HRMS for pesticide analysis. Present and Future.

Pesticide Residue Analysis by HRMS

Definition High Resolution MS (SANCO/12571/2013)

- Detection using mass spectrometers with high resolving power, typically > 20,000 FWHM
  - FWHM = Full-width at half maximum (of a peak)
  - *In case of sector field instruments the 10 % valley is used for calculation the mass resolving power (following this definition HR > 10000)*

Pesticide Residue Analysis by HRMS

- Typical Instruments on the market
  - ToF or q-ToF coupled to LC or GC
  - Orbitrap or q-Orbitrap coupled to LC or GC
  - Sector field instruments coupled to GC

Pesticide Residue Analysis by HRMS

Application of HRMS in Pesticide Residue Analysis

1. Qualitative Screening by using cut of limits (e.g. the Screening Detection Limit - SDL)
2. Complementary technique to classical detectors
   - Increase of available information for detected pesticides
3. Search for analytes of special interest (e.g. “find by formular”)
4. Search for “real unknown” by the using databases

Pesticide Residue Analysis by HRMS

Application of HRMS in Pesticide Residue Analysis

1. Qualitative Screening @ SDL
2. Complementary technique to classical detectors
3. Search for analytes of special interest
4. Search for “real unknown” by the using databases

Reporting possible in case of applying validated methods

- Results of applications 3 and 4 are typical for internal use, only

Screening in Pesticides Residue Analysis

Decision Qualitative Screening <-> Confirmatory Method

- Qualitative Screening
  - Pesticides never found or few findings in Europe
  - Detection @ 0.01 mg/kg (ß <= 5 %)
  - *Detection below MRL-level (not for MACCP)*
- Confirmatory Method
  - Pesticides frequently or sometimes found
  - Pesticides with unsatisfying SDL

Validation of qualitative screening

Data evaluation (at least 20 spiking experiments):
Spiked samples: for each pesticide within a commodity group
=> count no. of false negatives and calculate false negatives

Criterium:

False negative rate: ß ≤ 5%

Suspects detects in control samples: no criterion -> confirmation method

On-going AQC:
Re-assessment of false negatives over time, including other matrices

Validation of qualitative screening

Action to be taken if false negative rate > 5%?

- Adjust method -> normally not
  - Additional cleanup – loss of analytes
  -
- Adjust chromatography
  - Column type
  - Column length ⇧ (e.g. 150 mm instead of 50 mm or 100 mm)
  - Particle size ⇩ (e.g. 1.8 µm instead of 3 µm)
  - Eluents
  - Gradient

Validation of qualitative screening

Action to be taken if false negative rate > 5%?

- Optimize instrument
  - Increase resolution
  - Optimize your scanning
    (no scheduled or depending MS/MS experiments)
- Optimize search
  - Searching using peak profiles instead of centroid peaks lead to higher success rates
    - ➢ More time consuming
- Repeat at higher level

➢ Establish level for 95% confidence (ß ≤ 5 %)

QuEChERS

	QuEChERS
Sample amount	5 g matrix of interest (liquid whole egg, cow´s milk, cheese, meat)
Extraction	50 mL centrifuge tube
	Addition of internal standard: 100 µl ISTD, wait 10 min
	Addition of 10 mL water, shake Addition of 10 mL CAN 4 g $MgSO_4$ 1 g NaCl Citrate buffered (0,5 g Na_2H-citrate x 6 H_2O , 1 Na_3-citrate x 2 H_2O) Shake vigorously for 10 min Centrifugate for 6 min at 3000 g
Clean-up	15 mL centrifuge tube filled with : 900 mg $MgSO_4$ 150 mg PSA Add 6 mL supernatant Shake for 10 min Centrifugate for 6 min at 3000 g
Preparation before analysis	Transfer 5 mL into vial
Analysis	LC-MS/MS

SweEt

	SweEt for Food of Animal Origin
Sample amount	5 g matrix of interest (liquid whole egg, cow´s milk, cheese, meat, honey……)
Extraction	50 mL centrifuge tube
	Addition of internal standard: add 100 µl ISTD (optional 100 µl spiking solution), wait 10 min
	Addition of 10 mL water, shake or vortex (10 sec) - **(not for milk)** Addition of 10 mL ethyl acetate Shake vigorously for 10 min 5.0 ± 0.2 g Na_2SO_4 + 0.2 g C18 + 0.2 g PSA Shake vigorously for 30 min Centrifuge for 6 min at 3000 rpm
Preparation before analysis	Transfer 2 times 1 mL into LC-vials
Analysis	LC-MS/MS + LC-MS-TOF

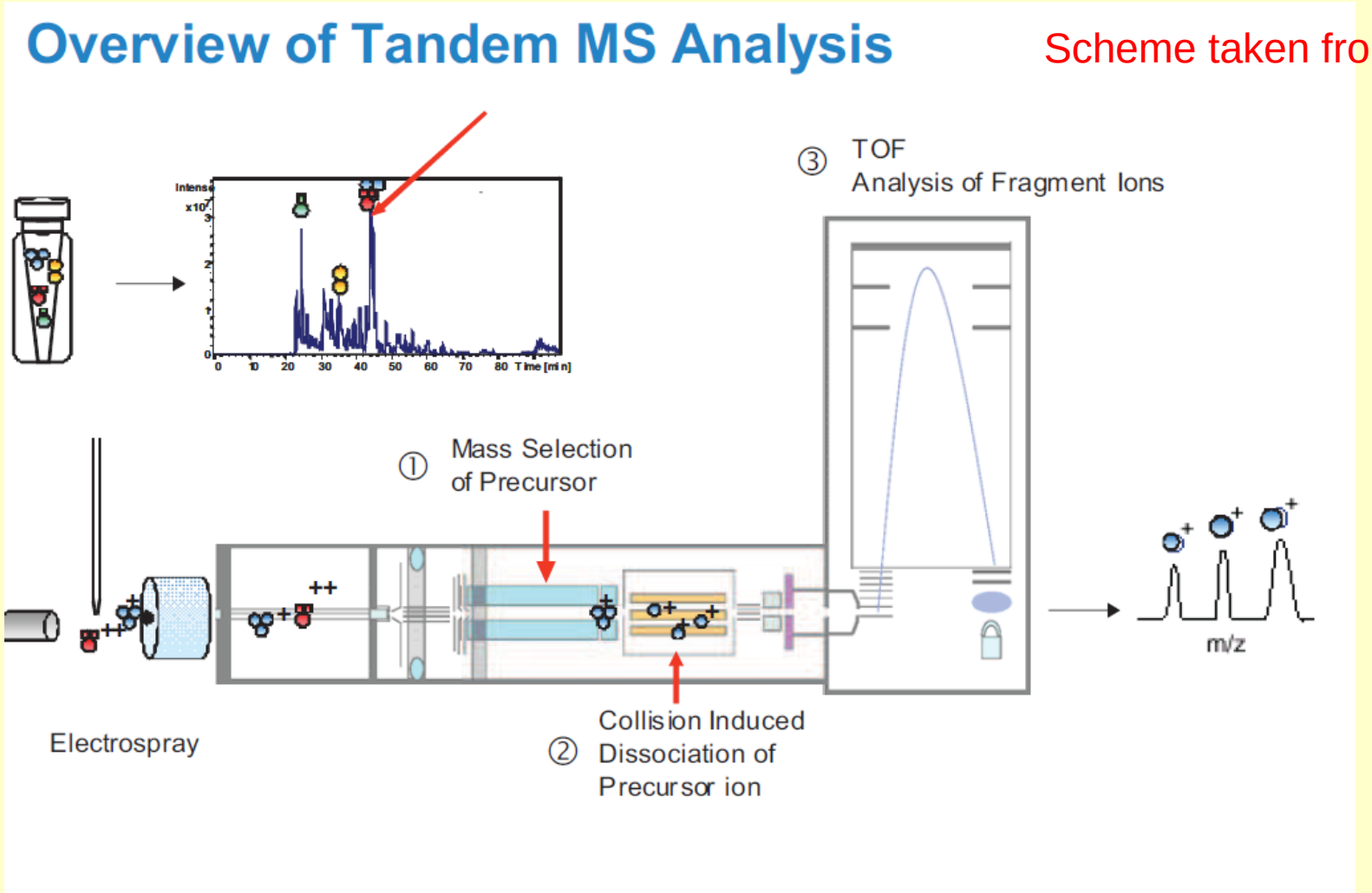
LC-MS-Q-TOF Conditions

- HPLC Methode1290 Series
- Simple method for „all“ analyts
- Injection volume 2 - 5 µl
- Column Zorbax Eclipse Plus C-18 HD, 150 x 2.1mm, 1.8 µm
- Gradient: solvent A = 5 mM NH_4Formiate; solvent B = ACN

Time (min)	% B	Flow (ml)
0	5	0.3
1	5	0.3
30	95	0.3
32.5	95	0.3
33	5	0.3

- Q-TOF Method
  - MSScan (sensitive scan) in 4 GHz-Modus
  - ~~Targeted MSMS (identification)~~
- Data base research (optimized for pesticides)

Workflow Screening



Workflow Screening

EXAMPLE: EXPERIMENTAL DESIGN OF A VALIDATION STUDY

Sample Treatment

- 241 analytes were spiked at 4 different levels

20 Blank matrices

- 10 different samples of hen´s eggs

5 spiking levels

- 0 mg/kg / 0.005 mg/kg / 0.010 mg/kg / 0.020 mg/kg / 0.040 mg/kg

Number of analyses

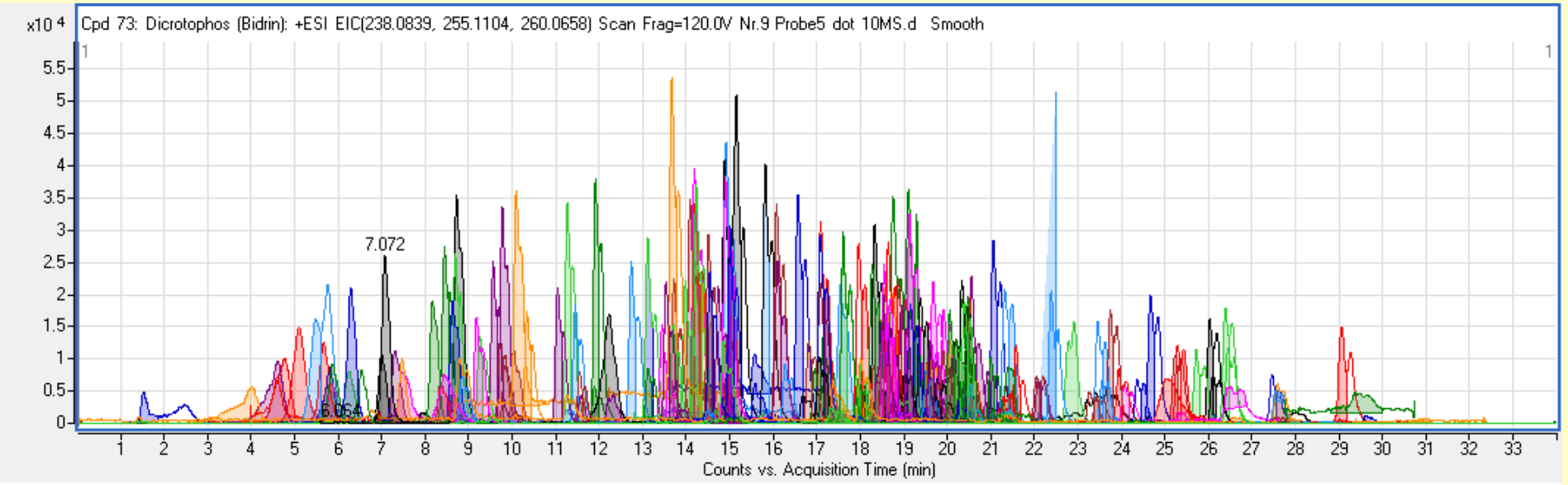
- In total 100 analyses
  (2 replicates of each sample analysed at 5 concentration levels)

QuEChERS clean up

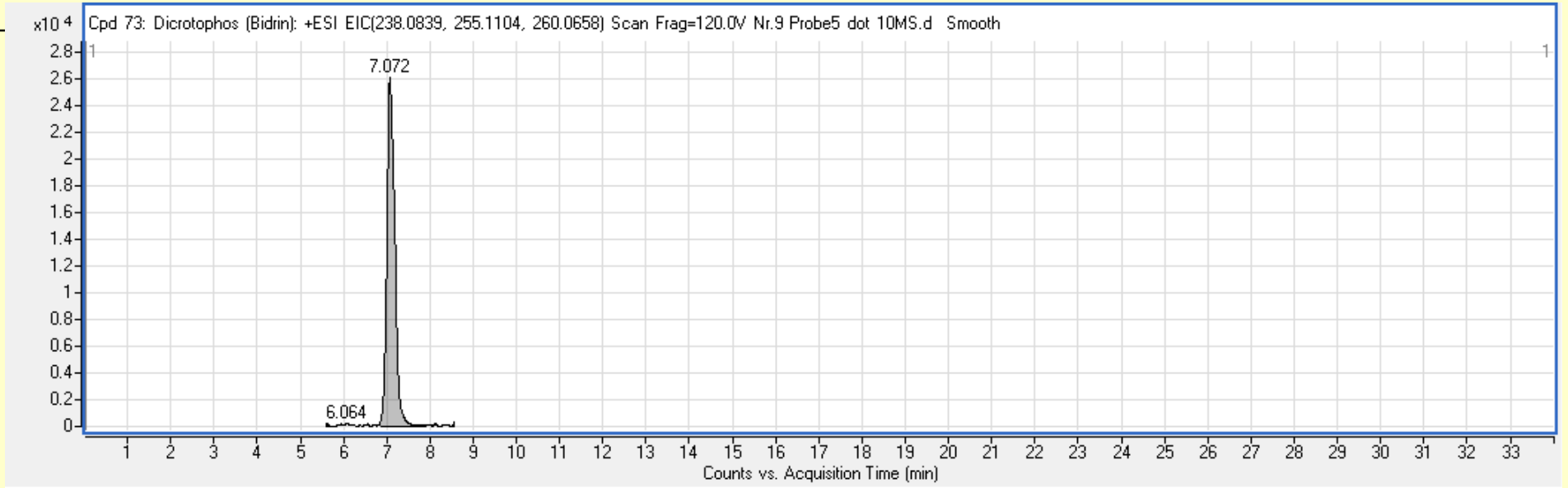
LC-MS-ToF (ESI pos, only)

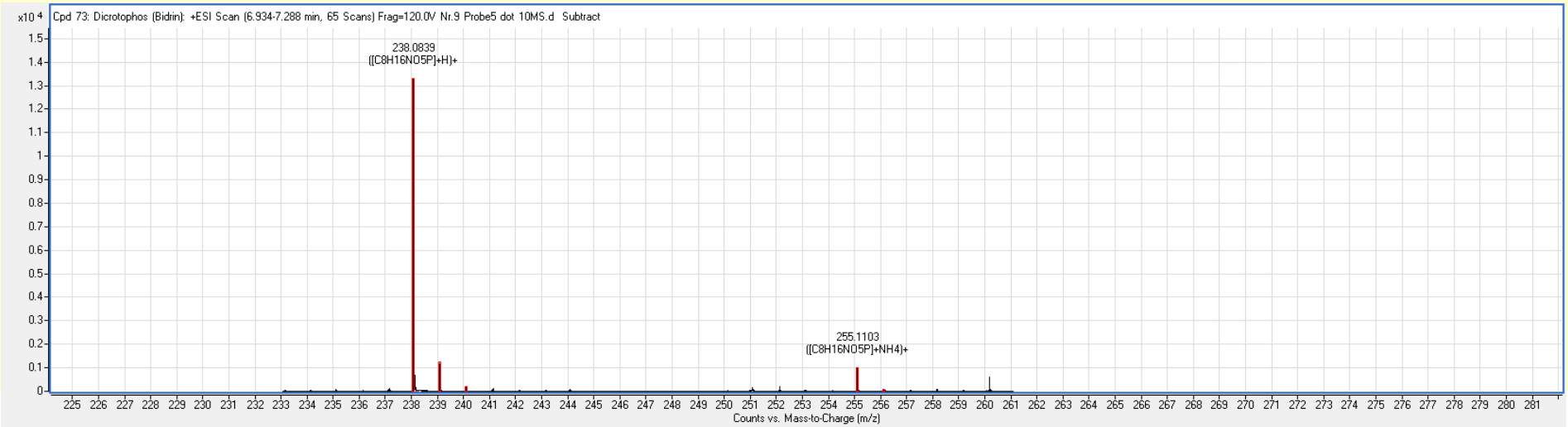
Evaluation against own database

Workflow Screening



Workflow Screening





Results of the Screening Validation Study (Egg)

Spiked Concentration [mg/kg]	**0.005**	**0.010**	**0.020**	**0.040**
Number of pesticides identified (Screening Detection Limit - SDL)	180	194	202	203
Ratio of pesticides identified at the spiked concentration	74.7%	80.5%	83.8%	84.2%

Results of the Screening Validation Study (Egg)

180 Pesticides with an obtained Screening Detection Limit (SDL) of 0.005 mg/kg:

1-(4-Chlorphenyl)urea, 4-Hydroxy-Cyprodinil CGA304075, Acetamiprid, Aldicarb-sulfoxid, Ametryne (Ametrex), Aminocarb, Amitraz-d12 (ISTD), Azoxystrobin, Baycor (Bitertanol), Benalaxyl, Bendiocarb, Benzoximate, Bifenazate (D 2341), Bixafen, Boscalid, Boscalid-M 510F01, Bromuconazole, Bupirimate, Buprofezin, Butafenacil, Butoxycarboxim, Carbaryl, Carbaryl-d7 (ISTD), Carbendazim, Carbendazim-d3 (ISTD), Carbetamid, Carbofuran, Carbofuran-3-hydroxy, Carboxin, Carfentrazone-ethyl, Chlorantraniliprole, Chloroxuron, Chlortoluron, Clethodim, Clofentezin, Clothianidin, Cyazofamid, Cycluron, Cyproconazole, Cyprodinil, Dichlobutrazol (Diclobutrazol), Dicrotophos (Bidrin), Diethofencarb, Difenoconazole, Diflubenzuron, Dimethoat, Dimethomorph, Dimoxystrobin, Diniconazole(I), Dinotefuran, Dioxacarb, Diuron, DMPF, Epoxiconazole, Etaconazole(I), Ethiofencarb, Ethiprole, Ethirimol, Etoxazole, Fenarimol, Fenazaquin, Fenbuconazole, Fenhexamid, Fenoxycarb, Fenpropidin, Fenpropidin-CGA289267, Fenpropimorph, Fenpyroximate, Fenthion-sulfoxide, Fenuron, Fluazifop-buthyl, Flubendiamide, Flufenacet (Fluthiamide) (BAY FOE 5043), Fluometuron, Fluoxastrobin, Fluquinconazole, Flusilazol, Flutolanil, Flutriafol, Forchlorfenuron, Fuberidazole, Furalaxyl, Halofenozide, Haloxyfop, Haloxyfop-ethoxyethyl, Haloxyfop-methyl, Hexaconazole, Hexythiazox, Hydramethylnon, Imazalil, Imidacloprid, Indoxacarb, Iprovalicarb, Isoproturon, Kresoxim, Kresoxim-methyl, Linuron, Malaoxon, Malathion, Mandipropamid, Mefenacet (Rancho), Metalaxyl, Metazachlor, Metconazole, Methabenzthiazuron, Methamidophos (Metamidophos), Methomyl, Methoprotryne, Methoxyfenozid, Metobromuron, Metribuzin, Mevinphos (Phosdrin), Mexacarbate (Zectran), Monocrotophos (Azodrin), Monolinuron (phenylurea), Moxidectin (Cydectin), Myclobutanil, Myclobutanil-RH9090, Neburon (Phosphoramidothioic acid), Nitenpyram, Nuarimol, Omethoat, Oxadixyl, Oxamyl, Paclobutrazole, Penconazole(I), Pencycuron, Pendimethalin, Phosmet, Picoxystrobin, Piperonyl-butoxide, Pirimicarb, Pirimicarb-desmethyl, Pirimiphos-methyl, Prochloraz, Promecarb, Propamocarb, Propargite, Propiconazole, Propoxur, Pymetrozine, Pyracarbolid, Pyraclostrobin, Pyridaben, Pyrimethanil, Pyriproxyfen, Quinoxyfen, Rotenone, Secbumeton, Siduron, Simetryn, Spinosyn A, Spirodiclofen, Spiromesifen, Spirotetramat-BYI03380-enol, Spirotetramat-BYI03380-monohydroxy, Spiroxamin, Sulfentrazone, Tebufenozid, Tebufenpyrad, Tebuthiuron, Temephos (Abate), Terbumeton, Terbutryn, Tetraconazole, Thiabendazole, Thiabendazole-5-hydroxy, Thiacloprid, Thiamethoxam, Thidiazuron, Thiophanate-methyl, Triadimefon, Triadimenole, Tricyclazole, Trifloxystrobin, Triflumizole, Triflumizol-FM-6-1, Vamidothion, Zoxamide

Results of the Screening Validation Study (Egg)

14 Pesticides with an obtained Screening Detection Limit (SDL) of 0.010 mg/kg:

Chlorfluazurone, Doramectin, Flonicamid, Flufenoxuron, Formetanate, Isoprocarb, Mepanipyrim, Mepronil, Metaflumizone, Phoxim, Spirotetramat, Tebuconazole, Trichlorfon, Triflumuron

8 Pesticides with an obtained Screening Detection Limit (SDL) of 0.020 mg/kg:

Aldicarb, Avermectin B1a, Cymoxanil (Curzate), Etofenprox, Fenthion, Isocarbophos, Ivermectin B1a, Spinetoram

1 Pesticide with an obtained Screening Detection Limit (SDL) of 0.040 mg/kg:

Fenthion-sulfon

7 Pesticides with no final Screening Detection Limit (SDL):

Prothioconazole (11 hits), Desmedipham (12), Spinosyn D (13, level 0.007 mg/kg), DMF (13, spiked was Amitraz), Methiocarb (14, all levels), Acibenzolar-S-methyl (CGA 245704) (17), Fenobucarb (Baycarb) (18, levels 10, 20, 40)

Results of the Screening Validation Study (Egg)

31 Pesticides with no detects under the conditions of the validation study:

4-Hydroxy-Chlorthalonil, Acephate, Alanycarb, Aldicarb-sulfone (Aldoxycarb), Amitraz, Benfuracarb, Carbofuran-3-hydroxy, Chlorpropham, Cyromazine, Emamectin-benzoate, Ethofumesate, Famoxadon, Fenamidone, Fipronil, Fipronil-sulfid, Fipronil-sulfon, Fluazinam (Shirlan), Fludioxonil, Furathiocarb, Hexaflumuron, Ioxynil, Ipconazole(I), Lufenuron, Mesotrione, Novaluron, Phenmedipham, Prometon, Prometryn, Propham, Teflubenzuron, Thiobencarb

Screening with LC-HRMS in Pesticides Residue Analysis

Useful tool to improve the scope of pesticide analysis

Remove rarely detected analytes from the quantifying detection system (LC-QQQ)

Include analytes with SDL above need cut offs (e.g. MRL values) into LC-QQQ methods, instead.

„Real“ unknown screening (e.g. find by formular)

- Time consuming (and often frustrating)
  - For identification: standards needed
  - For screening: knowledge of retention time important

Identification

Quantification

Identification

Semi-Quantification

New

Methodology

Complementary

GC-HRMS NEGATIVE CHEMICAL IONIZATION

1
- Experimental conditions
- Compounds analyzed
- Mass accurate *homemade* database

2
- Operational parameters
- Automated searching parameters

} Optimization

3
- Analytical parameters evaluated: a new combined criteria for detection. Typical mass accuracy
- Real samples

1. Experimental conditions

Injection volume: 2 µL

Mode: Splitless MM Inlet

Inyector temperature: 280 ºC

Agilent 7200 Q-TOF GC/MS

OVEN PROGRAM

Rate (ºC/min)	Value (ºC)	Hold Time (min)	Run Time (min)
	60	1	1
40	120	0	2.5
5	310	0	40.5

Post Run Time: 2 min

Post Run temperature: 310 ºC

BACKFLUSHING CAPABILITIES

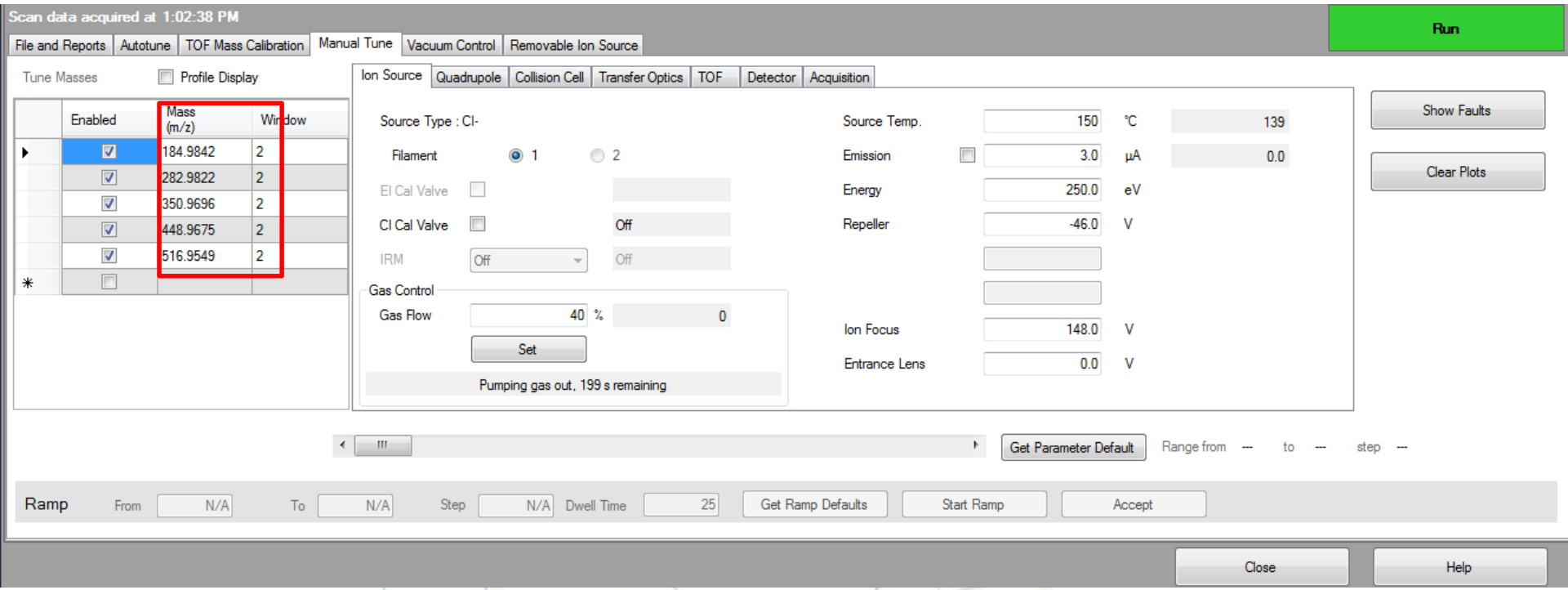
Retention time locked with constant flow

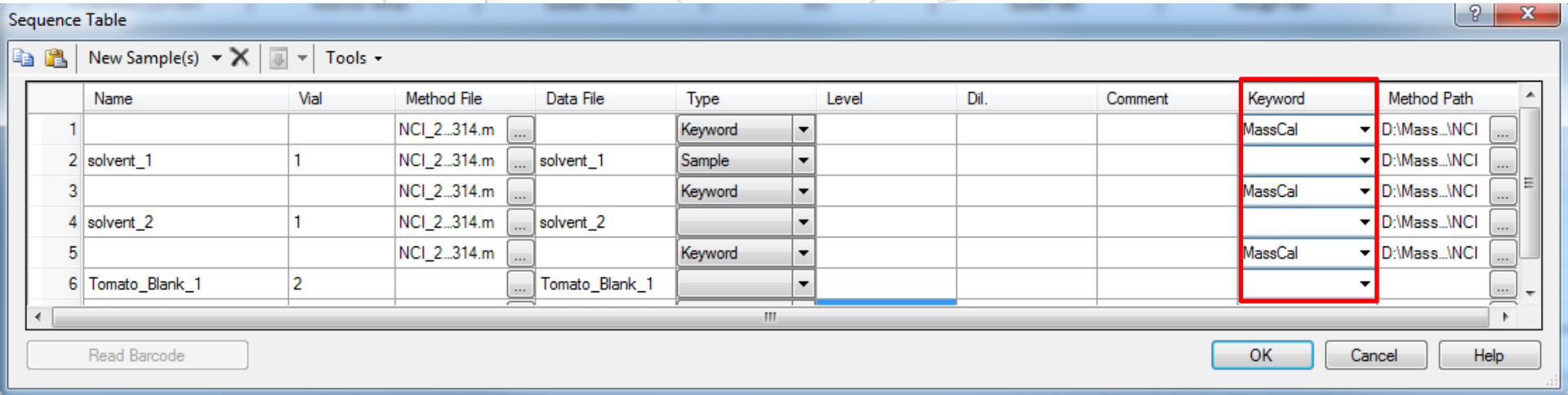
Chemical Ionization
Acquisition in full scan at 4 GHz

Ion source temperature: 150 ºC

Transfer line temperature: 280 ºC

TOF mass calibration





Compounds analyzed

#	Compound
1	Trifluralin
2	Dicloran
3	Lindane (HCH-Gamma)
4	Fonofos
5	Propyzamide
6	Chlorothalonil
7	Tefluthrin
8	Parathion-Methyl
9	Chlorpyriphos-Methyl
10	Vinclozolin
11	Tolclofos-Methyl
12	Heptachlor
13	Malaoxon
14	Fenitrothion
15	Dichlofluanid
16	Malathion
17	Chlorpyriphos
18	Parathion
19	Tetraconazole
20	Pendimethalin
21	Pyrifenox I
22	Tolylfluanid

#	Compound
23	Chlozolinate
24	Chlorfenvinphos
25	Fipronil
26	Chinomethionat
27	Methidathion
28	Pyrifenox II
29	Endosulfan alpha
30	Tetrachlorvinphos
31	Hexaconazole
32	Prothiofos
33	Dieldrin
34	Myclobutanil
35	Bupirimate
36	Chlorfenapyr
37	Endosulfan beta
38	Ethion
39	Ofurace
40	Carbophenothion
41	Quinoxyfen
42	Endosulfan Sulfate
43	Fenhexamid

#	Compound
44	Propiconazole
45	Trifloxystrobin
46	Nuarimol
47	Iprodione
48	Phosmet
49	Bifenthrin
50	Fenpropathrin
51	Bifenox
52	Tetradifon
53	Phosalone
54	Lambda-Cyhalothrin
55	Fenarimol
56	Pyrazophos
57	Acrinathrin
58	Pyridaben
59	Fluquinconazole
60	Cypermethrin
61	Flucythrinate I
62	Flucythrinate II
63	Fluvalinate-tau
64	Azoxystrobin

Accurate mass *homemade* database

#	Compound	Rt (min)	Exact Mass	Molecular Formula
1	Trifluralin*, **	13.888	335.1093	C13H16F3N3O4
2	Dicloran*	14.706	205.9650	C6H4Cl2N2O2
	Dicloran cluster		207.9622	C6H4Cl2N2O2
3	Lindane (HCH-Gamma)*	15.523	252.8912	C6H6Cl5
	Lindane (HCH-Gamma) cluster		254.8883	C6H6Cl5
4	Fonofos*	15.894	168.9911	C4H10OPS2
	Fonofos F1		109.0112	C6H5S
5	Propyzamide*	15.934	255.0218	C12H11Cl2NO
	Propyzamide F1		187.9670	C7H4Cl2NO
6	Chlorothalonil*	16.645	263.8816	C8Cl4N2
	Chlorothalonil cluster		265.8787	C8Cl4N2
	Chlorothalonil F1		229.9205	C8Cl3N2
7	Tefluthrin*	16.831	241.0243	C9H9O2ClF3
	Tefluthrin F1		205.0476	C9H8F3O2
8	Parathion-Methyl*	18.039	153.9963	C6H4NO2S
	Parathion-Methyl F1		263.0017	C8H10NO5PS
9	Chlorpyriphos-Methyl*	18.053	211.8895	C5HCl3NS
	Chlorpyriphos-Methyl F1		140.9775	C2H6O3PS

*** Quantifier ion**

**** Compounds fully identified with MSMS experiment**

2. Operational parameters in full scan stage

- Acquisition speed:

Black = 2 spectrum sec^{-1}

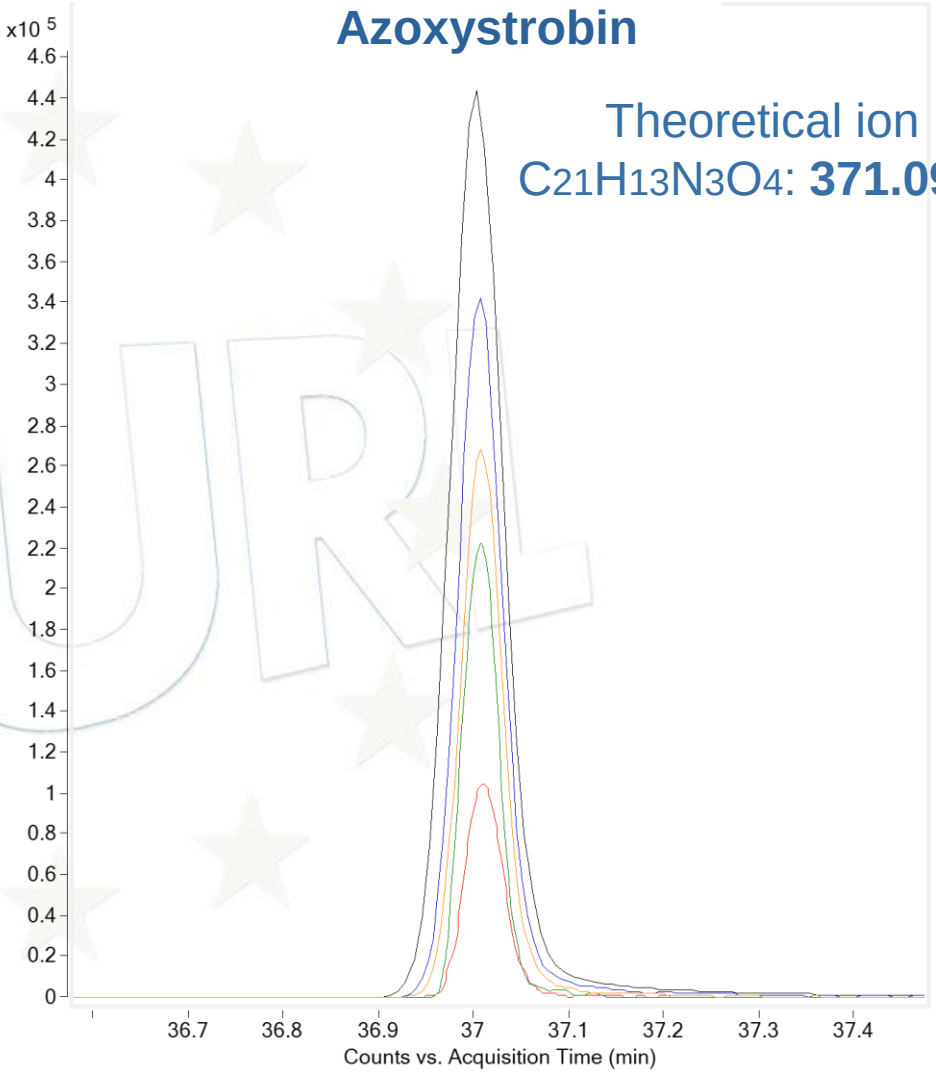
Blue = 3 spectrum sec^{-1}

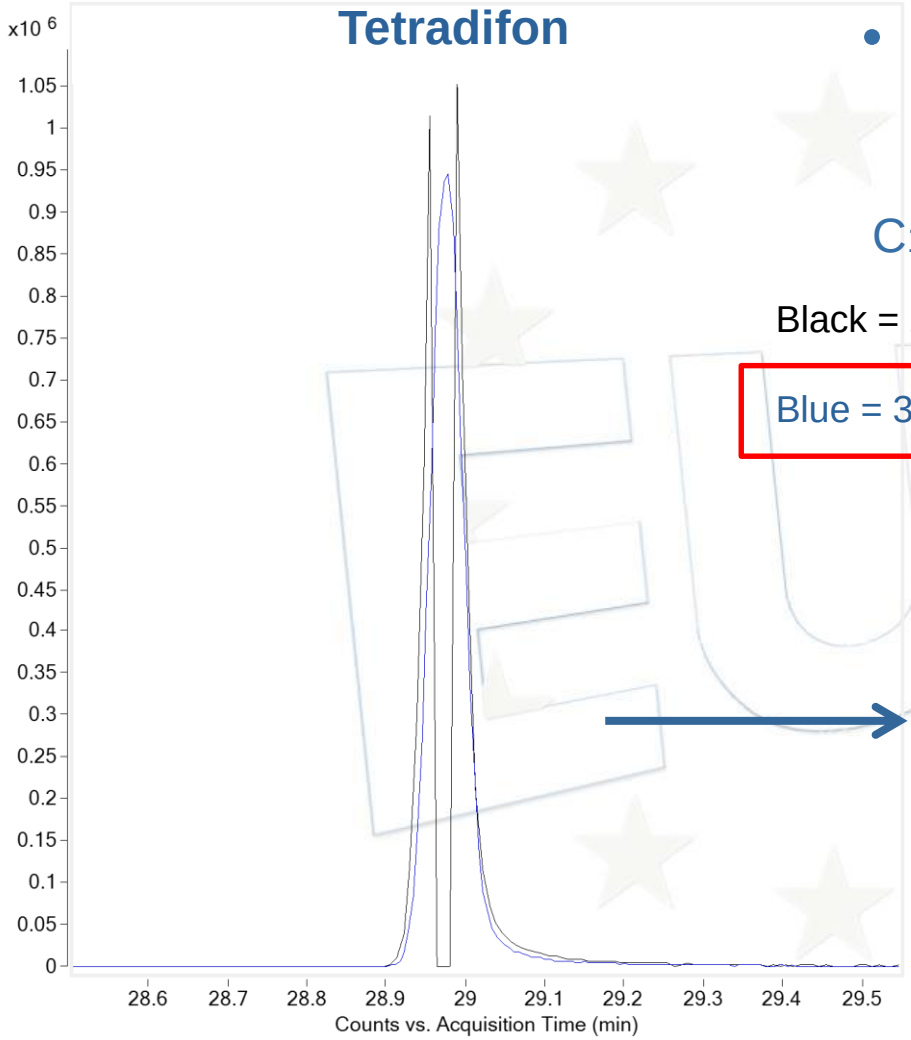
Orange = 4 spectrum sec^{-1}

Green = 5 spectrum sec^{-1}

Red = 10 spectrum sec^{-1}

Sensitivity





- Acquisition speed in full scan

Theoretical ion
$C_{12}H_5Cl_3O_2S$: 317.9081

Black = 2 spectrum sec^{-1}

Blue = 3 spectrum sec^{-1}

→ Saturation phenomenon!

Acquisition speed= 3 spectrum sec^{-1}

As expected, at major concentrations, saturation phenomena is evidenced.

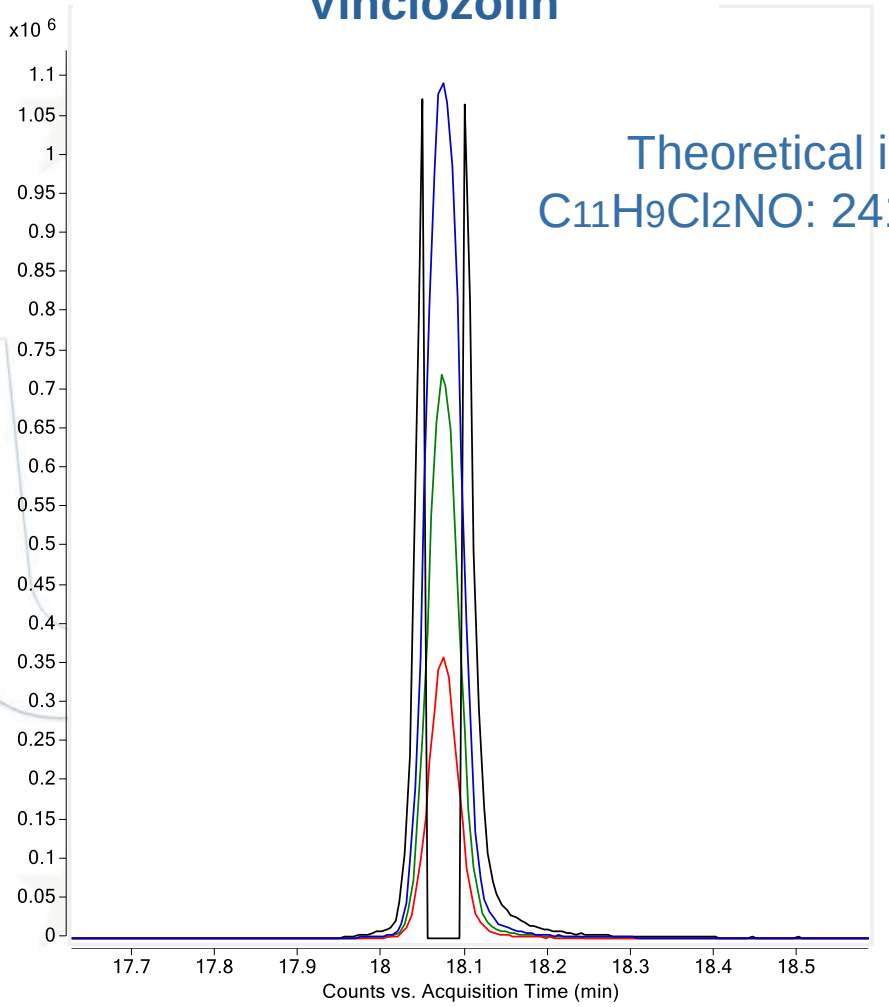
Black = 50 µg kg^{-1}

Blue = 20 µg kg^{-1}

Green = 10 µg kg^{-1}

Red = 5 µg kg^{-1}

Vinclozolin

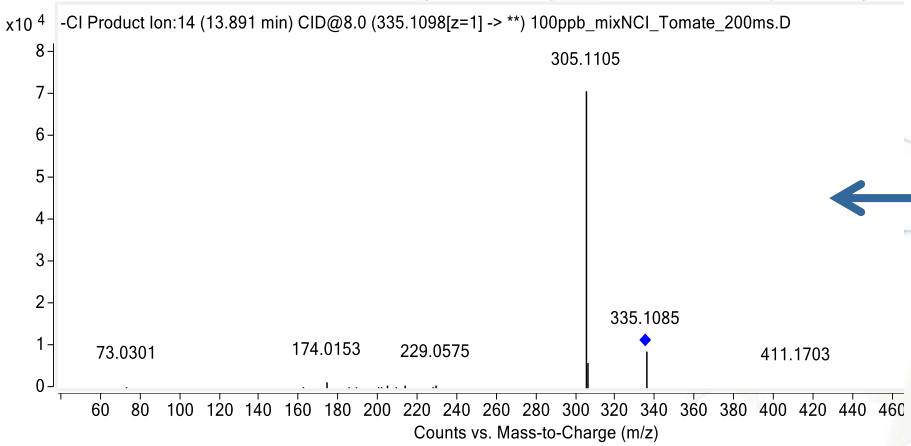


Theoretical ion $C_{11}H_9Cl_2NO$: 241.0061

2. Operational parameters in MSMS stage

- Quadrupole: medium MS resolution
- Speed of acquisition in MSMS experiments: 20, 100 and 200 ms spectrum^{-1} were evaluated.

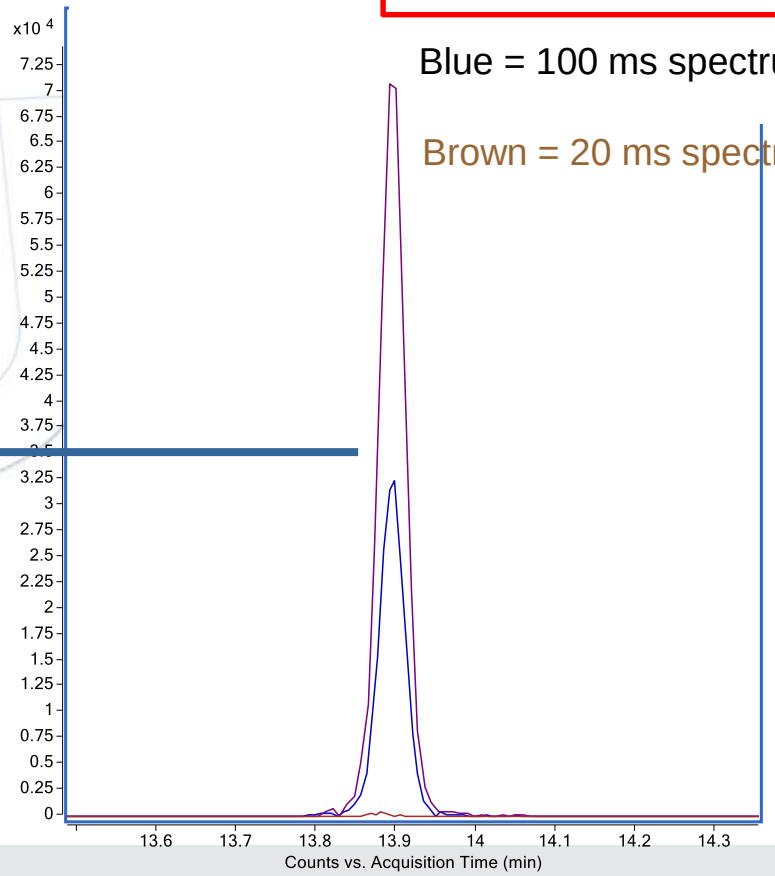
Trifluralin: 335.1098>>305.1118



Purple = 200 ms spectrum^{-1}

Blue = 100 ms spectrum $^{-1}$

Brown = 20 ms spectrum $^{-1}$



Compounds optimized in MS/MS

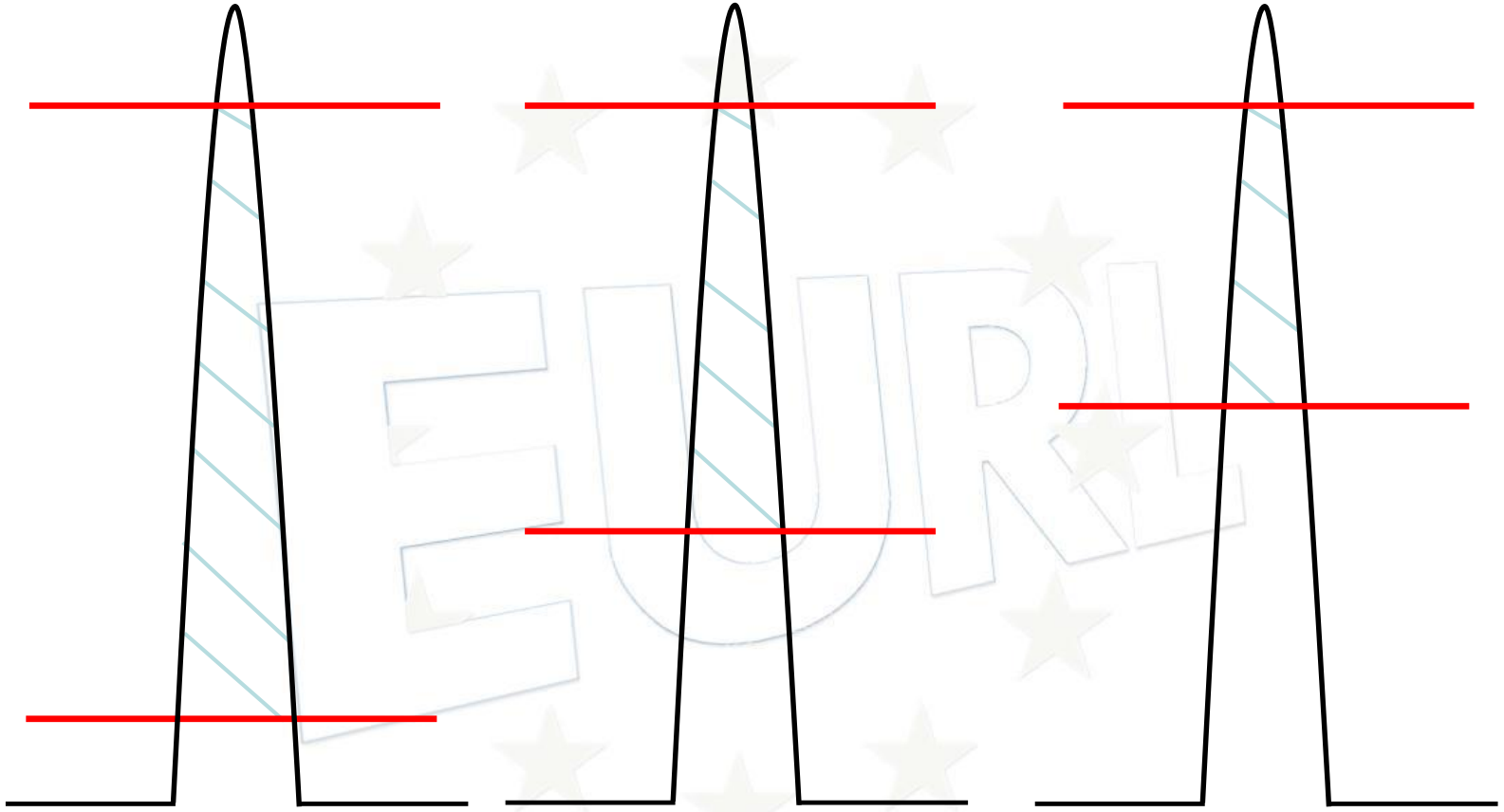
#	Compound	Rt (min)	Precursor ion (m/z)	Product ion (m/z)	Molecular Formula	CE (eV)	Error (ppm) at 10 µg kg^{-1}
1	Trifluralin	13.888	335.1093	305.1113	C13H16F3N2O3	8	1.3
16	Malathion	19.604	156.9547	141.9317	CH3O2PS2	20	8.5
19	Tetraconazole	20.320	116.9964	96.9901	C2F3O	5	7.2
20	Pendimethalin	21.137	281.1376	251.1396	C13H19N2O3	8	6.8
22	Tolylfluanid	21.322	212.0624	168.0119	C7H6NO2S	10	4.8
30	Tetrachlorvinphos	22.488	125.0004	78.9585	O3P	20	0.0
27	Methidathion	22.044	156.9547	141.9317	CH3O2PS2	20	3.5
39	Ofurace	25.739	245.1052	126.0191	C5H4NO3	10	7.9
45	Trifloxystrobin	26.433	190.0509	158.0242	C9H4NO2	8	1.9
50	Fenpropathrin	28.460	141.0916	97.1022	C7H13	10	0.0

Collisson energies were optimized
Trials with 3, 5, 8, 10, 20 and 30 eV were evaluated

2. Data processing method: automated searching parameter

- Masses tolerance: ± 10 ppm
- Retention time tolerance: ± 0.2 min
- Extract EIC and cleaned spectrum
- Exclude if above 10 % of saturation
- Average scans > 50 % of peak height
- Extract MS/MS spectrum per CE with precursor tolerance ± 10 ppm

Exclude if above 10% of saturation



Average scans
>10% of peak height

Average scans
>35% of peak height

Average scans
>50% of peak height

3. Analytical parameters evaluated

LOD: detection limits

Criteria of detection:

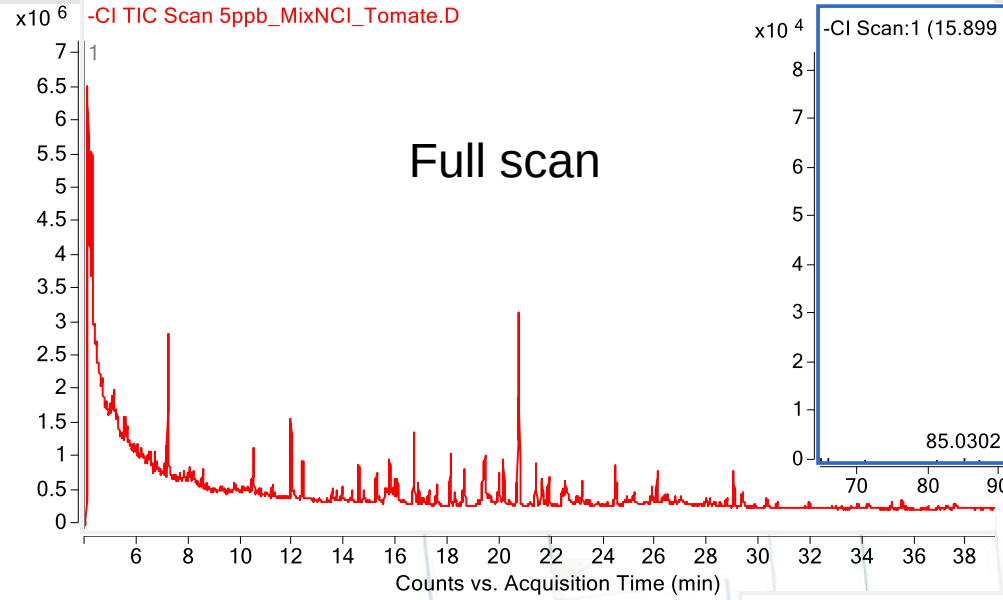
In the case of pesticides fully identified with full scan:

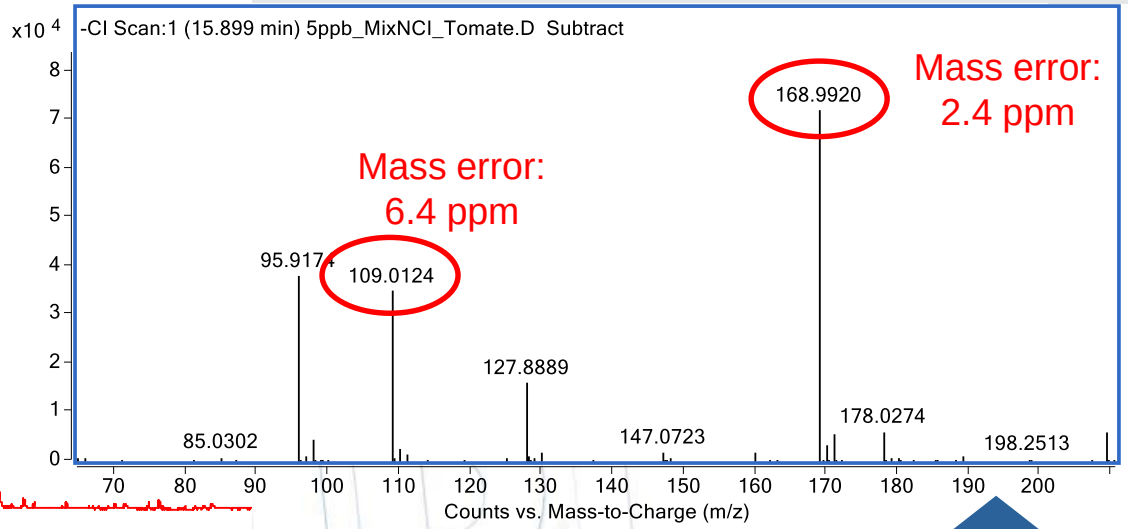
a) The two selected ions had to be present.

b) A signal-to-noise ratio higher than 3 for each ion.

c) At least one diagnostic ion with mass accuracy less than 5 ppm.

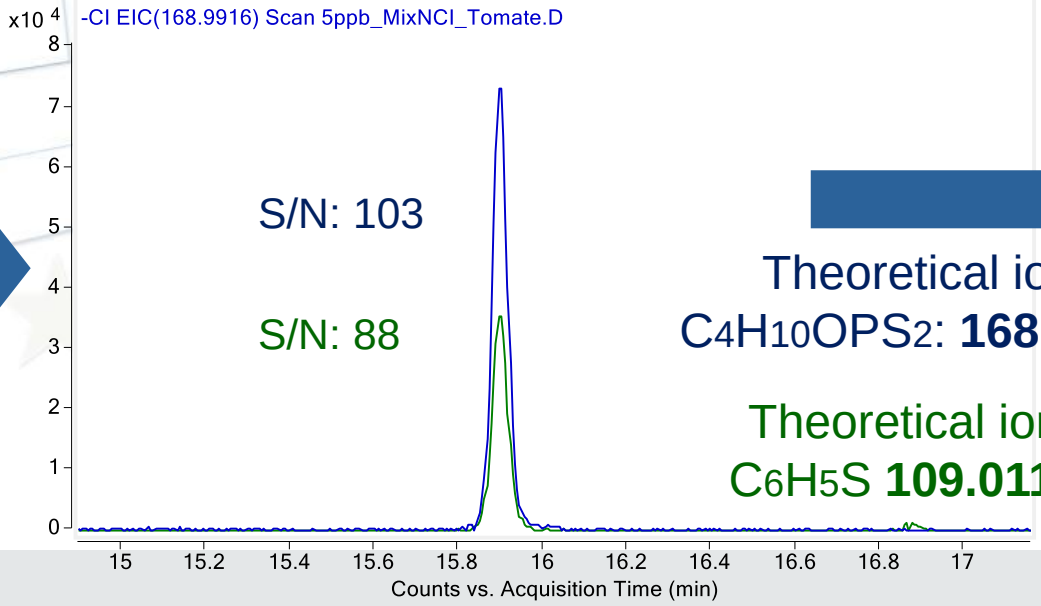
Example: **Fonofos** at 5 µg kg^{-1} in tomato





EIC

Theoretical ions ± 10 ppm



Theoretical ion
$C_4H_{10}OPS_2$: **168.9916**

Theoretical ion
C_6H_5S **109.0117**

3. Analytical parameters evaluated

LOD: detection limits

Criteria of detection:

In the case of other pesticides

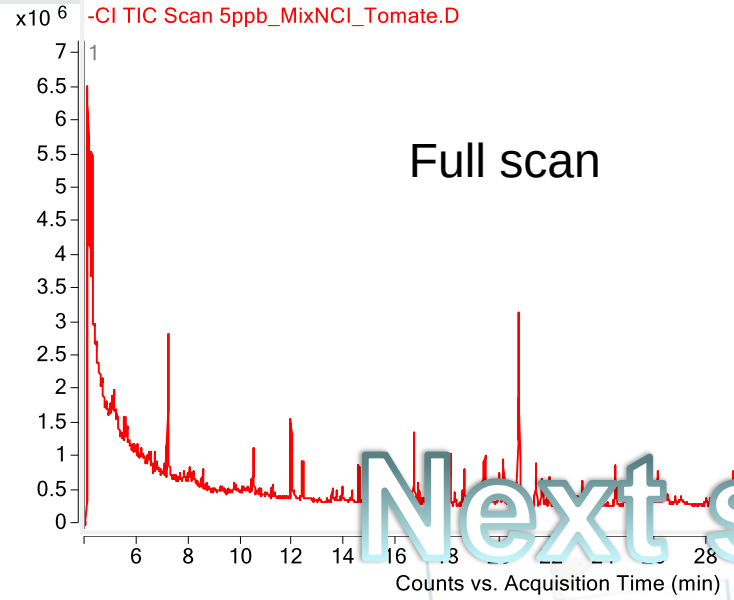
a) The selected ion in full scan had to be present.

b) A signal-to-noise ratio higher than 3.

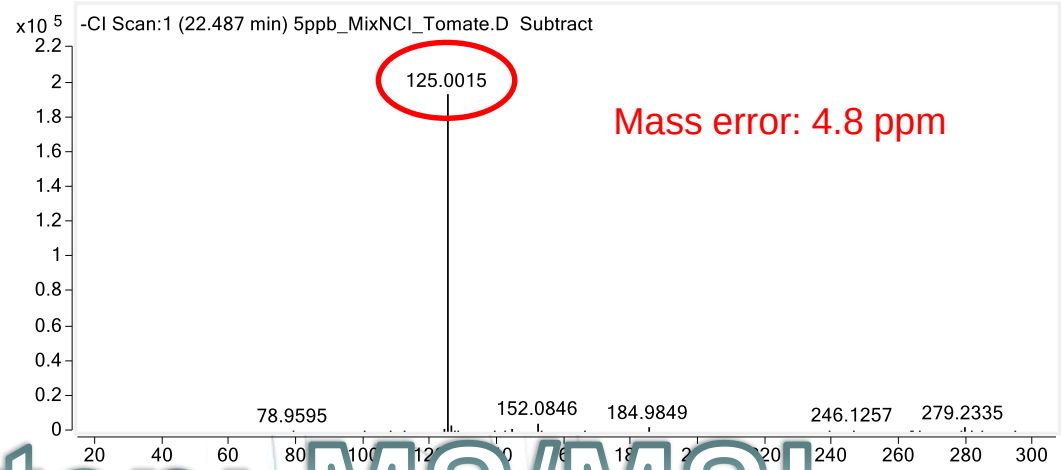
c) The presence of the transition in MSMS experiment is needed

d) At least one diagnostic ion with mass accuracy less than 5 ppm.

Example: **Tetrachlorvinphos** at 5 µg kg^{-1} in tomato



Full scan

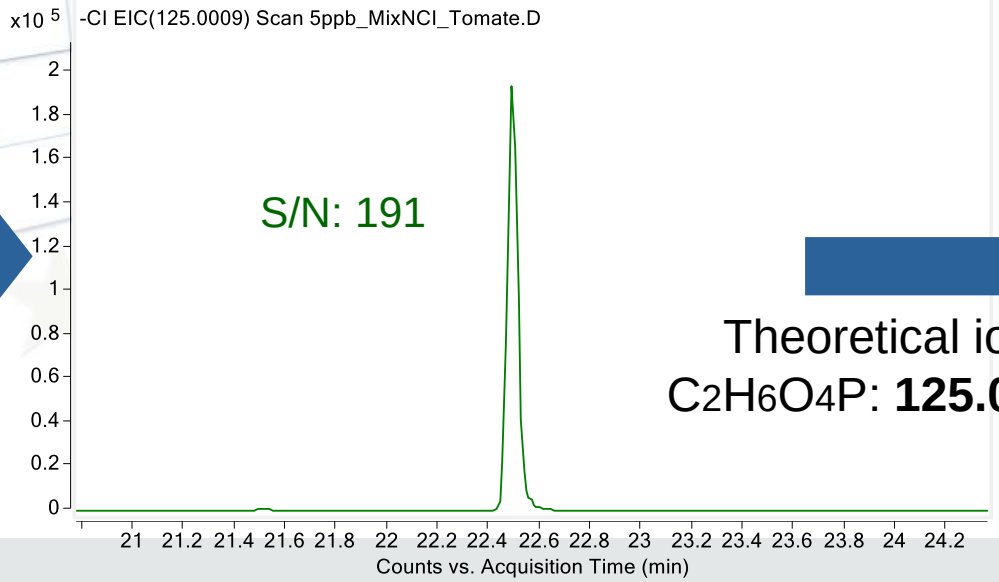


Mass error: 4.8 ppm

Next step: MS/MS!

EIC

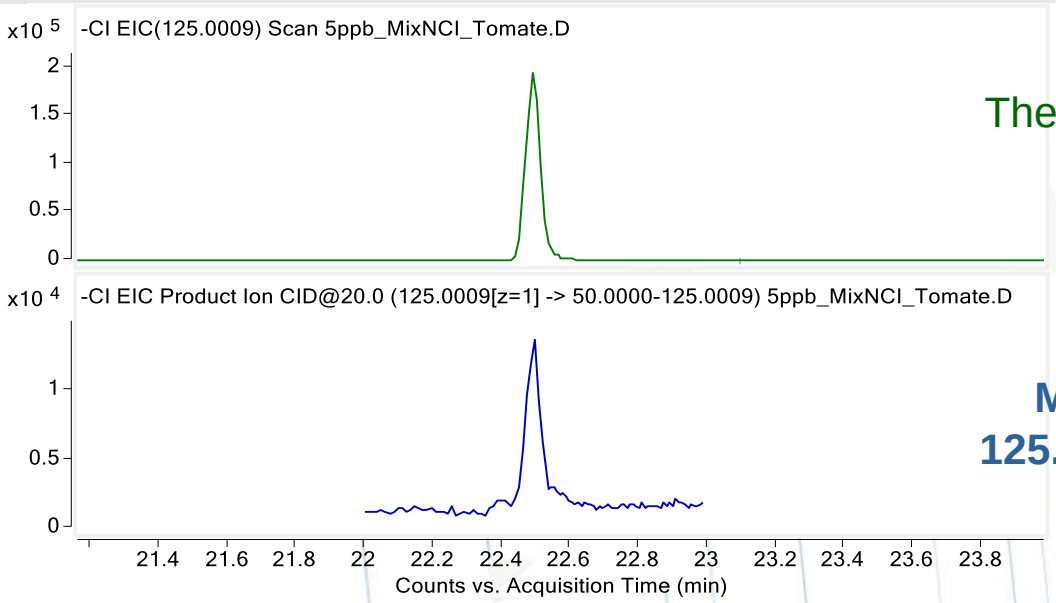
Theoretical ion ± 10 ppm



S/N: 191

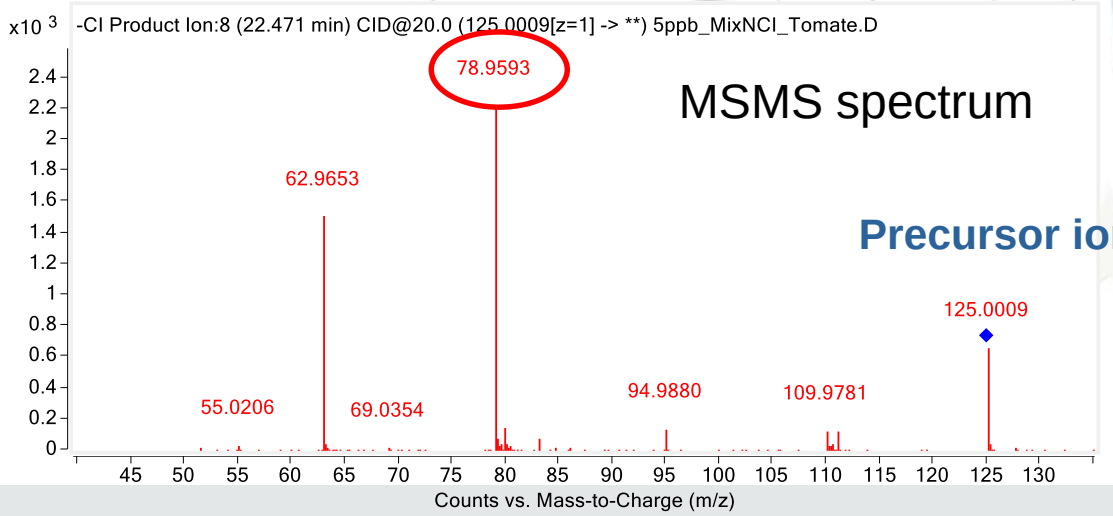
Theoretical ion $C_2H_6O_4P$: **125.0009**

Example: **Tetrachlorvinphos** at 5 µg kg^{-1} in tomato



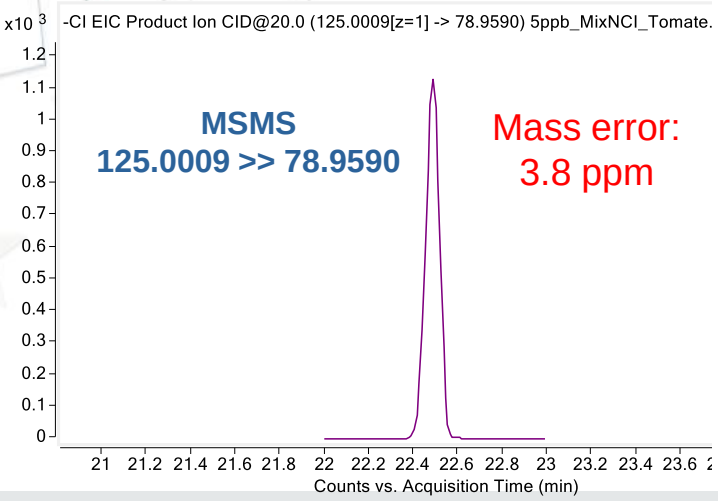
Theoretical ion**125.0009**
from **full scan**

MSMS experiment:
125.0009 >> 50-125.0009



MSMS spectrum

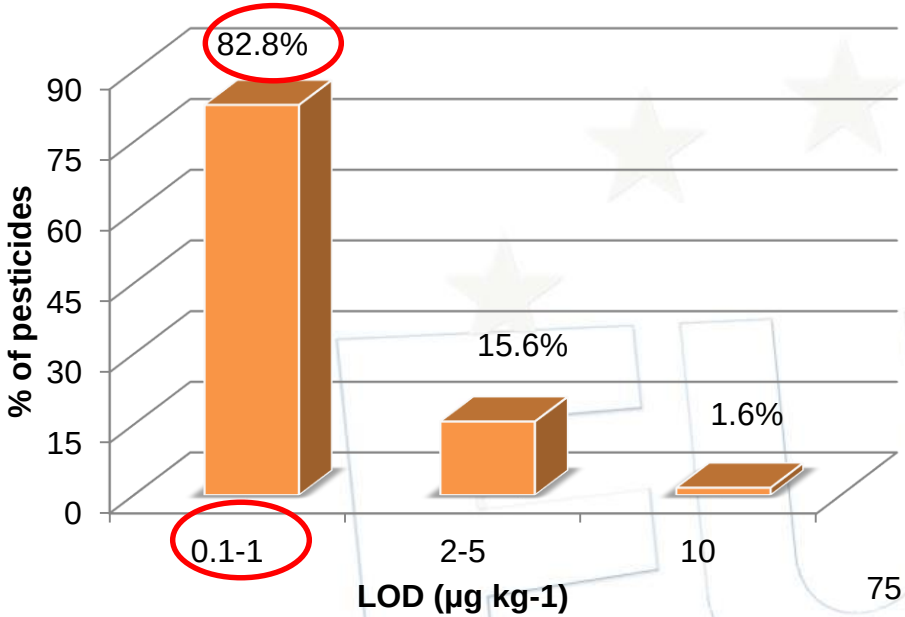
Precursor ion



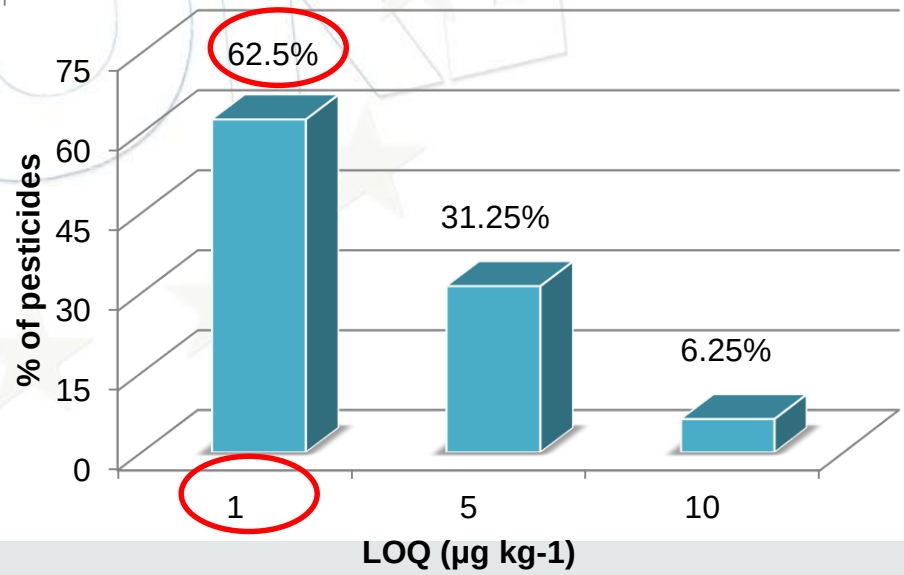
MSMS
125.0009 >> 78.9590

Mass error:
3.8 ppm

LODs


82.8%
15.6%
1.6%
90
75
60
45
30
15
0
% of pesticides
0.1-1
2-5
10
LOD (µg kg-1)

LOQs


62.5%
31.25%
6.25%
75
60
45
30
15
0
% of pesticides
1
5
10
LOQ (µg kg-1)

Linearity

Compound	Linear Range (ug/kg)	R^2
Trifluralin	5-20	0.9996
Dicloran	1-50	0.9973
Lindane	5-500	0.9996
Fonofos	1-20	0.9992
Propyzamide	5-500	0.9998
Chlorothalonil	1-10	0.9914
Tefluthrin	5-20	0.9980
Parathion-Me	1-200	0.9967
Chlorpyriphos-Me	1-50	0.9999
Vinclozolin	1-20	0.9938
Tolclofos-Methyl	1-200	0.9940
Heptachlor	10-200	0.9958
Malaoxon		
Fenitrothion	1-100	0.9991
Dichlofluanid	5-200	0.9969
Malathion	5-50	0.9992
Chlorpyriphos	1-50	0.9998
Parathion	1-200	0.9922
Tetraconazole	1-100	0.9972
Pendimethalin	5-200	0.9977
Pyrifenox I	5-500	0.9998
Tolylfluanid	5-10	1.0000

Compound	Linear Range (ug/kg)	R^2
Chlozolinate	5-20	0.9892
Chlorfenvinphos	5-20	0.9989
Fipronil	1-100	0.9978
Chinomethionat	1-10	0.9995
Methidathion	1-500	0.9949
Pyrifenox II	5-500	0.9999
Endosulfan alpha	1-200	0.9939
Tetrachlorvinphos	5-10	1.0000
Hexaconazole	1-100	0.9991
Prothiofos	1-50	0.9999
Dieldrin	1-200	0.9966
Myclobutanil	10-500	0.9931
Bupirimate	1-100	0.9995
Chlorfenapyr	1-20	0.9992
Endosulfan beta	1-500	0.9914
Ethion	1-20	0.9996
Ofurace	5-500	0.9998
Carbophenothion	1-20	0.9995
Quinoxyfen	5-200	0.9995
Endosulfan Sulfate	1-100	0.9988
Fenhexamid	5-500	0.9974

Compound	Linear Range (ug/kg)	R^2
Propiconazole	10-500	0.9994
Trifloxystrobin	10-200	0.9984
Nuarimol	5-500	0.9982
Iprodione	1-500	0.9963
Phosmet	1-50	0.9991
Bifenthrin	1-200	0.9998
Fenpropathrin	5-50	0.9999
Bifenox	1-50	0.9965
Tetradifon	1-20	0.9983
Phosalone	1-20	0.9992
λ-Cyhalothrin	1-50	0.9987
Fenarimol	1-500	0.9999
Pyrazophos	5-500	0.9963
Acrinathrin	1-20	0.9997
Pyridaben	1-200	0.9995
Fluquinconazole	1-200	0.9995
Cypermethrin	5-500	0.9990
Flucythrinate I	1-200	0.9988
Flucythrinate II	1-200	0.9995
Fluvalinate-tau	1-100	0.9995
Azoxystrobin	1-500	0.9994

Typical mass error of quantifier ion at 5 and 10 µg/kg in Tomato

Compound	Rt (min)	Exact Mass	Molecular Formula	Mass error (5µg kg^{-1})	Mass error (10µg kg^{-1})
Trifluralin	13.888	335.1093	C13H16F3N3O4	1.2	4.1
Dicloran	14.706	205.9650	C6H4Cl2N2O2	1.3	4.4
Lindane (HCH-Gamma)	15.523	252.8912	C6H6Cl5	0.0	5.4
Fonofos	15.894	168.9911	C4H10OPS2	1.4	4.9
Propyzamide	15.934	255.0218	C12H11Cl2NO	1.1	2.5
Chlorothalonil	16.645	263.8816	C8Cl4N2	2.5	2.5
Tefluthrin	16.831	241.0243	C9H9O2ClF3	3.3	2.5
Parathion-Methyl	18.039	153.9963	C6H4NO2S	2.8	3.7
Chlorpyriphos-Methyl	18.053	211.8895	C5HCl3NS	4.0	2.4
Vinclozolin	18.063	241.0061	C11H9Cl2NO	5.1	1.4
Tolclofos-Methyl	18.216	249.9620	C8H8ClO3PS	3.4	1.5
Heptachlor	18.246	263.9067	C10H4Cl4	3.8	0.3
Fenitrothion	19.118	168.0119	C7H6NO2S	2.1	2.8
Dichlofluanid	19.388	155.0041	C6H5NO2S	1.9	3.0
Malathion	19.604	156.9547	C2H6PO2S2	0.4	5.5
Chlorpyriphos	19.939	312.9496	C9H10Cl2NO3PS	3.4	0.7
Parathion	19.962	169.0088	C4H10O3PS	1.6	3.3
Tetraconazole	20.32	116.9964	C2HF4O	4.0	3.1
Pendimethalin	21.137	281.1376	C13H19N3O4	3.4	1.0
Pyrifenox I	21.299	226.0298	C13H7ClN2	2.4	2.4
Tolylfluanid	21.322	212.0619	C9H12N2O2S	0.7	0.1
Chlozolinate	21.354	287.0116	C12H11Cl2NO3	3.3	0.8
Chlorfenvinphos	21.506	153.0317	C4H10PO4	1.3	3.7
Fipronil	21.593	330.9668	C11H3ClF3N4OS	3.0	1.0
Chinomethionat	21.845	205.9972	C9H6N2S2	5.2	0.8
Methidathion	22.044	156.9547	C2H6PO2S2	1.1	4.1
Pyrifenox II	22.251	226.0298	C13H7ClN2	2.4	2.2
Endosulfan alpha	22.38	239.9067	C8H4Cl4	3.5	1.0
Tetrachlorvinphos	22.488	125.0004	C2H6O4P	2.7	3.8
Hexaconazole	22.972	221.0356	C10H8ClN3O	3.3	2.5

Compound	Rt (min)	Exact Mass	Molecular Formula	Mass error (5µg kg^{-1})	Mass error (10µg kg^{-1})
Prothiofos	23.139	236.9002	C7H3Cl2OS2	3.5	0.3
Dieldrin	23.332	234.8443	C5Cl5	2.0	1.4
Myclobutanil	23.683	288.1142	C15H17ClN4	-	0.3
Bupirimate	23.97	124.0068	C2H6NO3S	0.2	2.2
Chlorfenapyr	24.407	346.9198	C12H4BrClF3N2	1.8	1.1
Endosulfan beta	24.465	403.8169	C9H6Cl6O3S	1.2	1.4
Ethion	25.141	184.986	C4H10O2PS2	0.1	0.3
Ofurace	25.739	245.1052	C14H15NO3	3.4	3.7
Carbophenothion	25.837	184.986	C4H10O2PS2	3.6	5.9
Quinoxyfen	25.983	271.02	C15H7ClFNO	3.7	0.6
Endosulfan Sulfate	26.027	383.8351	C9H5Cl5O4S	3.0	0.4
Fenhexamid	26.132	265.087	C14H16ClNO2	5.0	0.8
Propiconazole	26.348	256.0044	C10H8Cl2N3O	0.9	2.1
Trifloxystrobin	26.433	190.0504	C10H8NO3	0.2	1.0
Nuarimol	26.714	278.0855	C17H11FN2O	2.8	0.5
Iprodione	27.747	301.0385	C12H13Cl2N3O2	0.9	0.6
Phosmet	27.92	156.9547	C2H6O2PS2	0.2	1.7
Bifenthrin	28.27	205.0471	C9H8F3O2	5.6	2.9
Fenpropathrin	28.46	141.0916	C8H13O2	1.3	0.6
Bifenox	28.694	340.9858	C14H9Cl2NO5	1.0	0.5
Tetradifon	28.971	317.9076	C12H5Cl3O2S	2.2	0.0
Phosalone	29.335	184.986	C4H10O2PS2	0.8	4.7
Lambda-Cyhalothrin	30.222	205.0476	C9H8F3O2	1.5	0.7
Fenarimol	30.266	294.056	C17H11ClN2O	2.4	0.2
Pyrazophos	30.609	169.0088	C4H10O3PS	1.4	2.2
Acrinathrin	30.653	333.0562	C12H11F6O4	1.0	0.4
Pyridaben	31.74	217.0202	C8H10ClN2OS	3.3	0.1
Fluquinconazole	31.884	339.0323	C16H7ClFN5O	0.6	0.4
Cypermethrin	33.315/33.516/33.652/33.729	206.998	C8H9Cl2O2	4.7	0.3
Flucythrinate I	33.759	199.0934	C11H13F2O	0.1	0.3
Flucythrinate II	34.136				
Fluvalinate-tau I	35.484/35.604				
Azoxystrobin	37.006	371.0906	C21H13N3O4	1.2	0.7

Mass error lower than 5 ppm

Real samples: fruit and vegetables

Real Sample	Compound	C (µg/Kg) GC-QqQ	C (µg/Kg) GC-QTOF
Apple	Bupirimate	<LOQ	4.1
	Chlorpyrifos	ND	<LOQ
Pear	Chlorpyrifos	<LOQ	4.9
	Chlorpyrifos-Methyl	12.2	16.7
	Iprodione	1274	1902.0
	Propiconazole	<LOQ	<LOQ
Mango	Chlorpyrifos	ND	<LOQ
	Iprodione	ND	2.6
Apple	Chlorpyrifos	12.8	17.0
	Lambda-Cyhalothrin	<LOQ	4.5
	Pyridaben	10.9	31.5
Mandarin	Chlorpyrifos	<LOQ	2.2
	Propiconazole	382.9	389.0
Tomato	Chlorpyrifos	ND	<LOQ
	Fenhexamid	21.4	12.4
Plum	Chlorfenapyr	ND	<LOQ
	Iprodione	1185.7	2936.0
Grapefruit	Chlorpyrfos	<LOQ	8.2
Onion	Chlorpyrifos	<LOQ	<LOQ

Real samples: fruit and vegetables

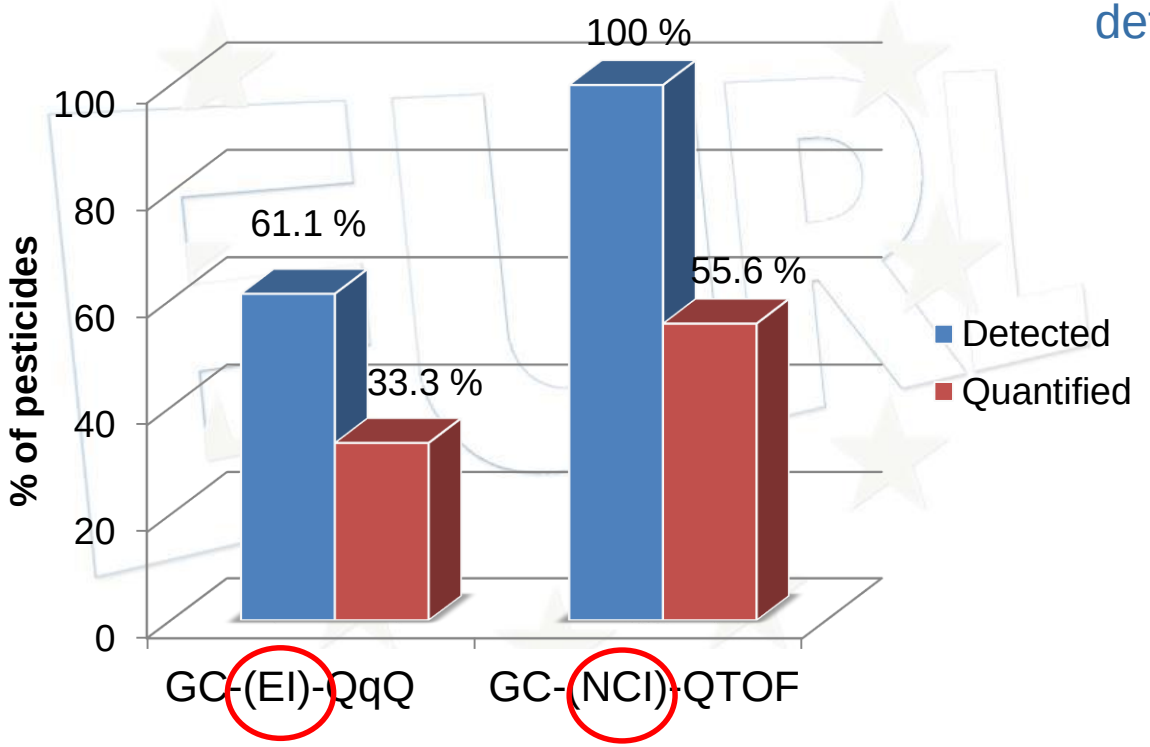
Real Sample	Compound	C (µg/Kg) GC-QqQ	C (µg/Kg) GC-QTOF
Lettuce	Chlorpyrifos	ND	<LOQ
Spinach	Chlorpyrifos	<LOQ	<LOQ
	Cypermethrin	191.5	269.9
Zucchini	Chlorpyrifos	ND	<LOQ
Beans	Azoxystrobin	15.1	16.1
Coliflower	Chlorpyrifos	<LOQ	<LOQ
Apple	Bupirimate	<LOQ	2.8
	Chlorpyrifos	ND	<LOQ
Papaya	Chlorfenapyr	ND	<LOQ
Tomato	Chlorpyrifos	ND	<LOQ
	Fenhexamid	19.6	13.7
Apple	Bupirimate	15.2	15.6
	Chlorpyrifos	ND	<LOQ
Lemon	Chlorpyrifos	ND	<LOQ
	Propiconazole	40.1	14.1
Cucumber	Chlorpyrifos	ND	<LOQ
Spring Onion	Bupirimate	<LOQ	3.4
	Lambda-Cyhalothrin	36.1	35.2

Real samples: herbs

Real Sample	Compound	C (µg/Kg) GC-QqQ	C (µg/Kg) GC-QTOF
Dill	Azoxystrobin	11.6	8.3
	Bupirimate	<LOQ	3.4
	Chlorpyrifos	30.4	21.4
	Chlorpyrifos-Methyl	ND	<LOQ
	Iprodione	191.1	125.1
Curly Parsley	Bupirimate	<LOQ	2.7
	Chlorothalonil	ND	1.0
	Chlorpyrifos	<LOQ	<LOQ
Rosemary	Chlorothalonil	ND	<LOQ
	Chlorpyrifos	20.2	14.2
	Chlorpyrifos-Methyl	ND	<LOQ
	Propizamide	ND	<LOQ
Thyme	Chlorothalonil	ND	<LOQ
	Chlorpyrifos	<LOQ	<LOQ
	Dicloran	ND	<LOQ
	Iprodione	11.0	28.6
	Propizamide	ND	8.6

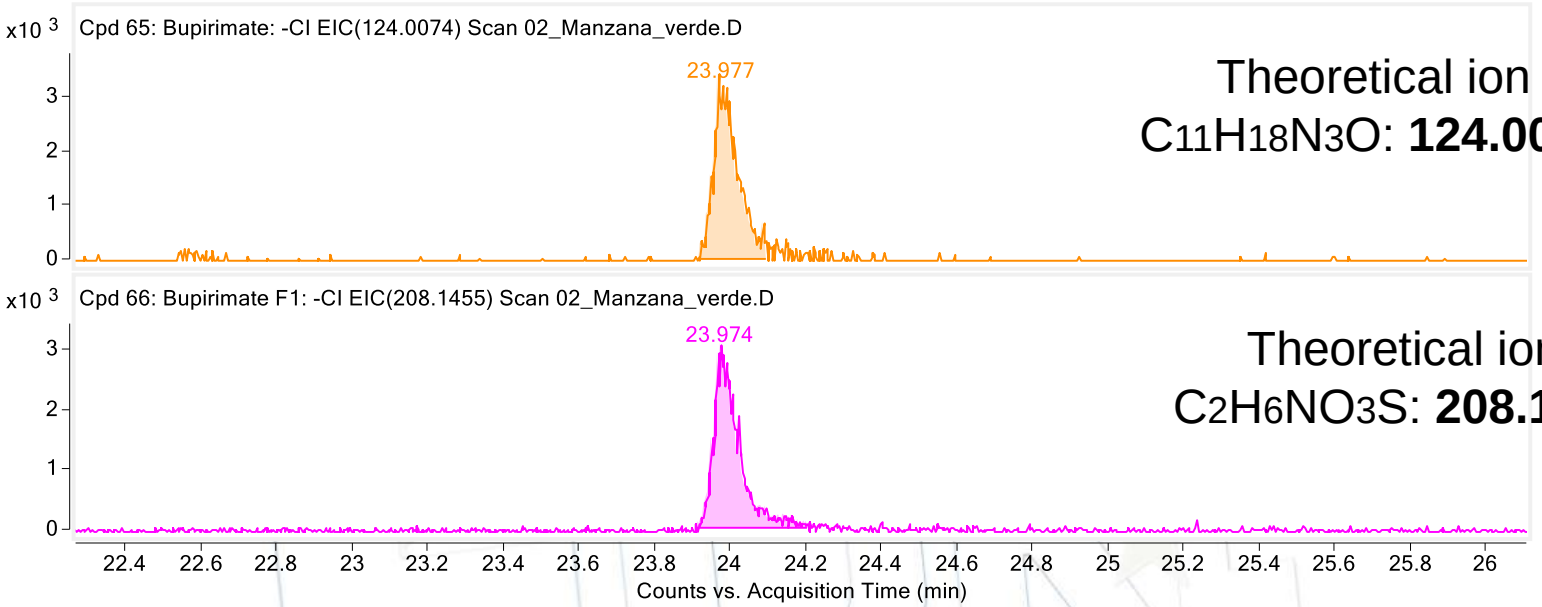
Real samples:
GC-QqQ vs GC-QTOF

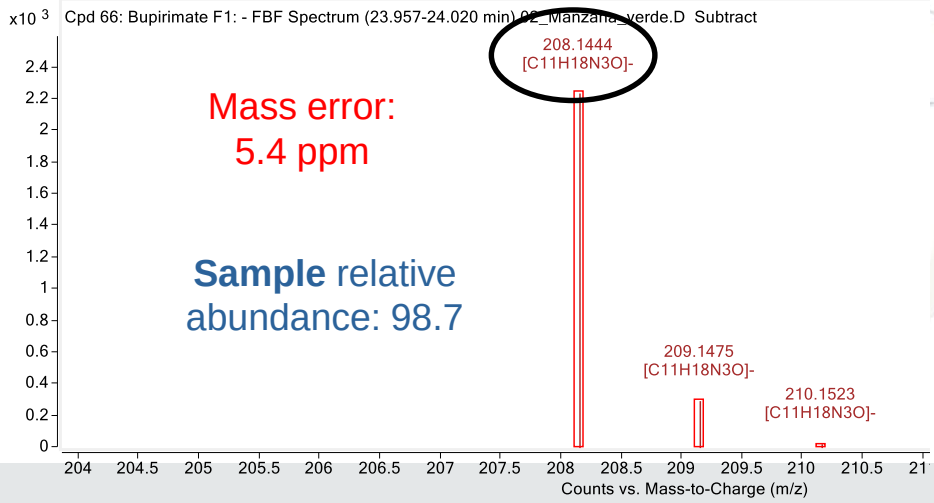
Total number of detected: 54

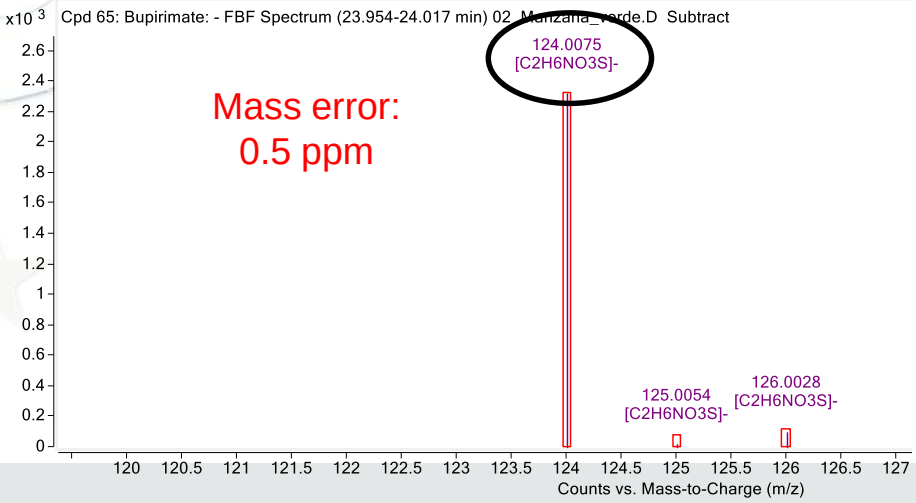


Automatic search

Bupiramate in green apple at 4.1 µg kg^{-1}

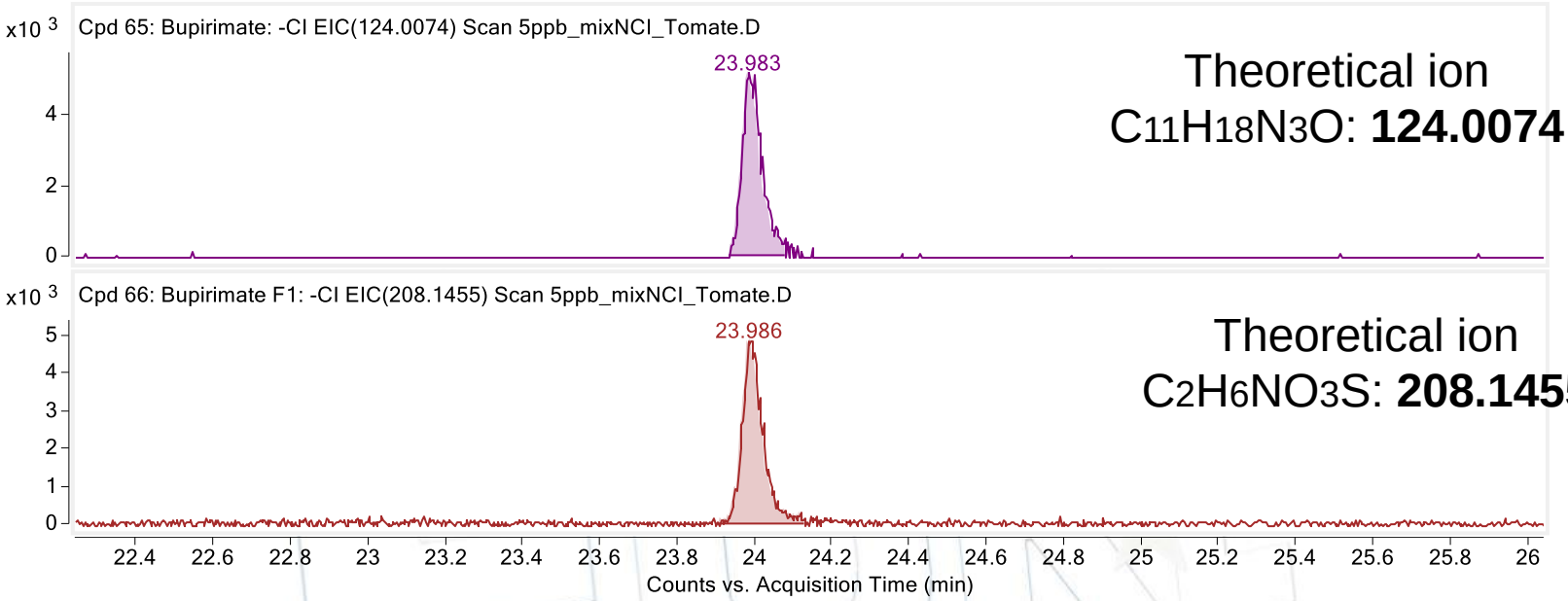


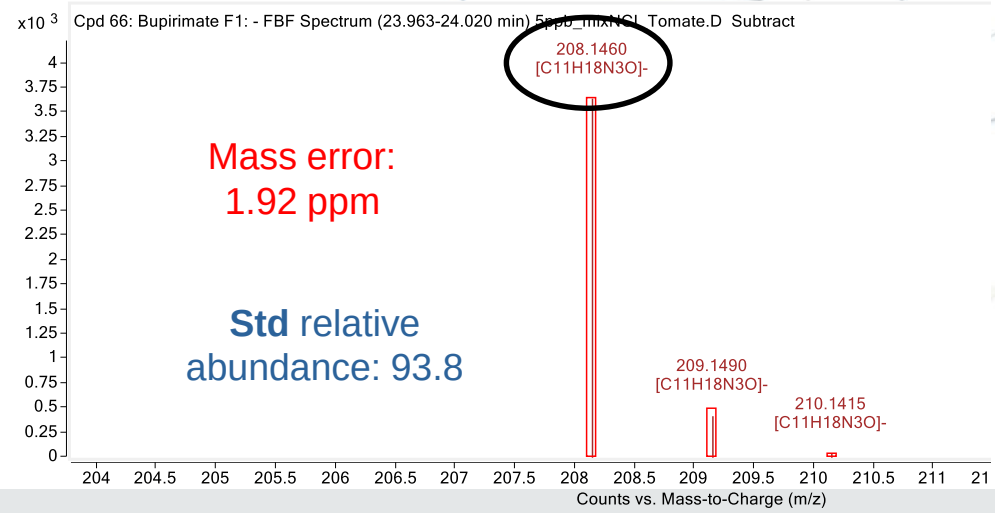


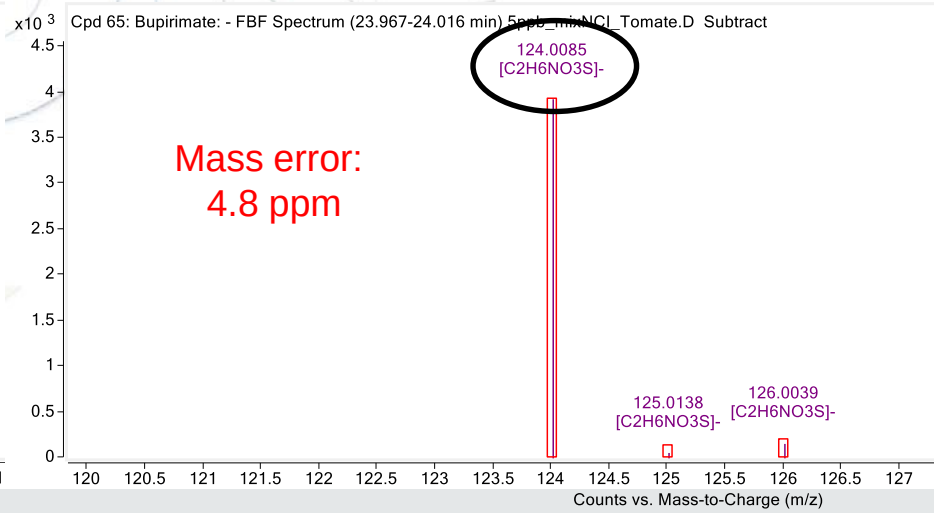


Automatic search

Std of bupiramate 5 µg kg^{-1}

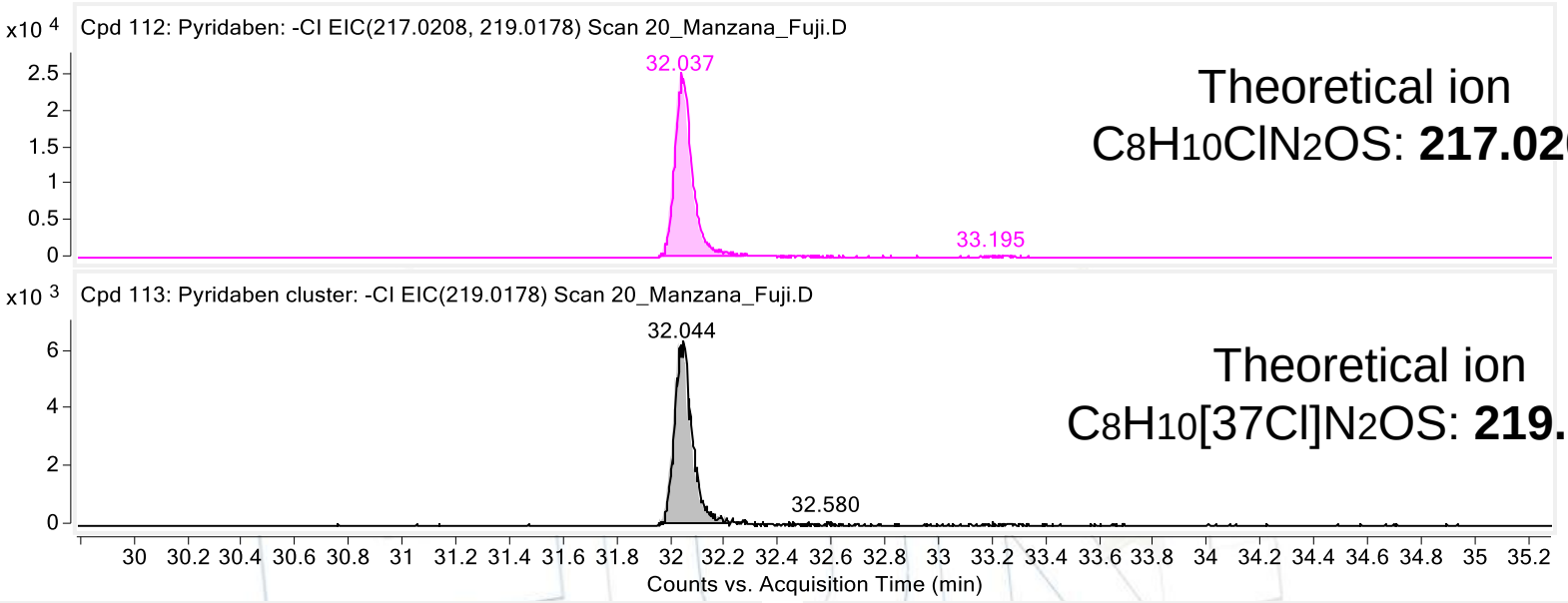


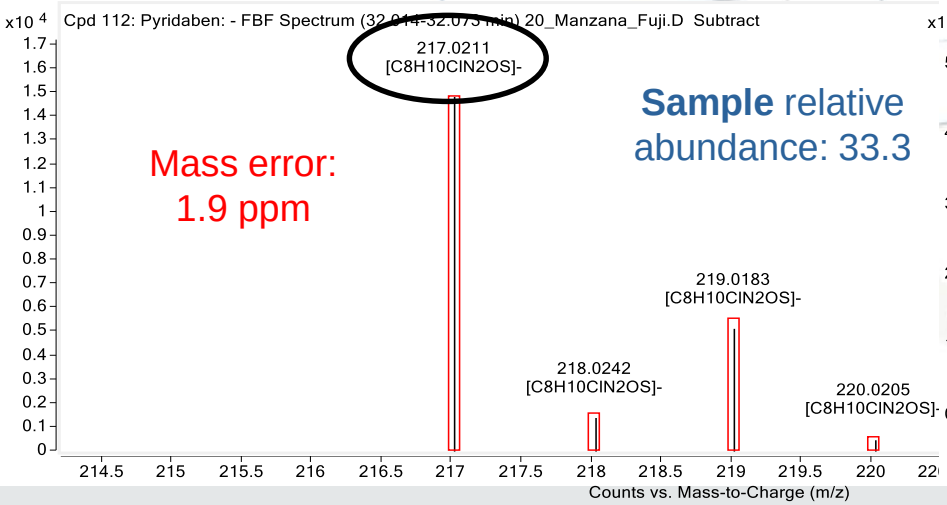


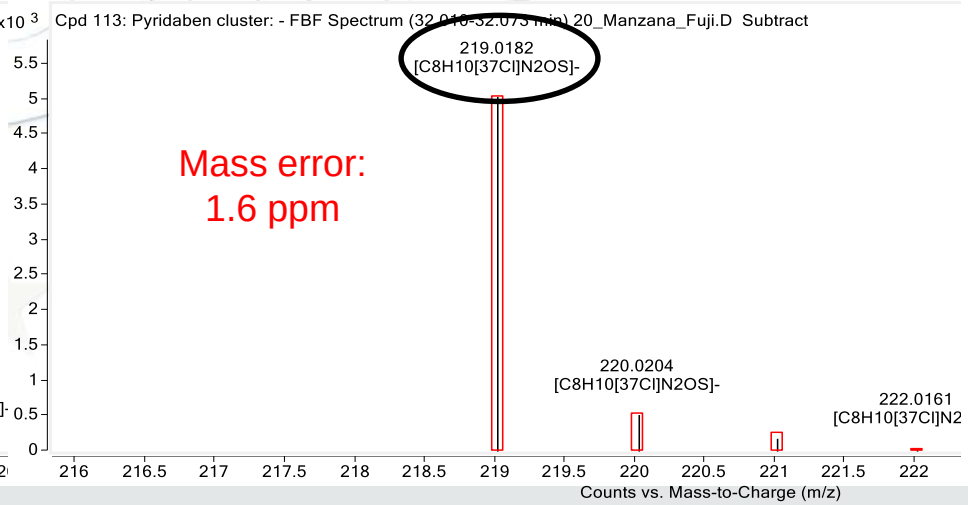


Automatic search

Pyridaben in apple at 31.5 µg kg^{-1}

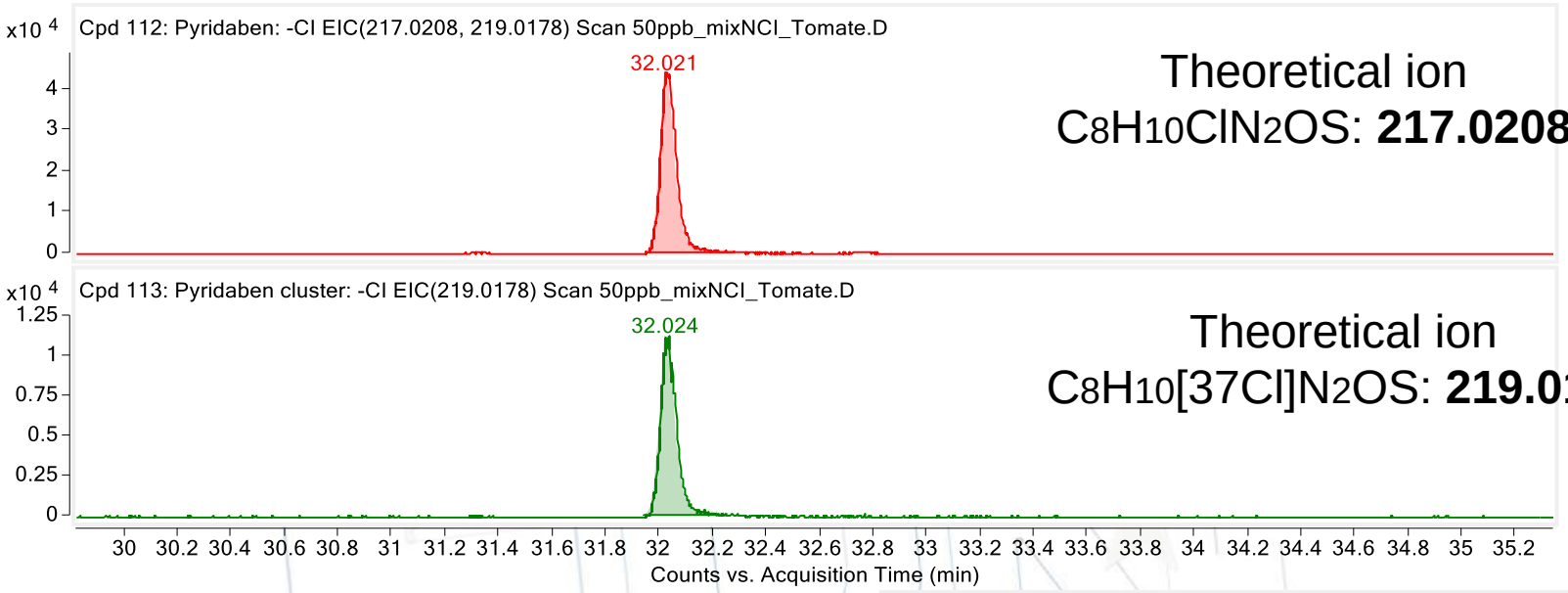


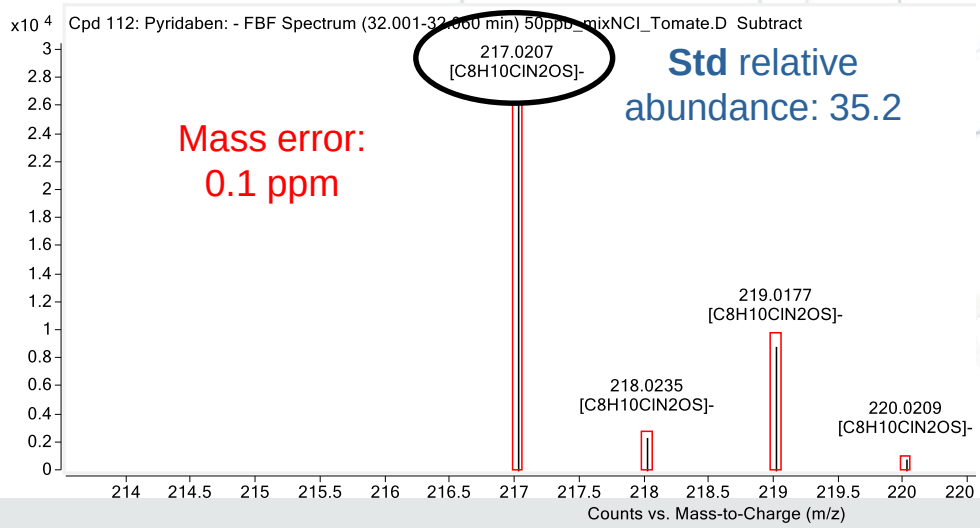


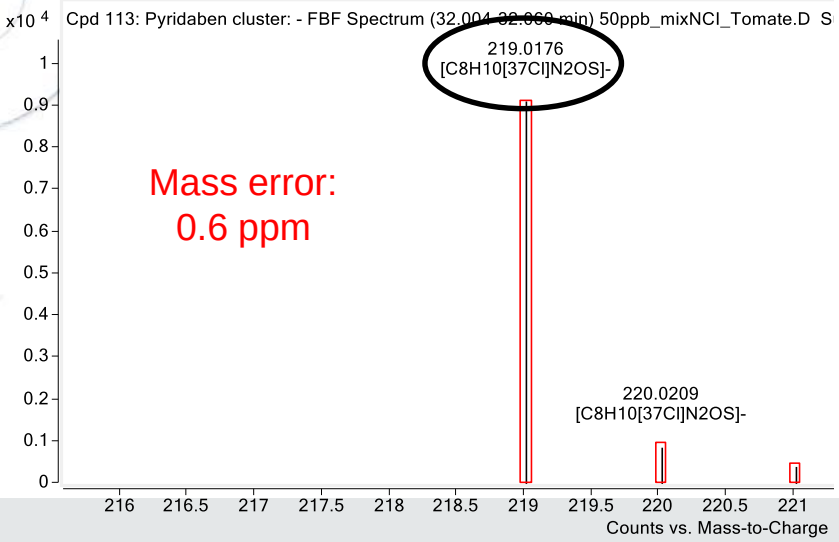


Automatic search

std of pyridaben at 50 µg kg^{-1}

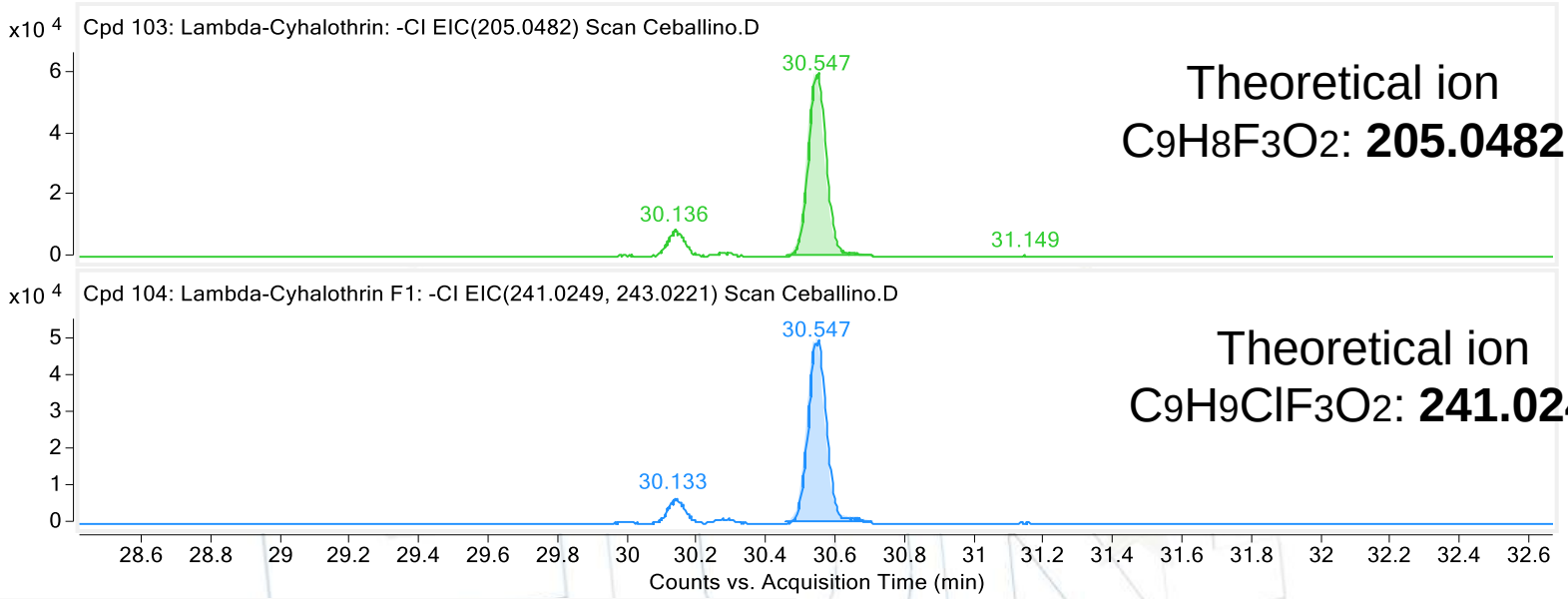


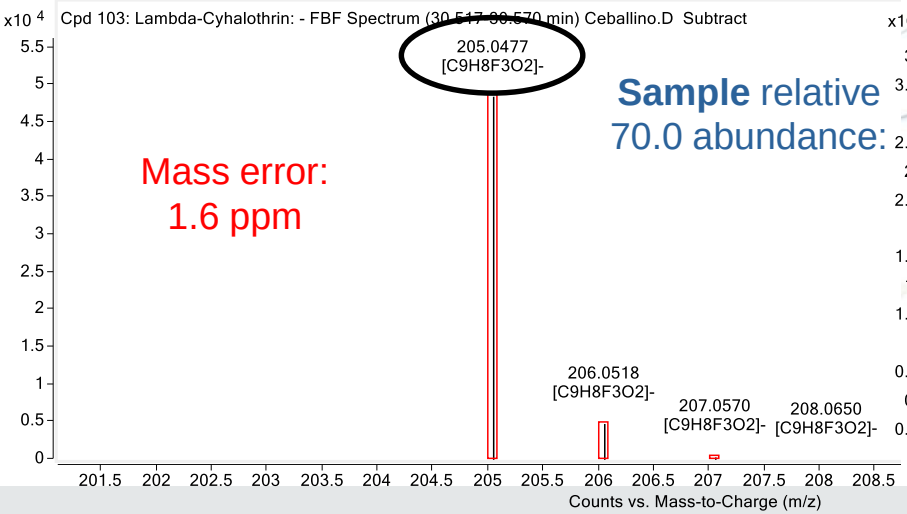


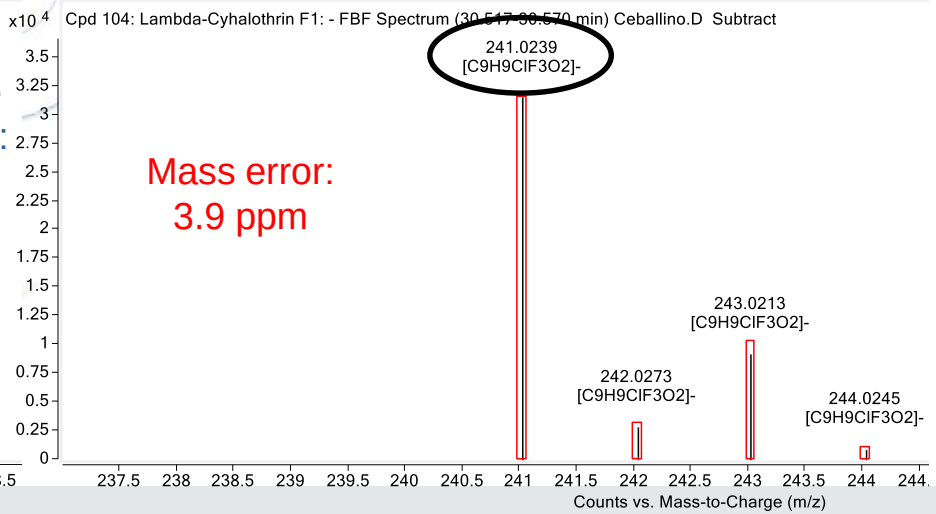


Automatic search

λ-cyalothrin in spring onion at 35 µg kg^{-1}

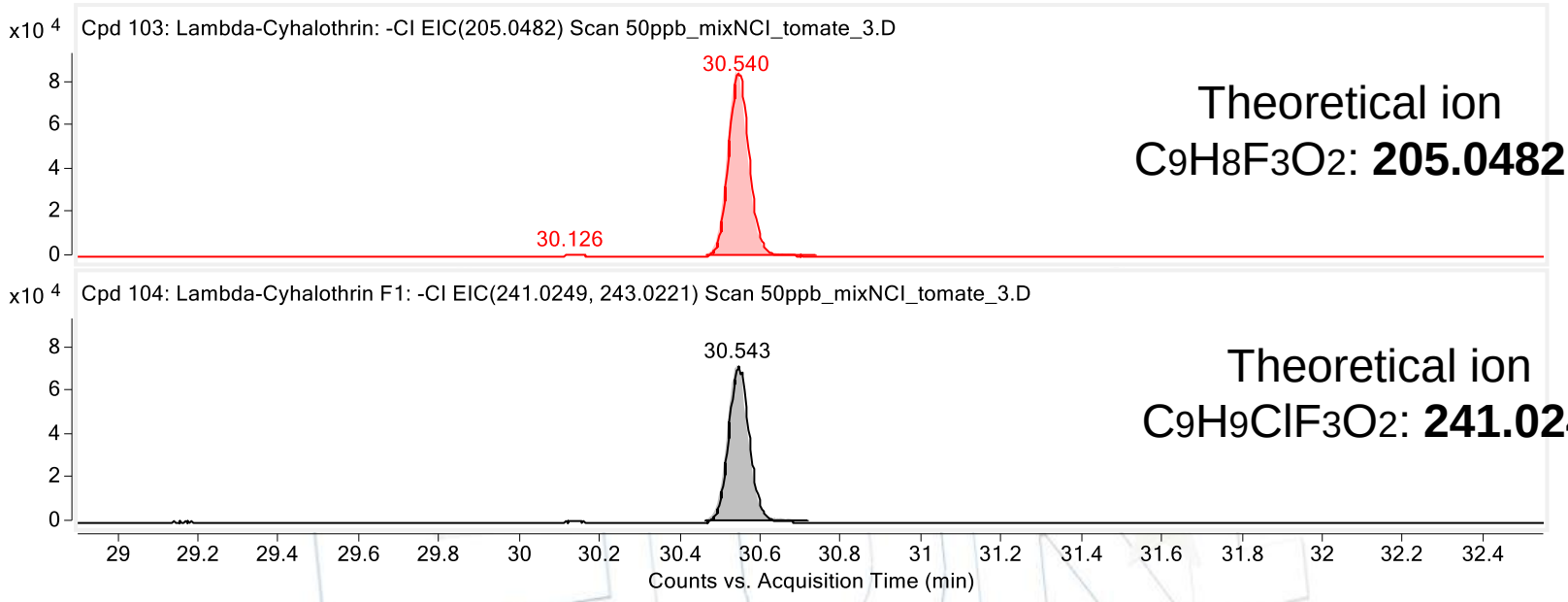


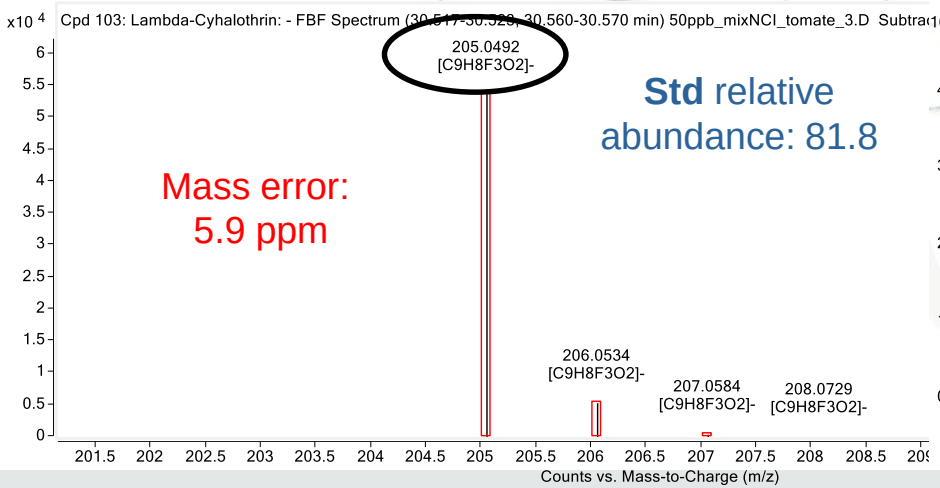


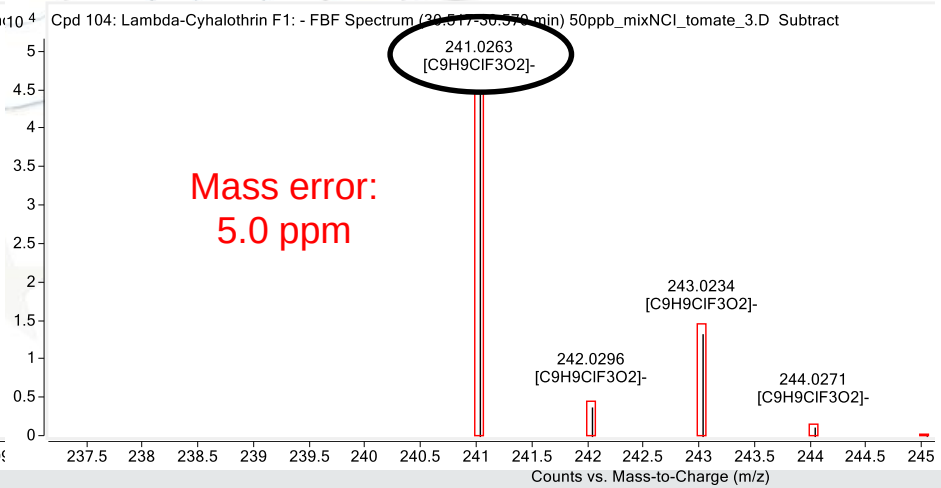


Automatic search

standard of λ-cyalothrin at 50 µg kg^{-1}







Thank You
for Your Attention

EURL EUROPEAN UNION REFERENCE LABORATORY