Fosetyl	High water content	Cucumber	0.02	3	103	5
	Fosetyl	High water content + acidic	Grapes	0.01	5	105	2
	Glufosinate	High water content + acidic	Grapes	0.05	5	96	10
	Glufosinate	Dry (cereals)	Barley	0.02	5	101	13
	Glufosinate	Dry (cereals)	Wheat flour	0.1	5	85	5
	Glufosinate	High water content	Apple	0.02	7	106	8
	Glufosinate	High water content	Cucumber	0.02	3	115	4
	Glyphosate	High water content + acidic	Grapes	0.02	12	112	8
	Glyphosate	High water content + acidic	Grapes	0.02	5	102	6
	Glyphosate	Dry (cereals)	Barley	0.02	5	105	8
	Glyphosate	Dry (pulses)*	Lentil	0.1	11	107	18
	Glyphosate	High oil content, dry (oily seeds, nuts)*	Bean, Soya	0.1	10	95	10
	Glyphosate	High water content	Apple	0.02	16	93	12
	Glyphosate	High water content	Cucumber	0.02	3	94	3

QuPPe Method 1.3: EURL acidified methanol

https://www.eurl-pesticides.eu/userfiles/file/EurlSRM/meth_QuPPe_PO_V11_1.pdf

Chromatographic separation



Time-managed multiple reaction monitoring (MRM) library, dwell time optimization and automated MS method creation

1: Experiment 1
2: Experiment 2
3: Experiment 3
4: Experiment 4
5: Experiment 5
6: Experiment 6
7: Experiment 7
8: Experiment 8
9: Experiment 9
10: Experiment 10
11: Experiment 11
12: Experiment 12
13: Experiment 13
14: Experiment 14
15: Experiment 15
16: Experiment 16
17: Experiment 17
18: Experiment 18
19: Experiment 19
20: Experiment 20
21: Experiment 21
22: Experiment 22
23: Experiment 23
24: Experiment 24
25: Experiment 25
26: Experiment 26
27: Experiment 27
28: Experiment 28
29: Experiment 29
30: Experiment 30
31: Experiment 31
32: Experiment 32
33: Experiment 33
34: Experiment 34
35: Experiment 35
36: Experiment 36
37: Experiment 37
38: Experiment 38
39: Experiment 39
40: Experiment 40
41: Experiment 41
42: Experiment 42
43: Experiment 43
44: Experiment 44
45: Experiment 45
46: Experiment 46
47: Experiment 47
48: Experiment 48
49: Experiment 49
50: Experiment 50
51: Experiment 51
52: Experiment 52
53: Experiment 53

Time Managed MRM

Current Catalog: System : Pesticides

New | Load | System : Pesticides | *Enter a compound catalog name* | Save As: | Delete

Selected	Name	Adduct	Q1 Mass	Polarity	RT	ΔRT	Fragment 1 Q2 Mass	CE1	EV1	CCL2-1	Fragment 2 Q2 Mass	CE2	EV2	CCL2-2	Fragment 3 Q2 Mass	CE3	EV3	CCL2-3	Fragment 4 Q2 Mass	CE4
☑	3-hydroxycarbofuran	+H	238.1	+	7.075	0.5	163	-23	25	-45	181	-19	25	-41	220	-13	25	-36		
☑	acephate	+H	184.1	+	1.716	0.8	143	-12	25	-29	125	-25	25	-41	95	-30	25	-45		
☑	acetamiprid	+H	223.2	+	8	0.5	126.1	-30	25	-49	99.1	-56	25	-73						
☑	carbaryl (sevin)	+H	202.1	+	10.15	0.5	145	-38	25	-54	127	-42	25	-58	130	-55	25	-70		
☑	carbofuran	+H	222.2	+	9.842	0.5	165.2	-16	25	-37	123.1	-28	25	-47						
☑	chlorantraniliprole	+H	484	+	12.329	0.5	452.8	-20	25	-66	285.8	-18	25	-65						
☑	clothianidin	+H	250	+	6.529	0.5	169.1	-16	25	-39	132	-26	25	-48						
☑	cyromazine	+H	167.2	+	2.052	0.8	68	-30	25	-44	85	-30	25	-44	108	-29	25	-43		
☑	diflubenzuron	+H	311	+	13.456	0.5	158.2	-20	25	-49	141.2	-48	25	-74	227	-8	25	-38		
☑	dinotefuran	+H	203.1	+	3.033	0.7	114.1	-20	25	-38	129	-16	25	-35						
☑	imazalil	+H	297.1	+	14.087	0.7	159.2	-31	25	-58	201	-25	25	-52	255.1	-25	25	-52	161.2	-31
☑	imidacloprid	+H	256.2	+	7.411	0.5	209	-18	25	-42	175.2	-26	25	-49						
☑	methamidophos	+H	142	+	1.331	0.5	94	-20	25	-32	112	-20	25	-32	124.9	-20	25	-32		

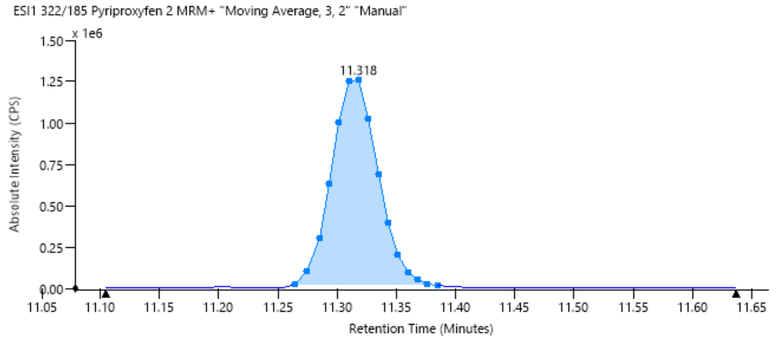
Synonyms

Transfer To Timed MRM

Anticipated Cycle Time (sec): 0.8

Polarity	Name	Q1 Mass	Q2 Mass	Expected RT (min)	Delta RT (min)
Positive	3-hydroxycarbofuran-1	238.1	163	7.075	0.5
Positive	3-hydroxycarbofuran-2	238.1	181	7.075	0.5
Positive	3-hydroxycarbofuran-3	238.1	220	7.075	0.5
Positive	acephate-1	184.1	143	1.716	0.8
Positive	acephate-2	184.1	125	1.716	0.8
Positive	acephate-3	184.1	95	1.716	0.8
Positive	acetamiprid-1	223.2	126.1	8	0.5
Positive	acetamiprid-2	223.2	99.1	8	0.5
Positive	carbaryl (sevin)-1	202.1	145	10.15	0.5
Positive	carbaryl (sevin)-2	202.1	127	10.15	0.5
Positive	carbaryl (sevin)-3	202.1	130	10.15	0.5
Positive	carbofuran-1	222.2	165.2	9.842	0.5
Positive	carbofuran-2	222.2	123.1	9.842	0.5
Positive	chlorantraniliprole-1	484	452.8	12.329	0.5
Positive	chlorantraniliprole-2	484	285.8	12.329	0.5
Positive	clothianidin-1	250	169.1	6.529	0.5
Positive	clothianidin-2	250	132	6.529	0.5
Positive	cyromazine-1	167.2	68	2.052	0.8

Apply | Cancel



Dwell time optimization

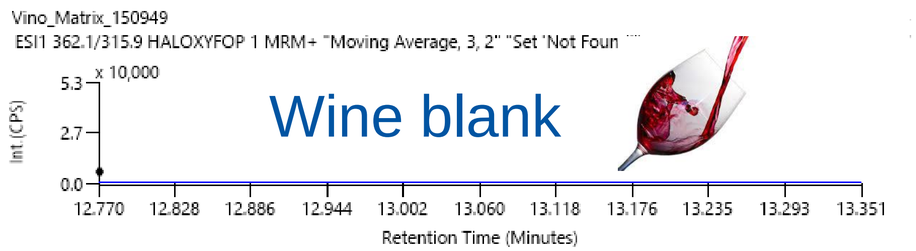
Peak width = 8 sec

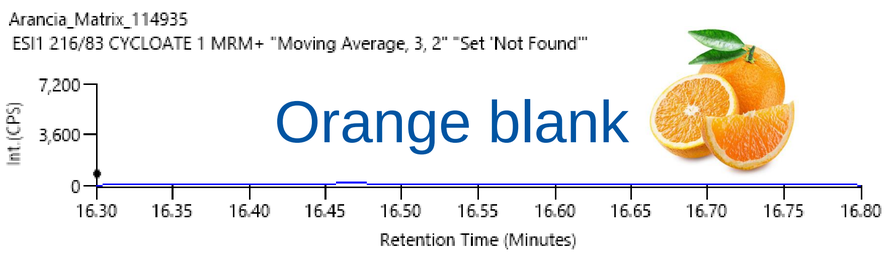
Anticipated cycle time = 0.55 sec

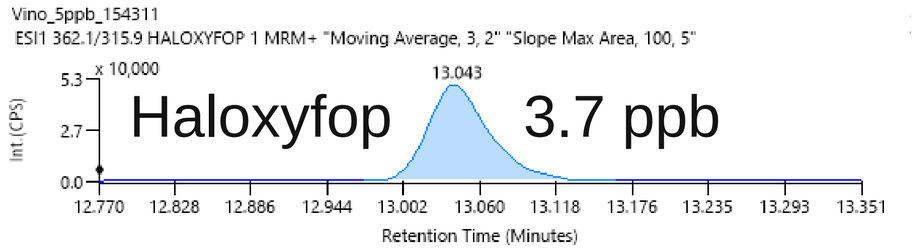
→ Data points across peak:

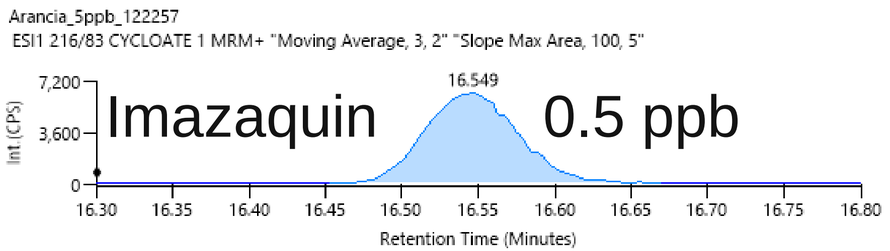
8/0.55 = 15 data points

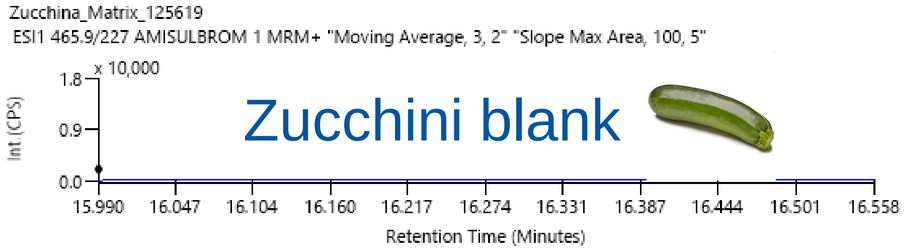
Pesticides in foods – spiked blank samples

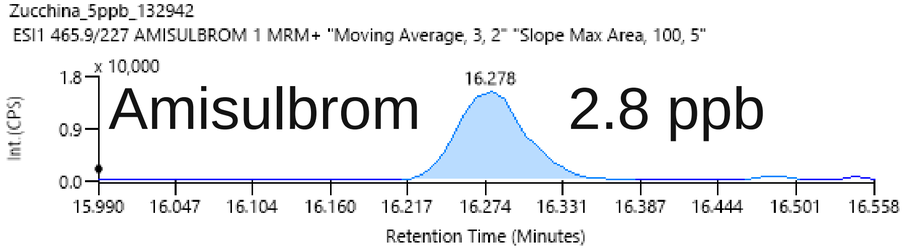


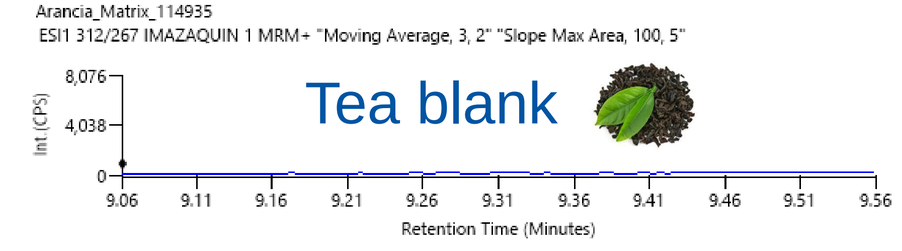


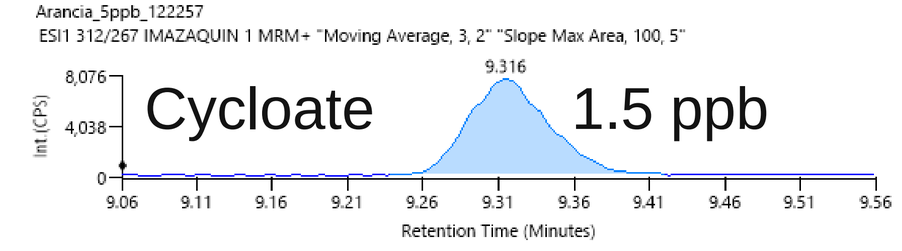




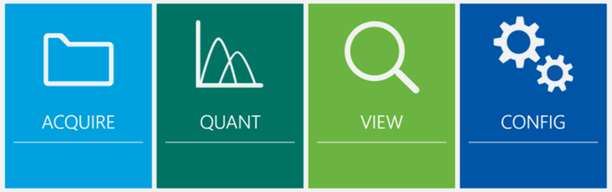


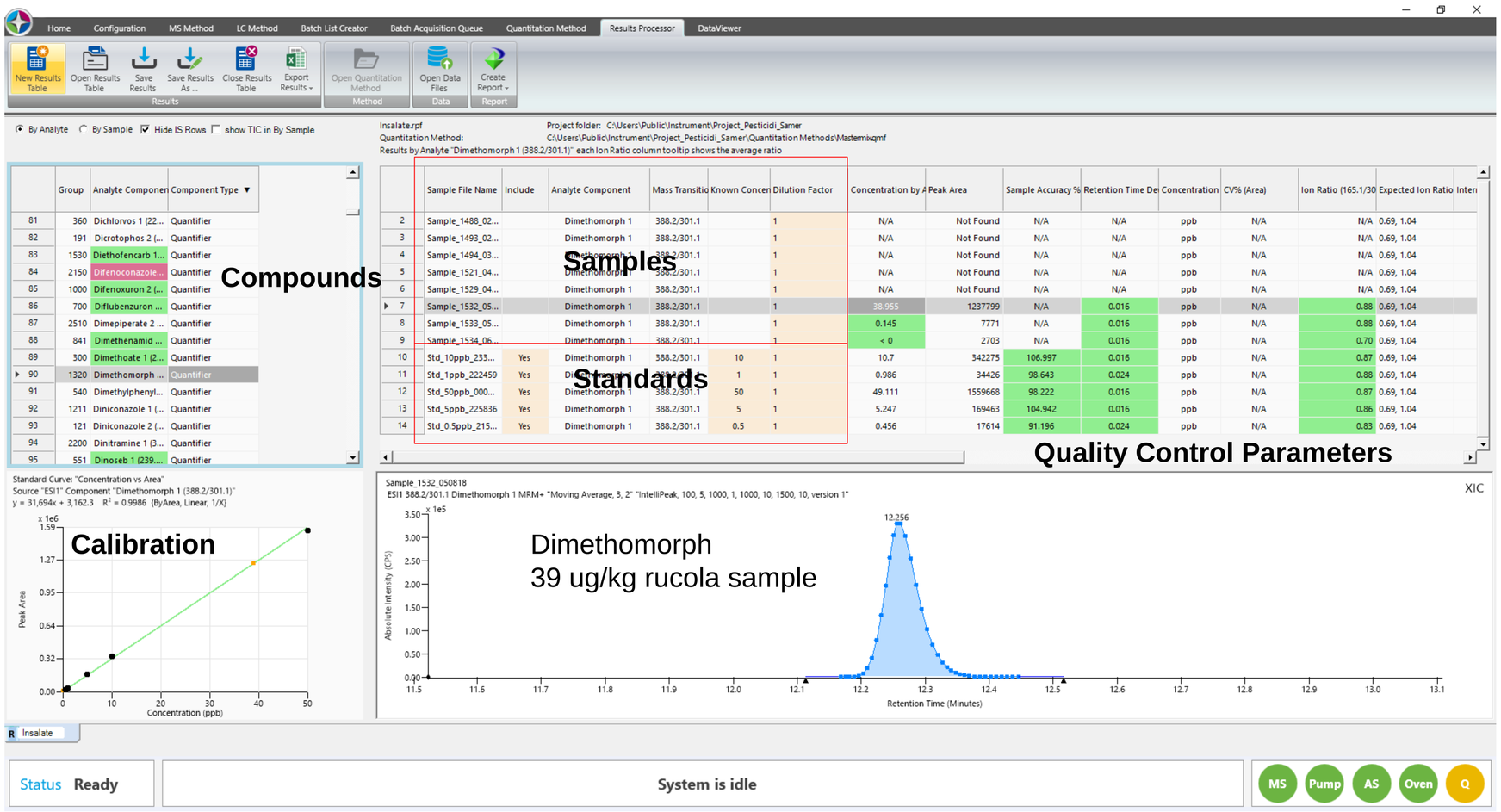


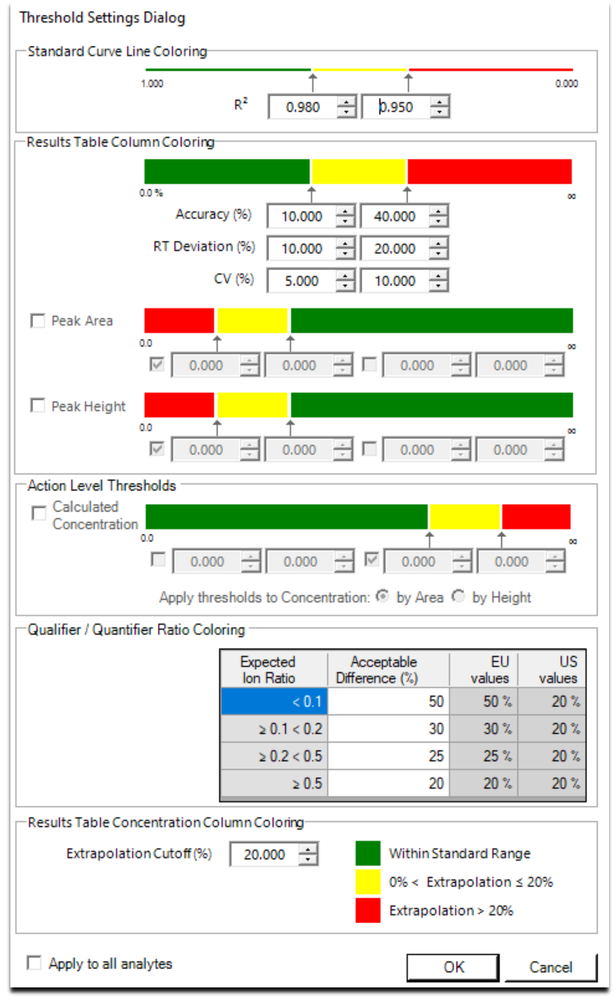




Simplicity™ Software







Color coding for rapid identification of “positive” samples

<1 ug/kg <10 ug/kg >10 ug/kg (general MRL)

QSight Outside

LX50 UHPLC

Small Footprint, Vertical Design:
Compact 50 cm x 50 cm x 110 cm
no benchtop needed.

PerkinElmer

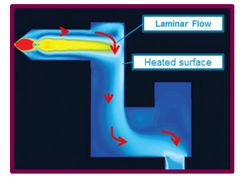
QSight Inside - Innovative and patented technologies – flow-based MS

Dual Source: Two independent probes provide true multiplexing flexibility

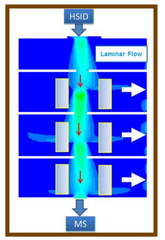
StayClean™ Source: Self cleaning design delivers maximum sensitivity and exceptional uptime

Unifield™ Detector: Patented technology counts positive and negative ions without high voltage switching

HSID™ Interface: Provides high S/N and reproducible results, with no optimization or regular maintenance



Laminar Flow Ion Guide™: Highly efficient field–free transmission



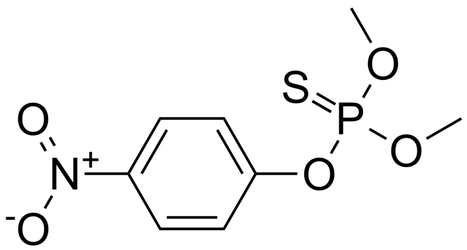
Modular: Plug-and-play design for ease of service

PerkinElmer

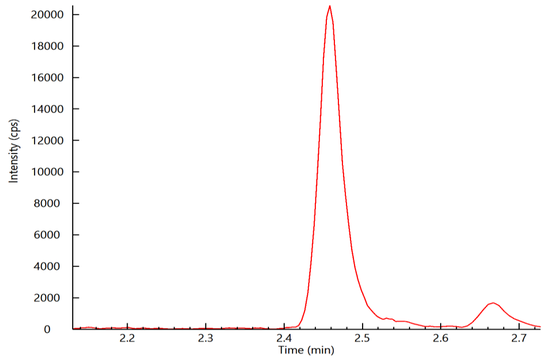
Selected Applications

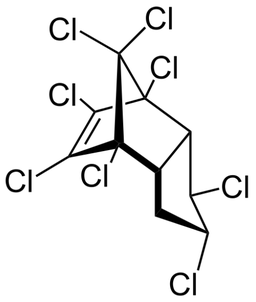
PerkinElmer

Dual Source: Use of APCI for GC amenable compounds

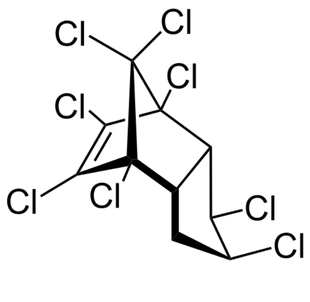


Methyl Parathion S/N = 200



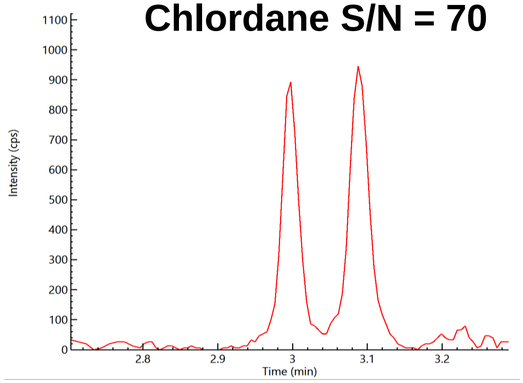


trans

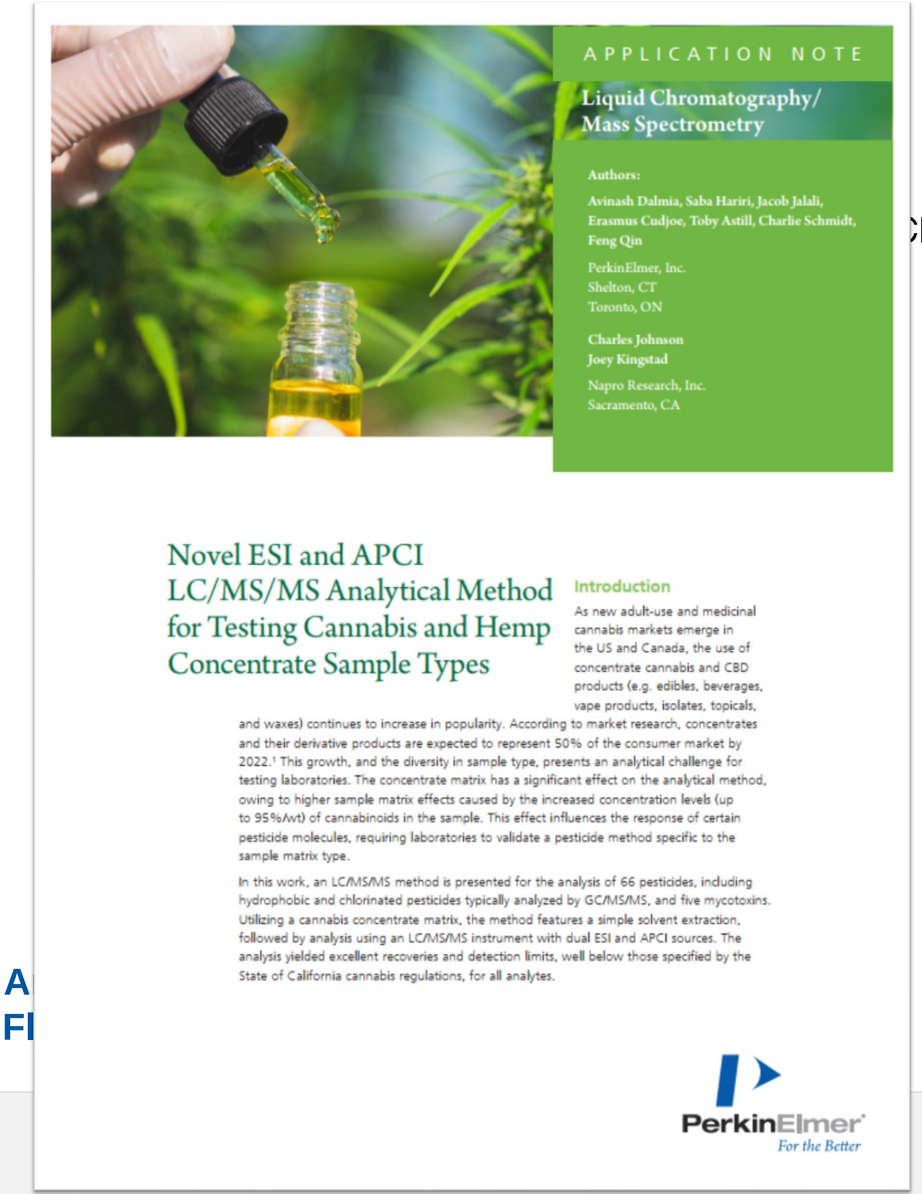


cis

Chlordane S/N = 70

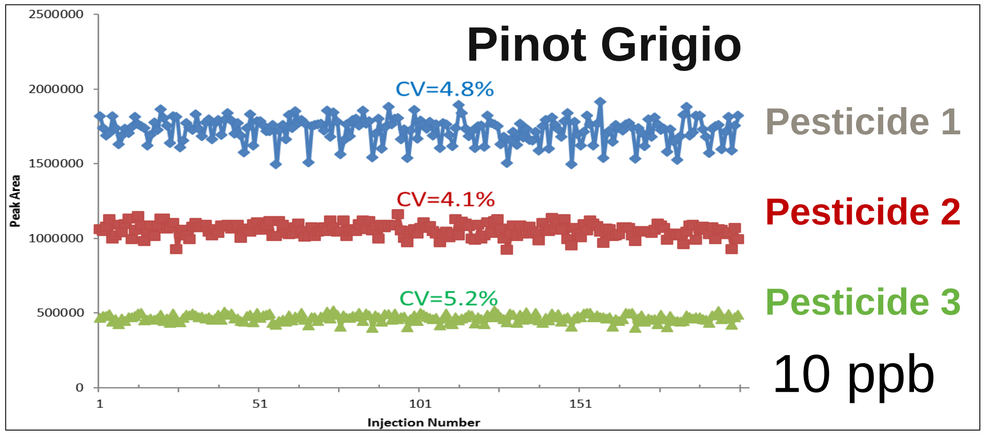


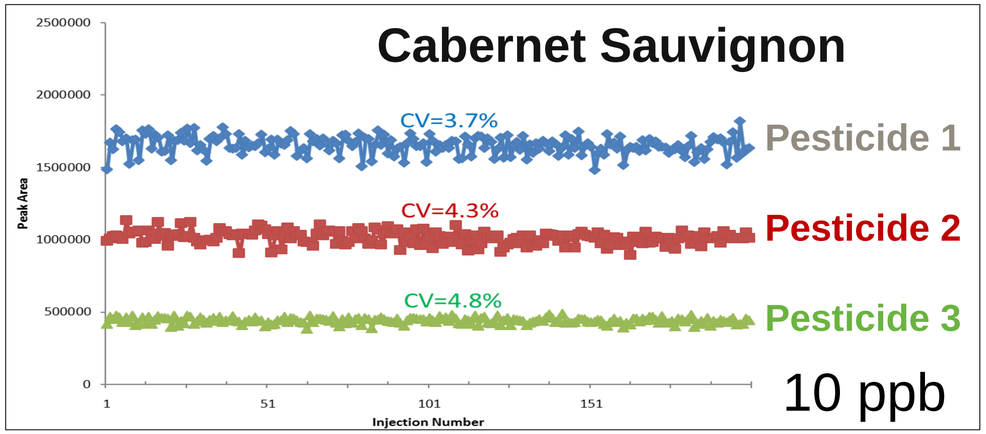
Response for Four A
10x diluted Cannabis Fl



StayClean™/HSID™: “No Dilute” Just Shoot - pesticides in wine

200 injections

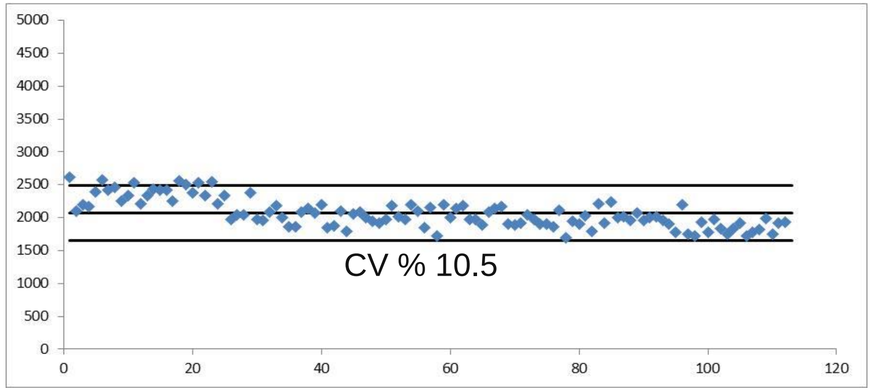




1. Dimethenamid, 2. Pyriproxyfen, 3. Benthiavalicarb-isopropyl

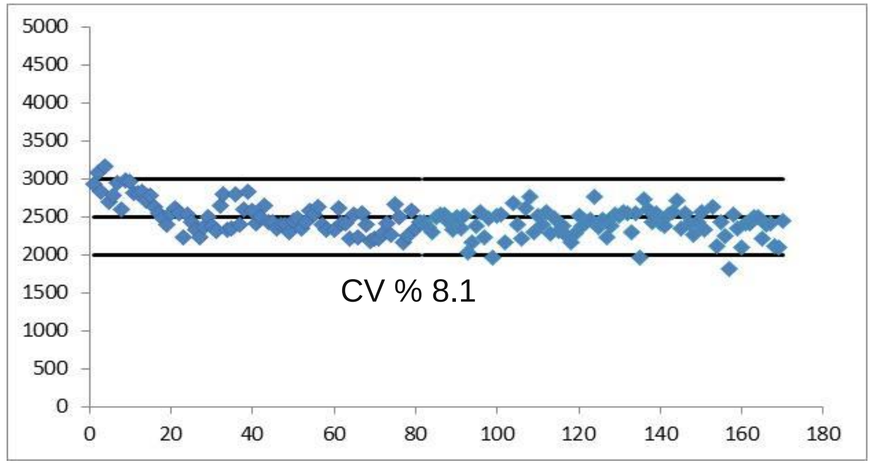
270 injections

Analysis 1 - glyphosate



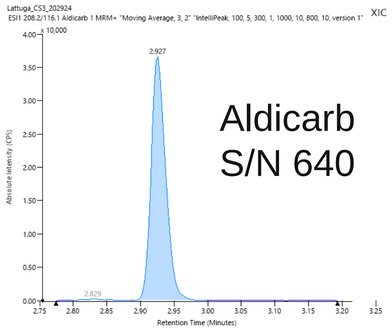
50 ppb

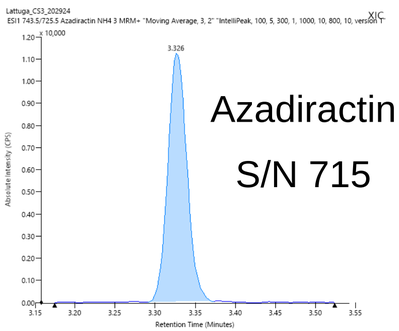
Analysis 2 - glyphosate

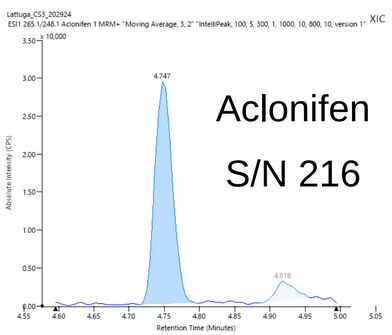


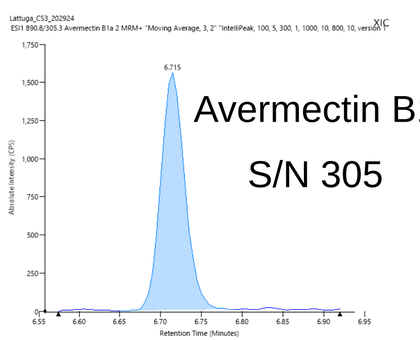
PerkinElmer

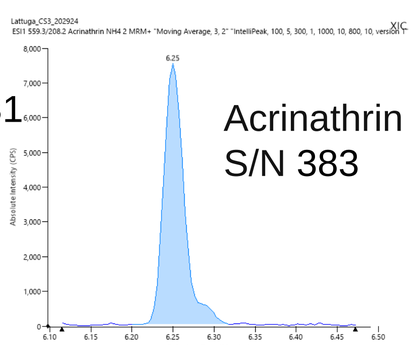
Laminar Flow Ion Guide™ - challenging pesticides – 10 ppb in lettuce

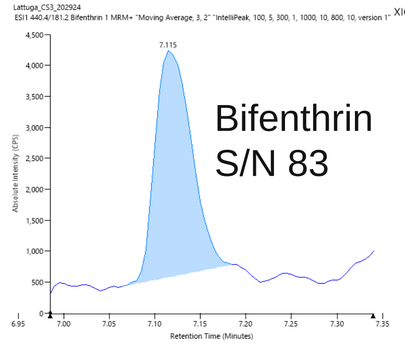


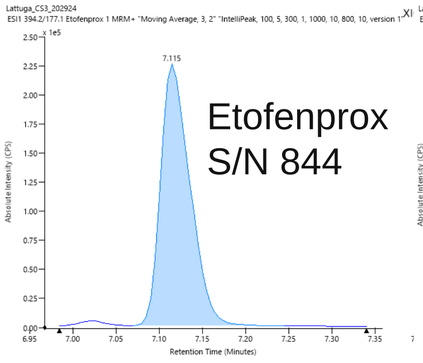


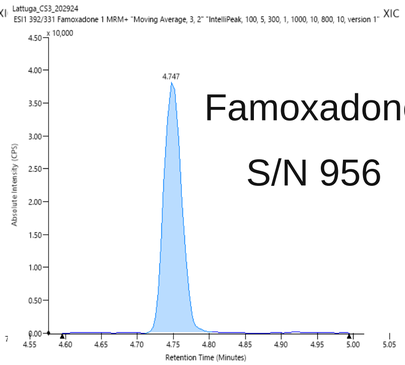


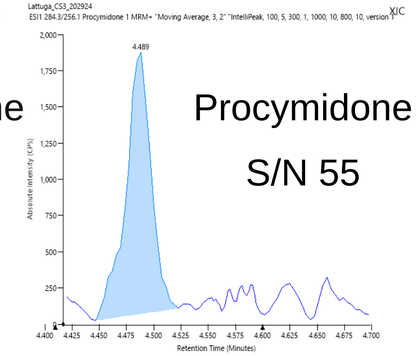


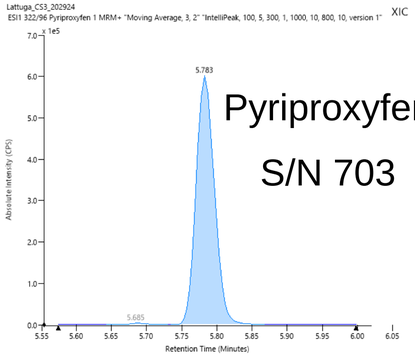


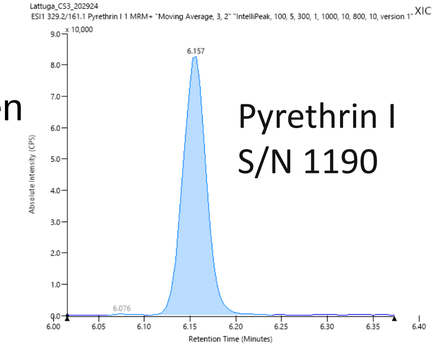


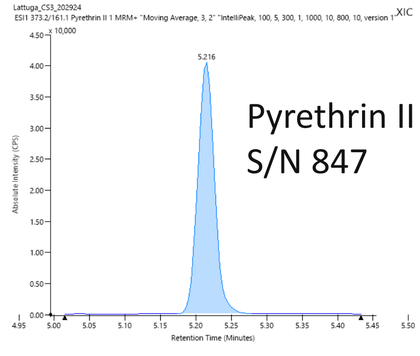


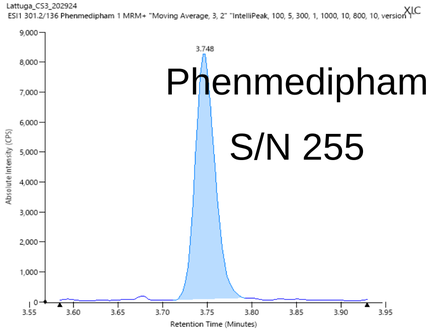


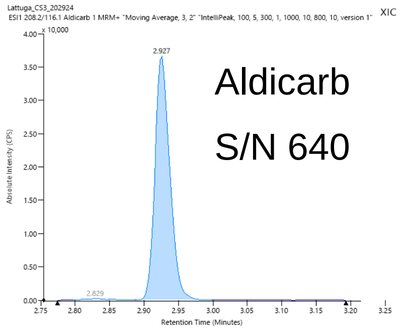


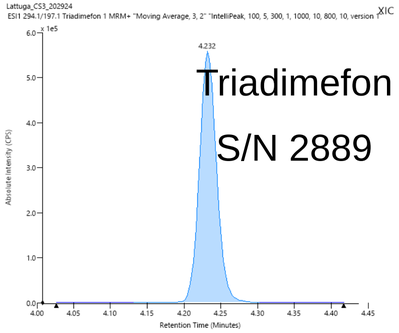


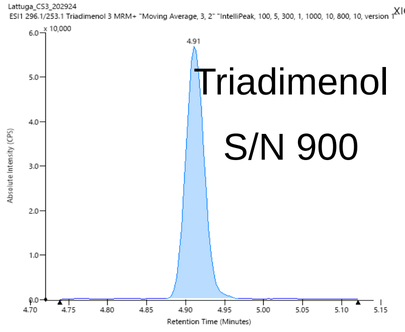


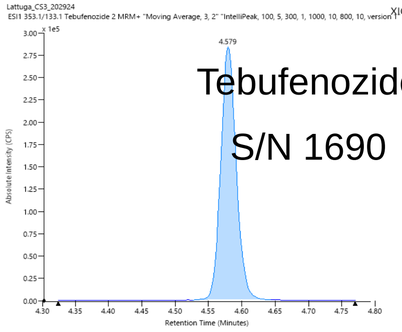


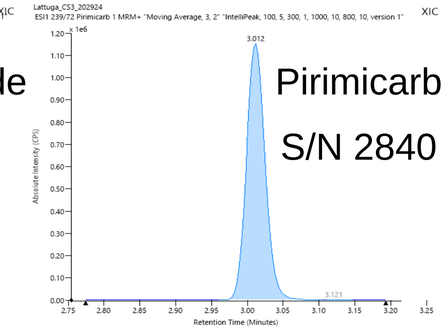












PerkinElmer

UniField Detector™: Multi-residue method with 500+ pesticides

Sample preparation:

- 10 g of vegetable/fruits (orange, apple, lettuce, endive, olives, black chickpeas)
- QuEChERS extraction and clean-up
- 45 mg of porous graphitic carbon (PGC) for highly pigmented fruit and vegetables
- IS addition

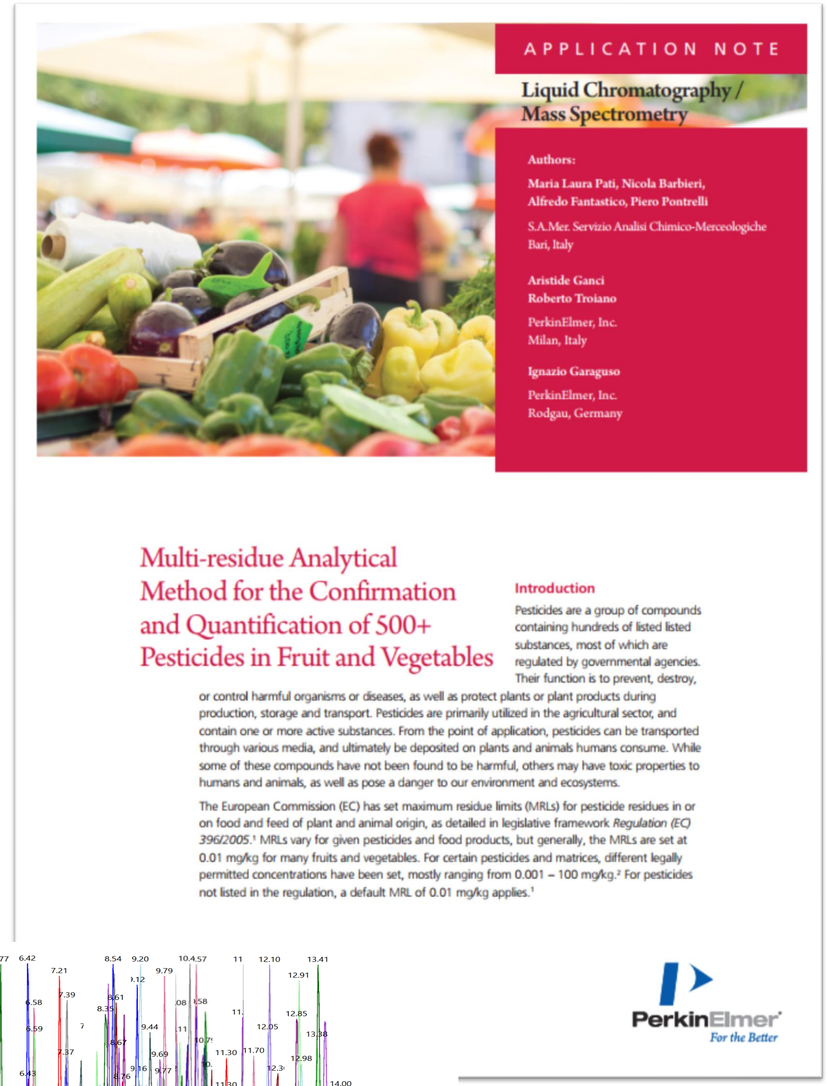
LC parameters:

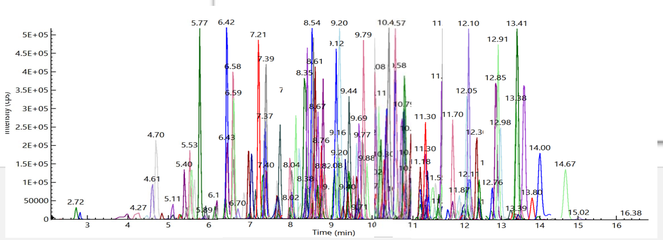
- Flow Rate: 0.4 ml/min
- Column: C18, 2.7µm, 4.6x100mm
- Column Temperature: 40°C
- Sample Temperature: 10°C
- Injection volume: 10 µl
- Mobile Phase A: 9mM $AcNH_4$ in H_2O – ACN (90:10,v:v), 0.1 % FA
- Mobile Phase B: 1mM $AcNH_4$ in H_2O – ACN (10:90,v:v), 0.1 % FA

Step	Time (min)	%A	%B
1	0	100	0
2	10	0	100
3	15	0	100
4	16	100	0
5	20	100	0

MS parameters

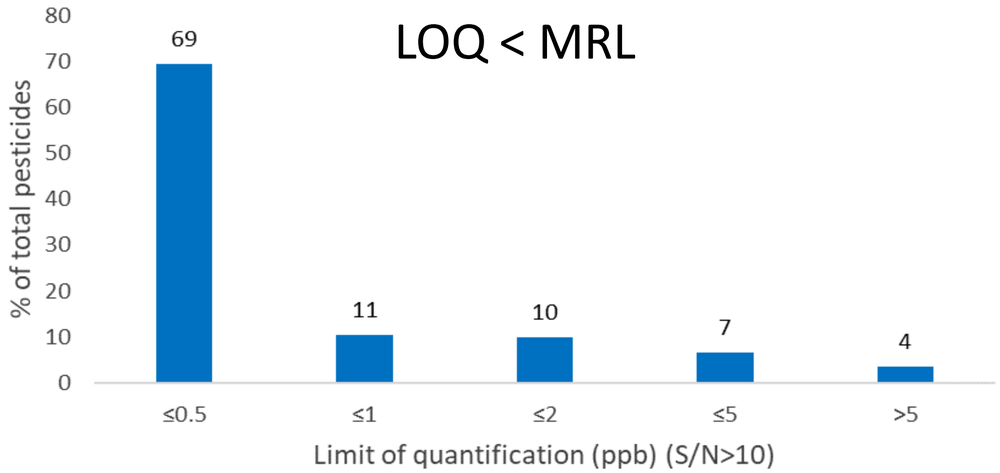
- Instrument: QSight 220
- Source: Electrospray with polarity switching
- Spray Voltage: 5000V/-4800V
- Nebulizer Gas : 350
- Drying Gas : 120
- Source Temperature : 340°C
- HSID Temperature : 200°C
- Detection Mode: Time-managed MRM™

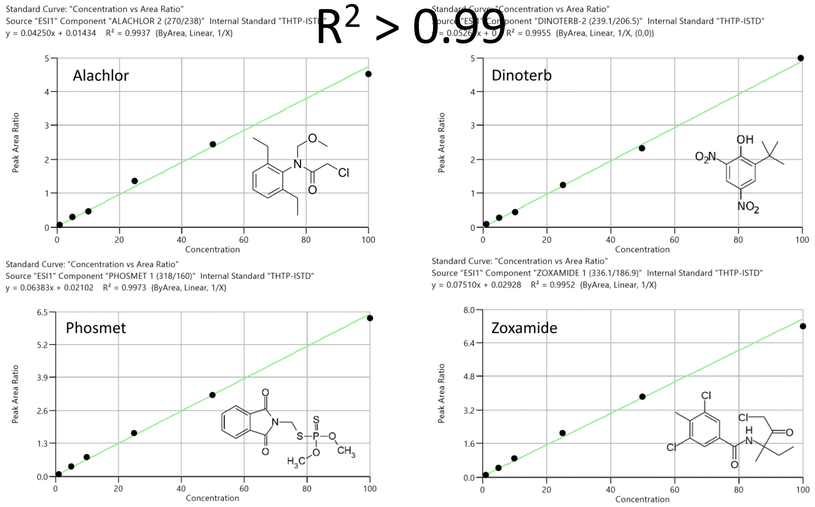


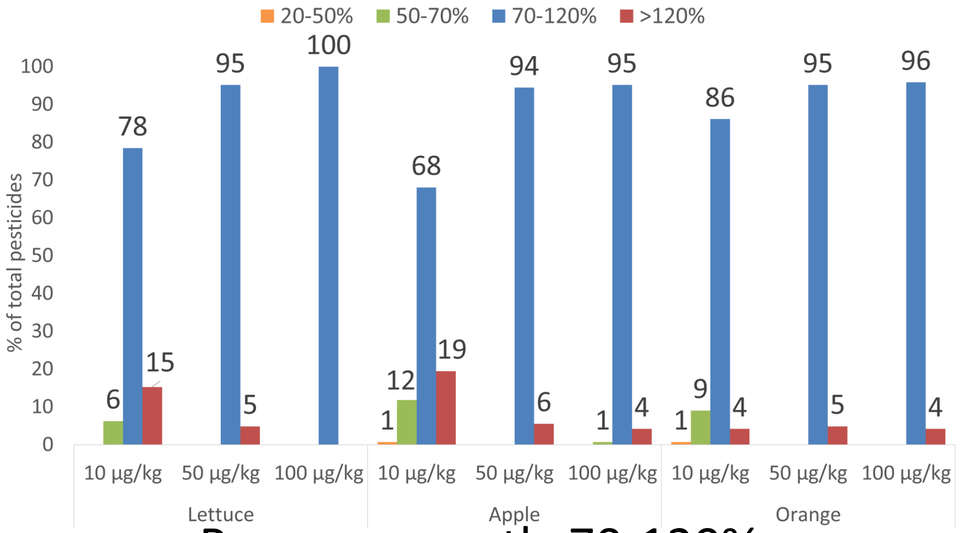


PerkinElmer

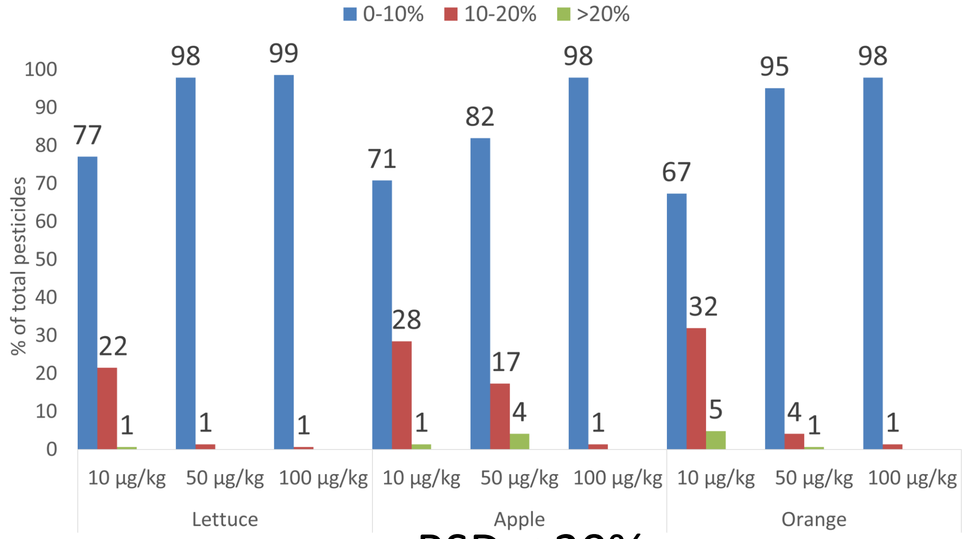
Method performance – LOQ, linearity, recovery and repeatability







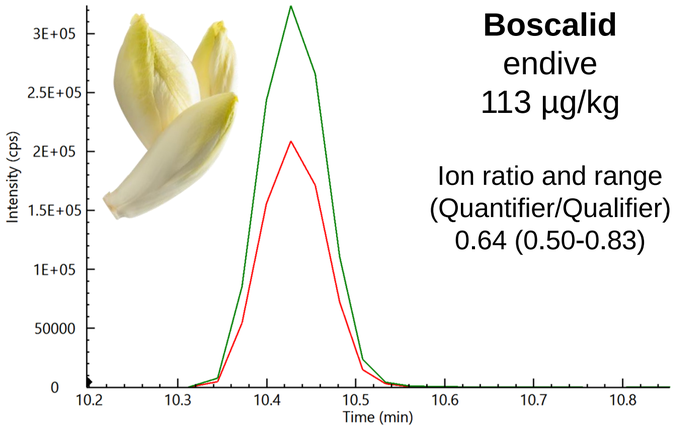
Recovery mostly 70-120%



RSD < 20%

Examples of positively quantified pesticides at varying concentrations

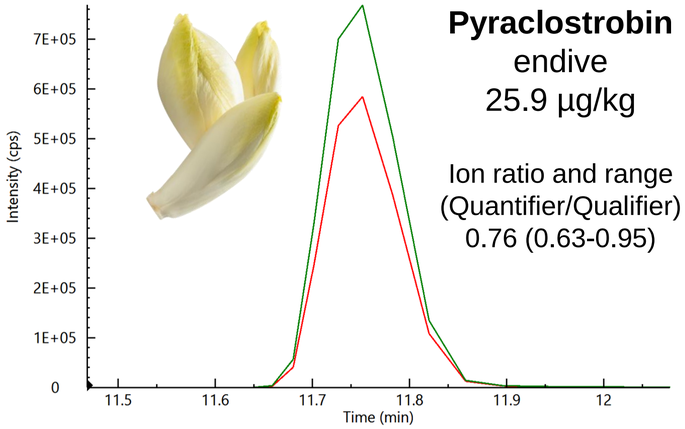
EIC +MRM 343.10/140.00 (34 pairs) EV: 25 V CC: -29 V Exp "Experiment 58" Boscalid 2
Number of Scans: 24
Smoothing Level: 1
Max: 3.24E+5 cps



Boscalid
endive
113 µg/kg

Ion ratio and range
(Quantifier/Qualifier)
0.64 (0.50-0.83)

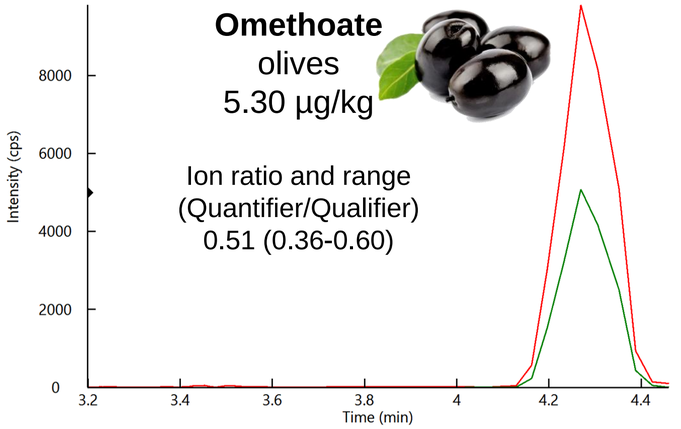
EIC +MRM 388.10/163.00 (20 pairs) EV: 25 V CC: -37 V Exp "Experiment 73" Pyraclostrobin 2
Number of Scans: 22
Smoothing Level: 1
Max: 7.69E+5 cps



Pyraclostrobin
endive
25.9 µg/kg

Ion ratio and range
(Quantifier/Qualifier)
0.76 (0.63-0.95)

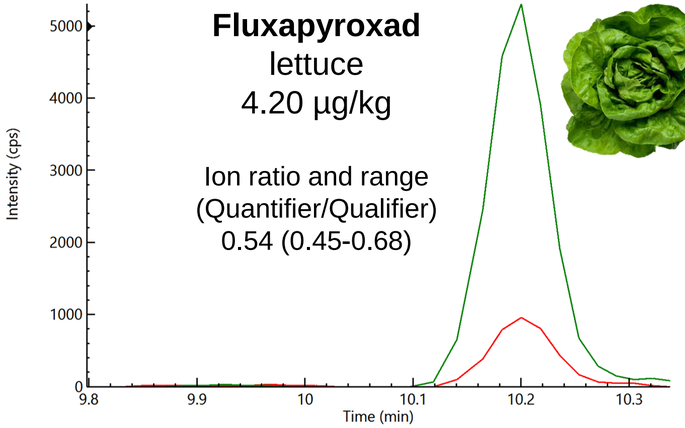
EIC +MRM 214.10/124.90 (6 pairs) EV: 10 V CC: -31 V Exp "Experiment 5" Omethoate 2
Number of Scans: 68
Smoothing Level: 1
Max: 9.81E+3 cps



Omethoate
olives
5.30 µg/kg

Ion ratio and range
(Quantifier/Qualifier)
0.51 (0.36-0.60)

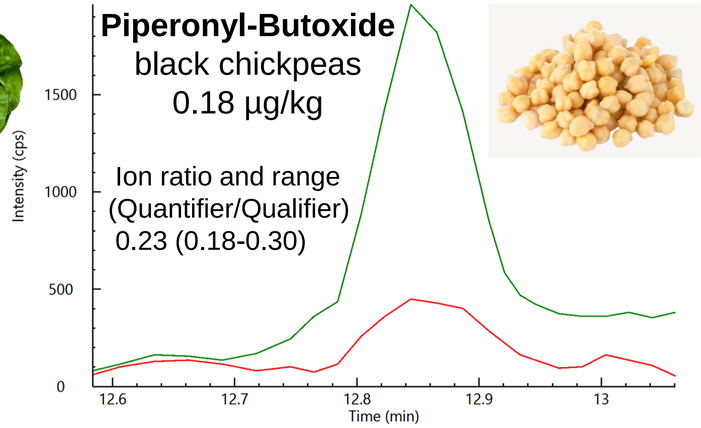
EIC -MRM 380.00/220.00 (2 pairs) EV: -1 V CC: 54 V Exp "Experiment 52" Fluxapyroxad 1
Number of Scans: 29
Smoothing Level: 1
Max: 5.31E+3 cps



Fluxapyroxad
lettuce
4.20 µg/kg

Ion ratio and range
(Quantifier/Qualifier)
0.54 (0.45-0.68)

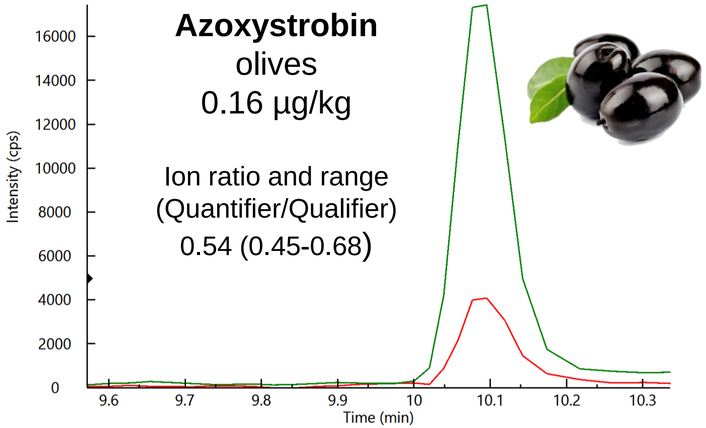
EIC +MRM 356.20/119.00 (6 pairs) EV: 12 V CC: -67 V Exp "Experiment 82" Piperonyl-Butoxide 2
Number of Scans: 24
Smoothing Level: 1
Max: 5.32E+2 cps



Piperonyl-Butoxide
black chickpeas
0.18 µg/kg

Ion ratio and range
(Quantifier/Qualifier)
0.23 (0.18-0.30)

EIC +MRM 404.10/344.10 (18 pairs) EV: 25 V CC: -35 V Exp "Experiment 53" Azoxystrobin 2
Number of Scans: 29
Smoothing Level: 1
Max: 1.74E+4 cps

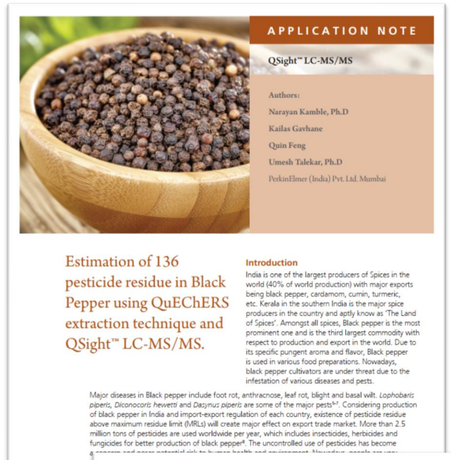


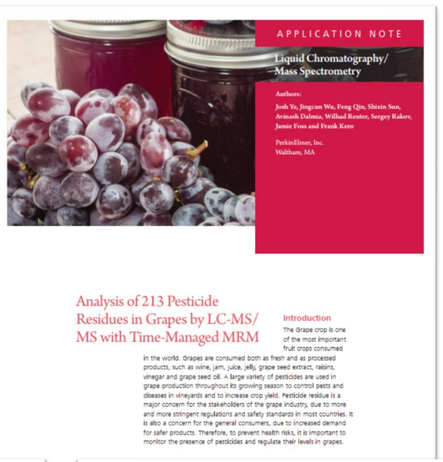
Azoxystrobin
olives
0.16 µg/kg

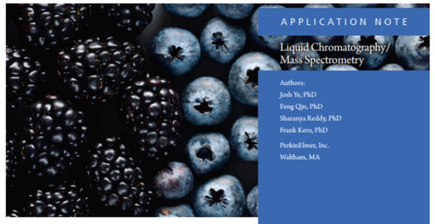
Ion ratio and range
(Quantifier/Qualifier)
0.54 (0.45-0.68)

PerkinElmer

Overview of Application Notes for Pesticide Analysis in Foods







QSight 420 for Rapid, High Sensitivity Analysis of Marine Toxins Causing Diarrheic Shellfish Poisoning in Mussels

Sheng-Suan (Victor) Cai, Senior Field Application Scientist

April 23, 2020

PerkinElmer®
For the Better

HUMAN HEALTH • ENVIRONMENTAL HEALTH

Introduction/Background

- Why this method?
  - Method developed for Washington State Dept. of Health
  - Lock-out spec: LOQ: 50 ppt for DTX2, 200 ppt for OA and DTX1
- Marine toxins causing diarrheic shellfish poisoning (DSP)
- Test Methods
  - Mouse Bioassay
  - HPLC-FLD, Derivatization
  - LC-MS/MS, High Sensitivity and Specificity

QSight 420 LX50 UHPLC-MS/MS System

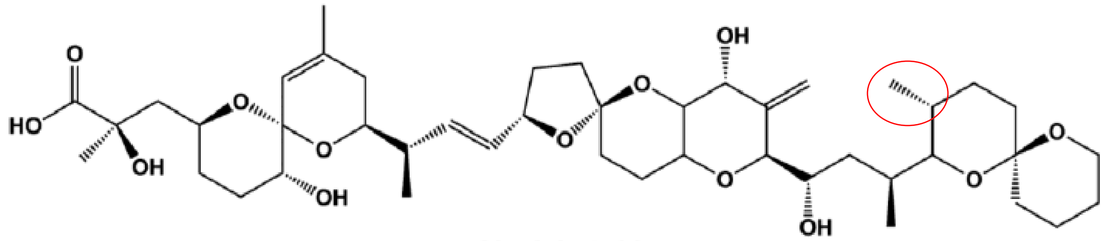
Triple Quad Mass Spec, Equipped with UHPLC and Dual ESI and APCI Ion Sources.

PerkinElmer

Target Analytes

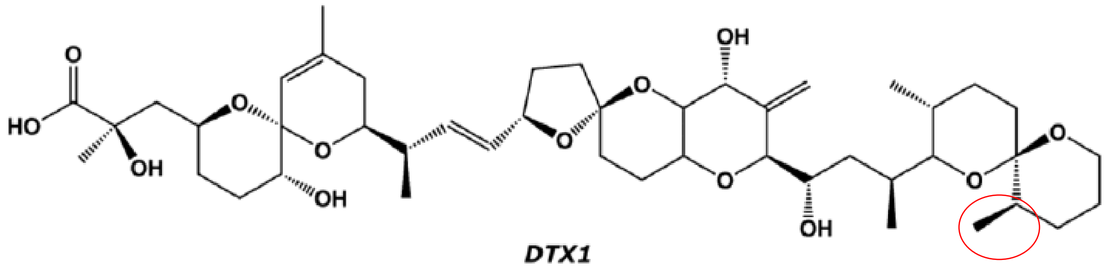
- A: Okadaic Acid (OA)
- B: Dinophysistoxin-1 (DTX1)
- C: Dinophysistoxin-2 (DTX2)

A



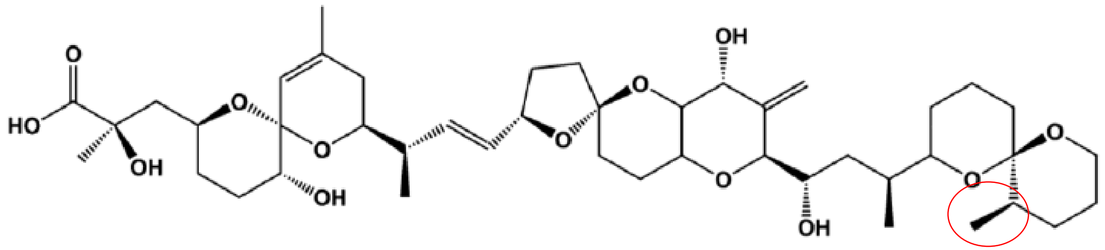
Okadaic Acid

B



DTX1

C



DTX2

A and C are isomers, sharing exactly same MRM transitions.
B has an additional methyl group

PerkinElmer

MRM Transitions and Mass Dependent Parameters

Analyte	MRM Transition	Dwell Time (ms)	EV	CC L2	CC	Resolution (Q1:Q2)
OA	803.4 > 255.3	100	-136	352	54	Unit_Unit
OA	803.4 > 113.1	100	-136	268	76	Unit_Unit
DTX2	803.4 > 255.3	100	-110	328	54	Unit_Unit
DTX2	803.4 > 113.1	100	-131	244	73	Unit_Unit
DTX1	817.5 > 255.3	100	-118	290	54	Unit_Unit
DTX1	817.5 > 113.1	100	-124	260	81	Unit_Unit

- OA and DTX2 share same transitions, but fully separated by RT on column.
- Three mass dependent parameters optimized by AutoTune.
- EV = Entrance Voltage, CC L2 = Collision Cell Lense2, CC = Collision Energy.

PerkinElmer

Rapid and Simple Sample Prep Procedure

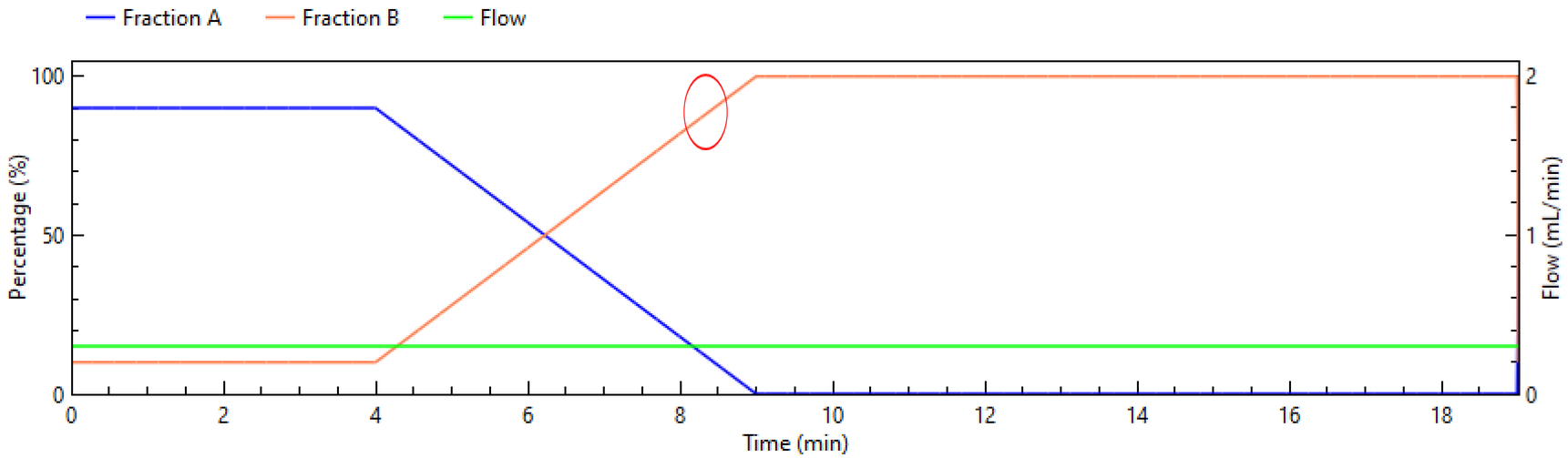
- Weigh 1g of mussel homogenate in a 15-mL test tube.
- Add 1 mL methanol.
- Vortex for 2 min
- Centrifuge for 2 min at 3500 rpm.
- Put in a freezer at -10 ^{o}C for 30 min
- Centrifuge immediately for 2 more min at 3500 rpm.
- Transfer supernatant immediately to a 1.5-mL micro-centrifuge tube.
- Centrifuge at 14,000 rpm at 0 ^{o}C for 10 min.
- Transfer supernatant immediately to 0.22 µm Nylon filter and collect in a 2-mL HPLC injection vial for negative ESI UHPLC-MS/MS analysis.

- StayClean® ion source allows direct injection analysis of sample extracts with good data quality.

PerkinElmer

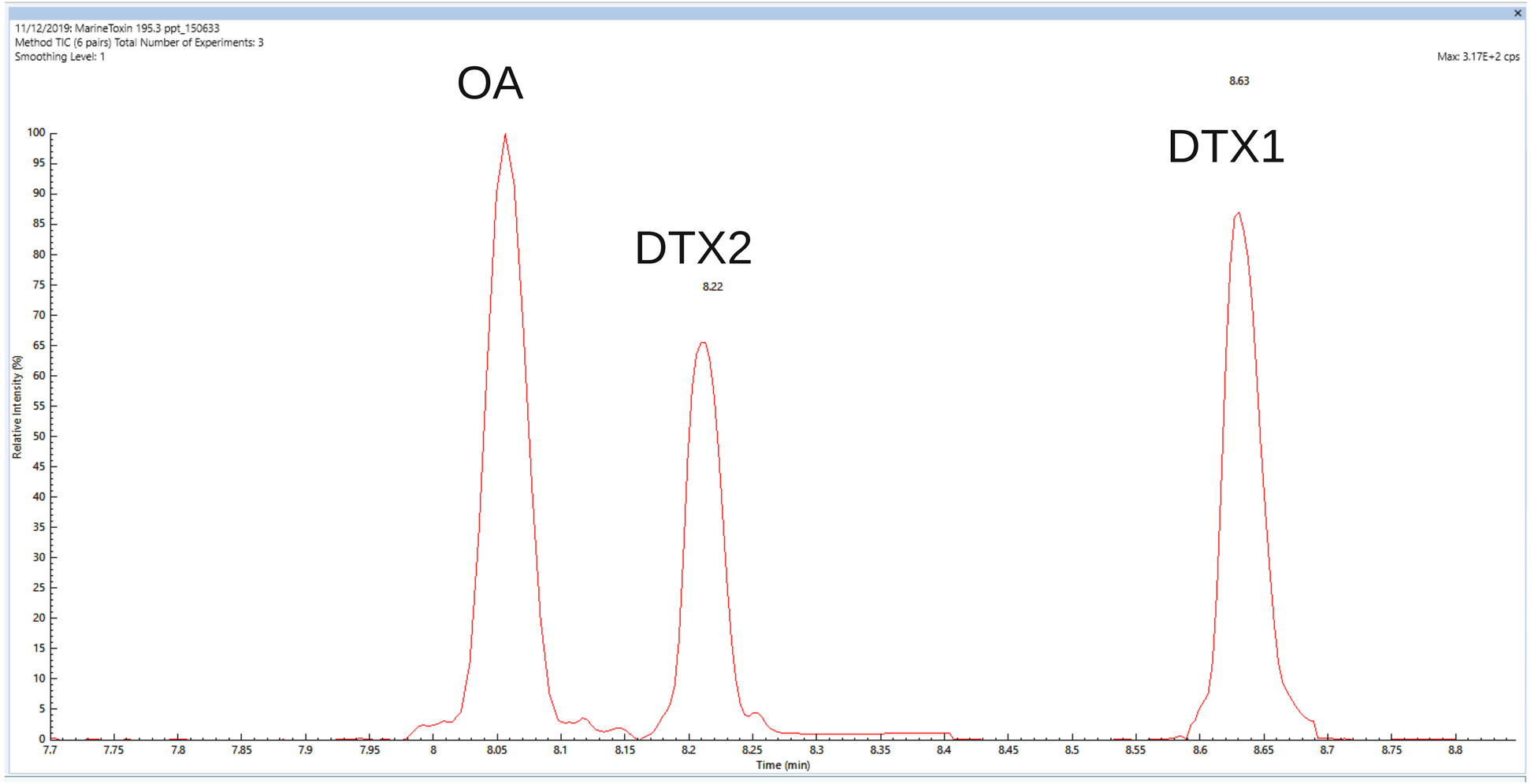
LC Conditions

- UHPLC column: Zorbax Eclipse Plus C_{18} (2.1 x 50 mm, 1.8 µm).
- Mobile phase A: Water, B: Acetonitrile. Both contain 0.1% formic acid and 2 mM ammonium formate
- Wash solvent: 10% MeOH in Water, 250 µL
- Oven temp: 40°C, Flow rate: 0.3 mL/min
- Injection volume: 10 µL
- Gradient elution: Hold 10%B for 4 min. Linear gradient to 100%B in 5 min. Hold 100%B for 10 min.



RT: OA = 8.05 min, DTX2 = 8.21 min, DTX1 = 8.63 min.

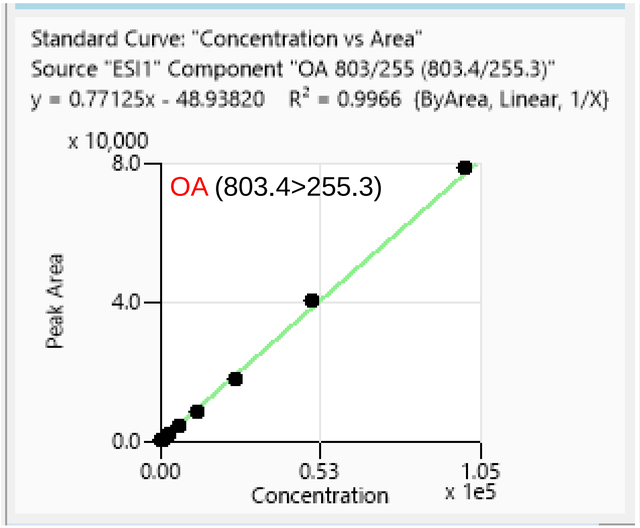
Column Separation, 195.3 ppt

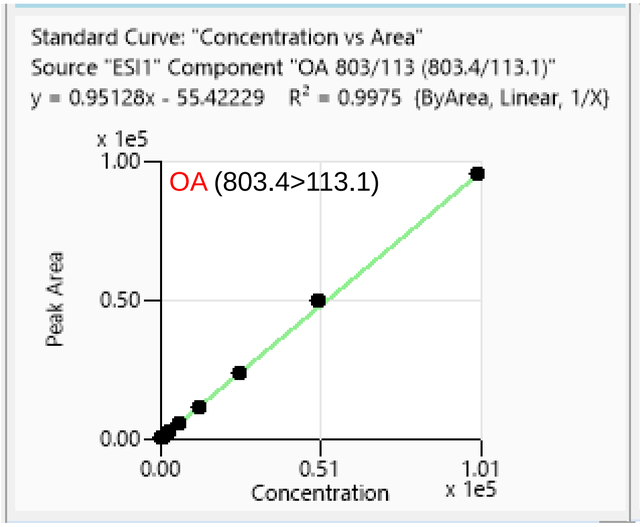


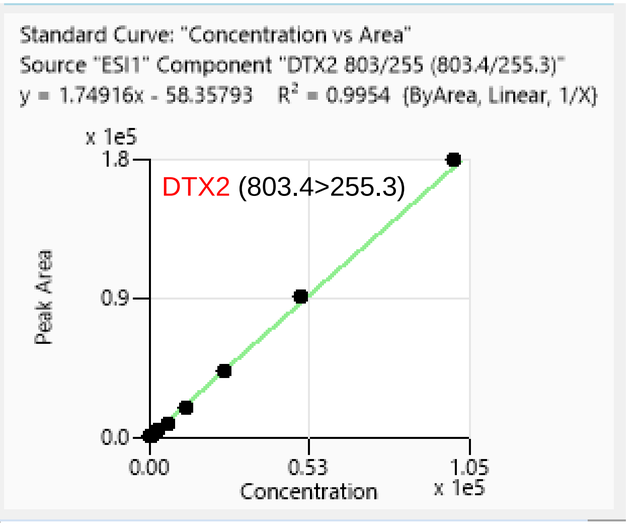
RT: OA = 8.05 min, DTX2 = 8.22 min, DTX1 = 8.63 min. Peak Width = 6 sec. at base

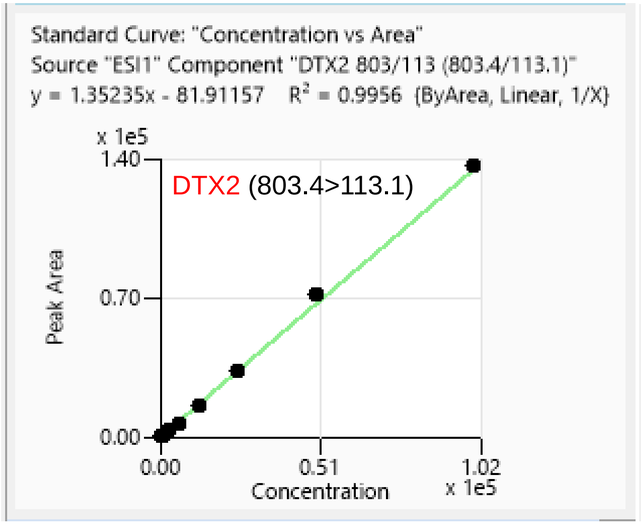
PerkinElmer

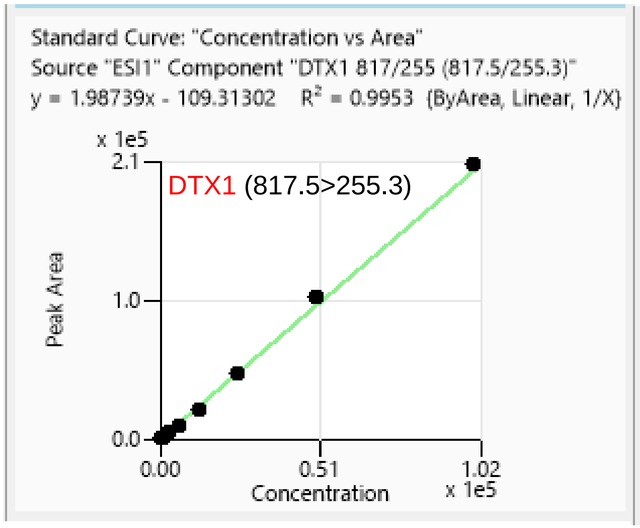
Calibration Curves

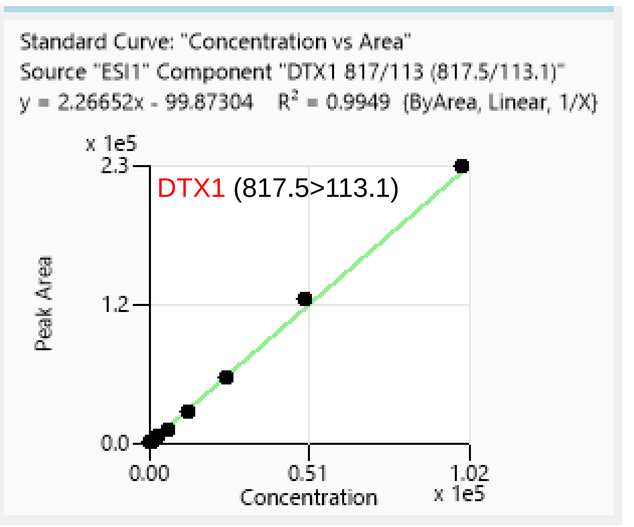












PerkinElmer

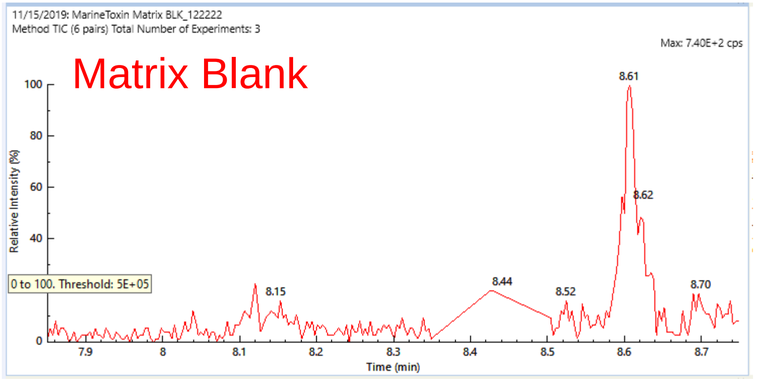
Linearity

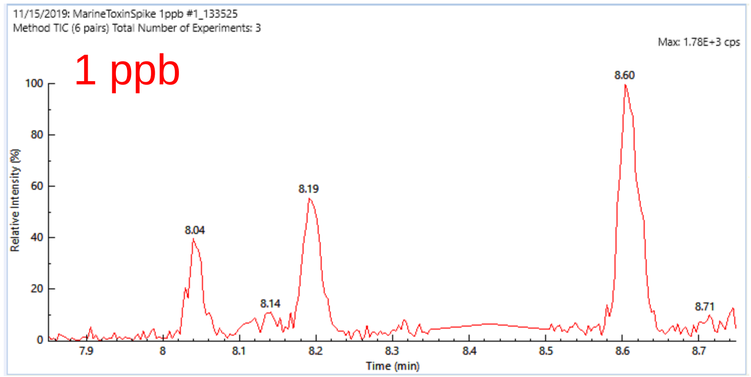
Analyte	MRM Transition	Calibration Range (ppt)	Regression Equation	R^2
OA	803.4 > 255.3	97.7 - 100,000	y = 0.77125x - 48.93820	0.9966
OA	803.4 > 113.1	48.8 - 100,000	y = 0.95128x - 55.42229	0.9975
DTX2	803.4 > 255.3	24.4 - 100,000	y = 1.74916x - 58.35793	0.9954
DTX2	803.4 > 113.1	48.8 - 100,000	y = 1.35235x - 81.91157	0.9956
DTX1	817.5 > 255.3	48.8 - 100,000	y = 1.98739x - 109.31302	0.9953
DTX1	817.5 > 113.1	48.8 - 100,000	y = 2.26652x - 99.87304	0.9949

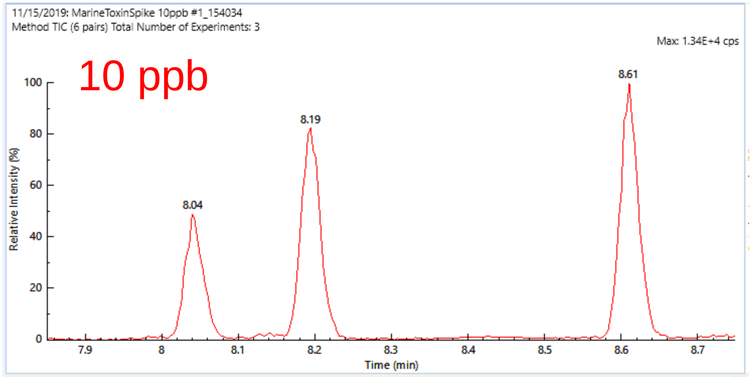
Calibration Range: Low ppt to 100 ppb. All $R^2 \geq 0.995$

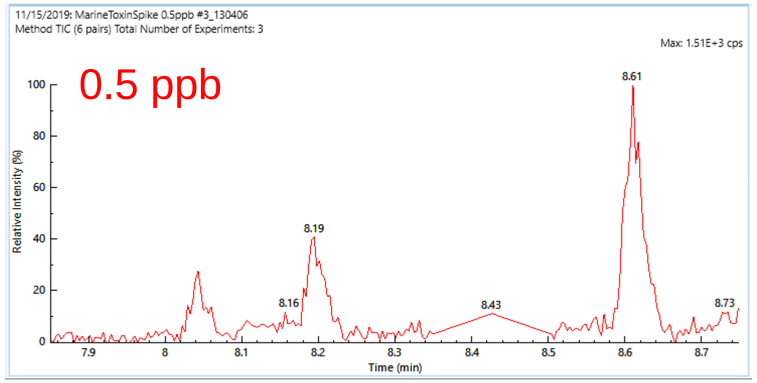
PerkinElmer

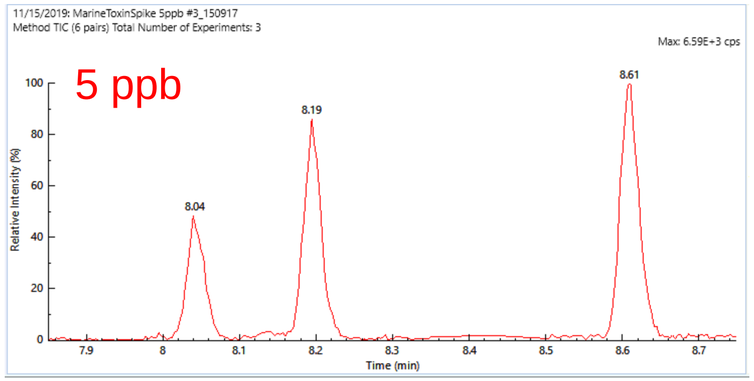
Matrix Blank vs. Matrix Spike (Without Smoothing)

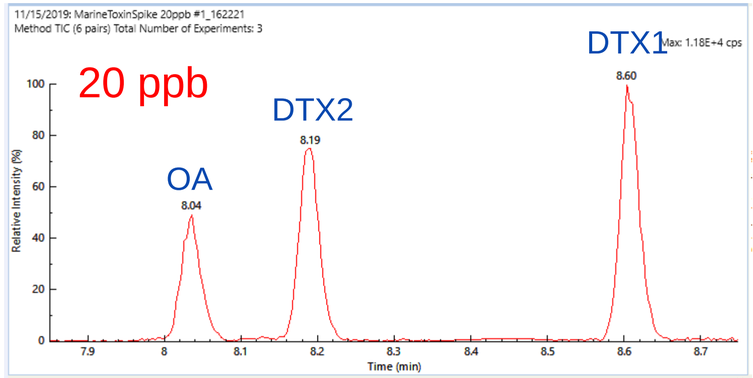












- Control samples contain low ppt level of analytes.
- OA = 91-107 ppt, DTX2 = 45-64 ppt, DTX1 = 277-299 ppt.
- Combined action limits = 160 ppb (OA equivalent)

PerkinElmer

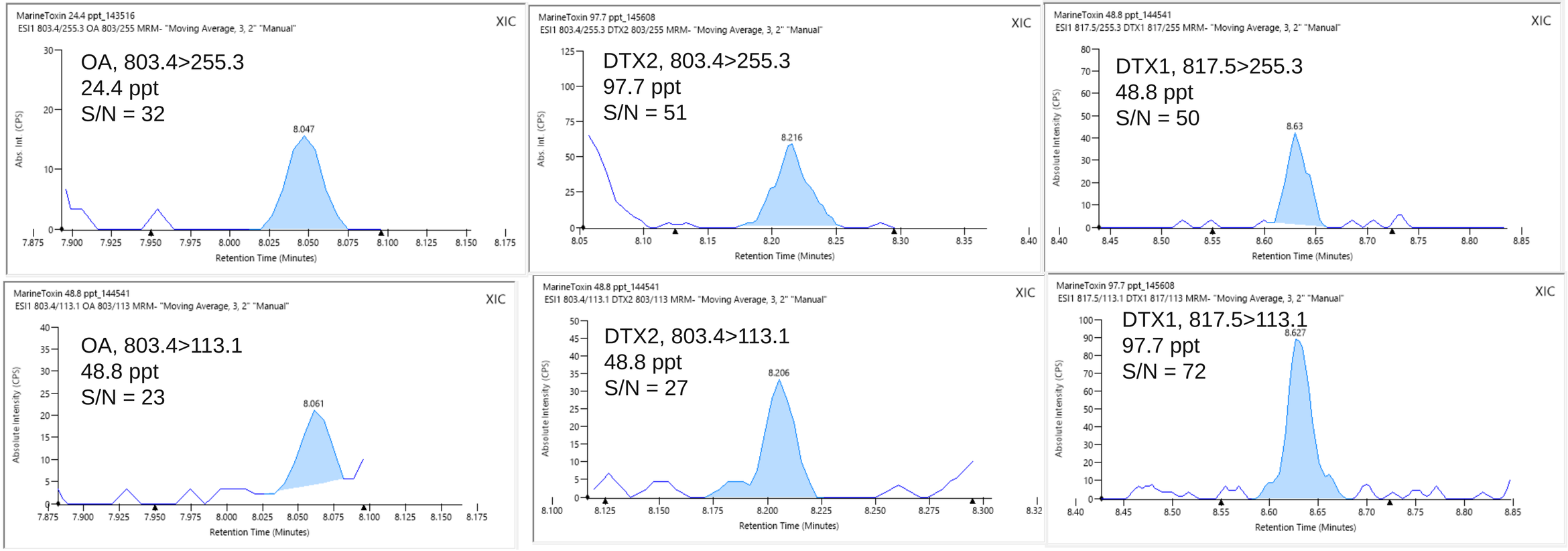
Spiked Recovery

Analyte	MRM Transition	0.5 ppb		1 ppb		5 ppb		10 ppb		20 ppb	
		%Rec	StDev	%Rec	StDev	%Rec	StDev	%Rec	StDev	%Rec	StDev
OA	803.4 > 255.3	90.9	14.8	100.5	19.0	123.1	18.7	122.5	2.4	114.7	8.3
OA	803.4 > 113.1	88.6	20.1	105.1	10.8	121.0	19.7	116.9	6.3	112.3	9.2
DTX2	803.4 > 255.3	92.5	29.4	102.9	7.7	119.1	17.3	126.4	5.9	107.3	6.7
DTX2	803.4 > 113.1	75.6	15.7	84.2	3.0	112.3	15.4	109.3	10.8	102.8	8.6
DTX1	817.5 > 255.3	78.0	31.3	94.0	9.1	89.9	9.2	97.4	5.2	90.8	3.9
DTX1	817.5 > 113.1	77.6	36.6	92.8	5.7	94.3	12.0	97.1	4.4	91.3	6.5

- Spike level: 0.5, 1, 5, 10 and 20 ppb
- % Rec: Average of triplicate analyses
- StDev: Standard deviation of triplicate analyses.

PerkinElmer

Instrument Sensitivity (Low ppt level injections)



- Low ppt level injections of standard mix on column.
- Injection volume = 10 µL
- SNR Method: Peak to Peak
- Smoothing Properties: Mean (3, 2). Noise Reduction

PerkinElmer

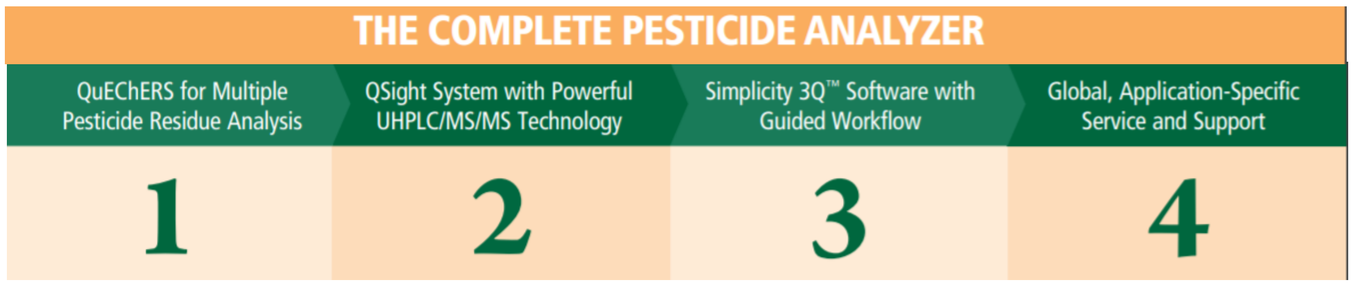
“Estimated” Limit of Quantification (LOQ, 10 x S/N)

Analyte	MRM Transition	RT (min)	LOQ (ppt)
OA	803.4 > 255.3	8.05	25
OA	803.4 > 113.1	8.05	26
DTX2	803.4 > 255.3	8.21	56
DTX2	803.4 > 113.1	8.21	20
DTX1	817.5 > 255.3	8.63	57
DTX1	817.5 > 113.1	8.63	26

- Control samples contain low ppt level of analytes.
- Low ppt level matrix spike tests difficult to perform.
- LOQ estimated from 0.5 ppb spike recovery tests. Background subtraction was performed for calculation of LOQ.

Conclusions

- Optimized workflow – from sample to result
- Sample preparation: easy/customized QuEChERS or… no sample preparation
- QSight flow-based mass spectrometry
  - Sensitive multi-residue method - EU MRL limits
  - Challenging contaminants in complex foods (ESI / APCI)
  - Instrument robustness and no frequent maintenance needed (StayClean™ / HSID™)



PerkinElmer

Merci pour votre attention

Christophe Clarysse - Christian Missitch

PerkinElmer