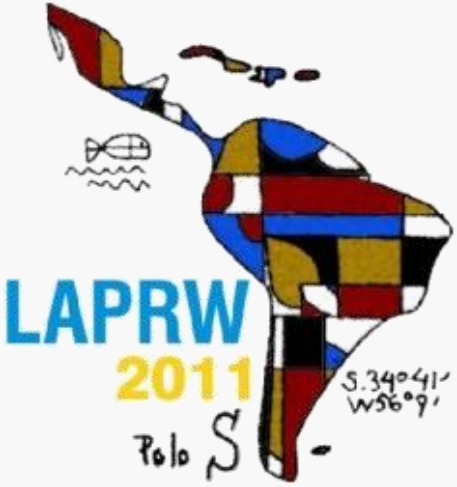




3rd Latin American
Pesticide Residue Workshop
Radisson Montevideo Victoria Plaza Hotel / Montevideo / URUGUAY
8-11 de Mayo, 2011

New Advances In Liquid Chromatography Mass Spectrometry For Pesticide Residue Analysis

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UNIVERSITY OF ALMERÍA


BLAUPUNKT
1,3 km
21:59
0:03 h
1.6 km
50 km/h

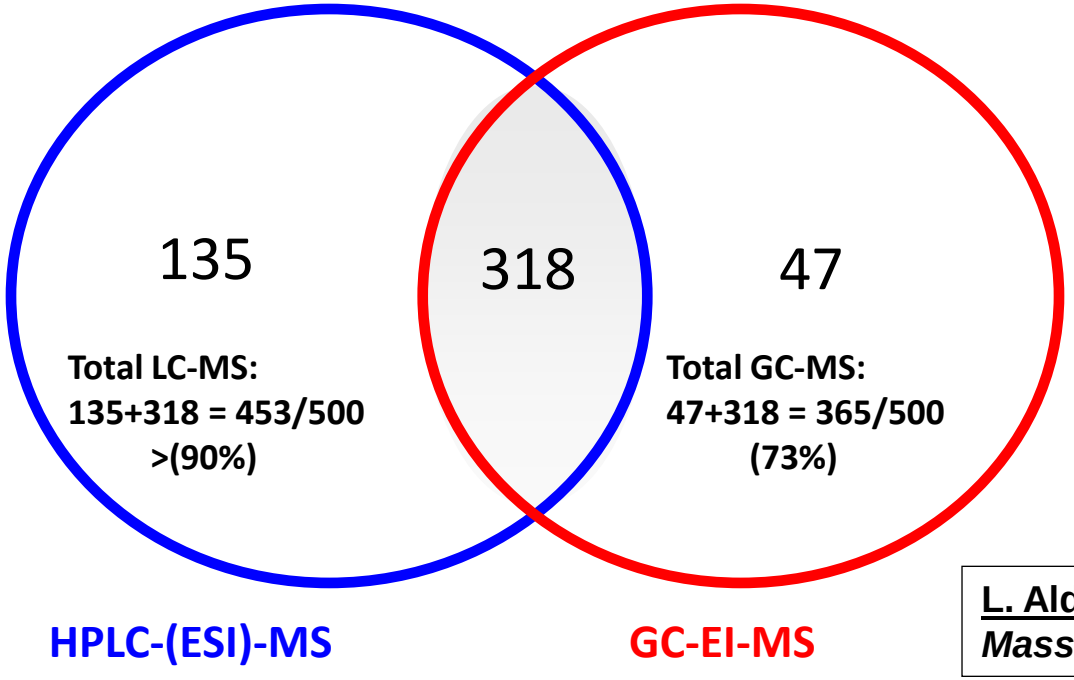
LC-ESI-MS
(APCI)

LC-ESI-TQ-MS/MS
LC-ESI-QLiT-MS/MS
LC-ESI-QTOF-MS/MS

APPI, ESI/APCI,
DART, DESI,LTP…….

New ionization sources for LC-MS

Pesticide Residue Analysis by hyphenated chromatographic/mass spectrometric techniques

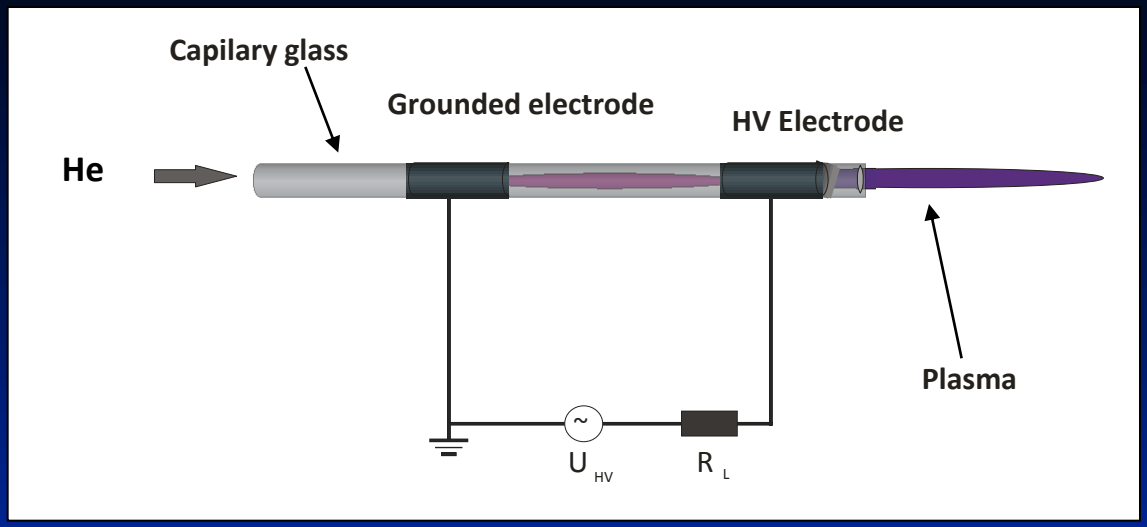


L. Alder et al,
Mass Spectrometry Reviews 25 (2006)

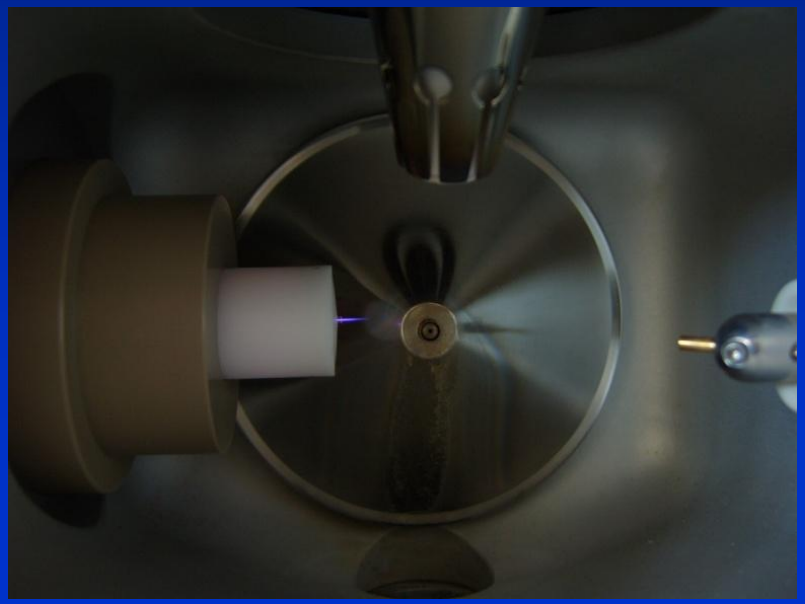
Green chemistry

1. **Design/synthesize chemicals that degrades easily after use**
2. **Avoid derivatization reactions (excesive use of reagents)**

Dielectric Barrier Discharge ionization for LC-MS



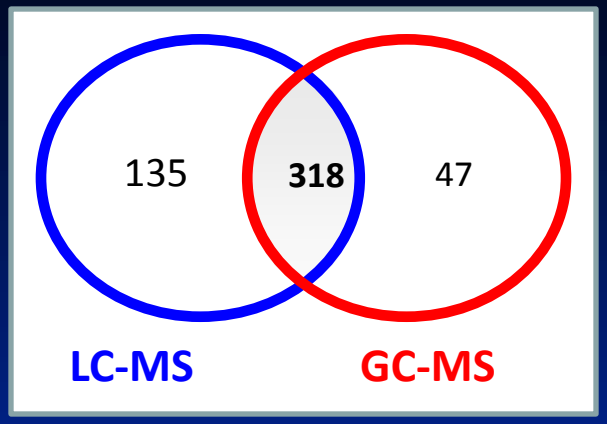
DBDI generates both positive and negative ions



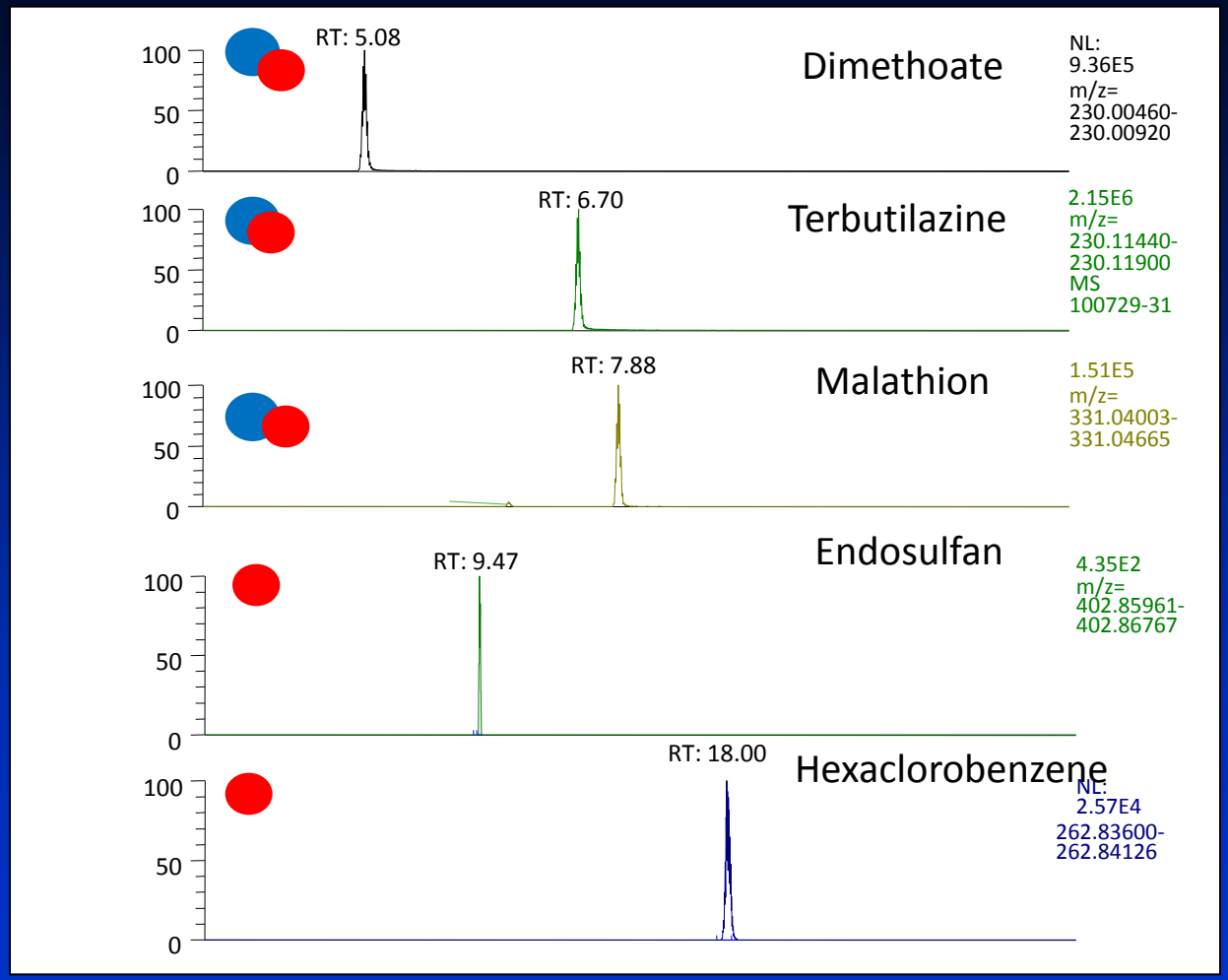
Anal. Chem. 81 (2009) 10239

Dielectric Barrier Discharge ionization for LC-MS

LC-DBDI-MS. Example of aplication



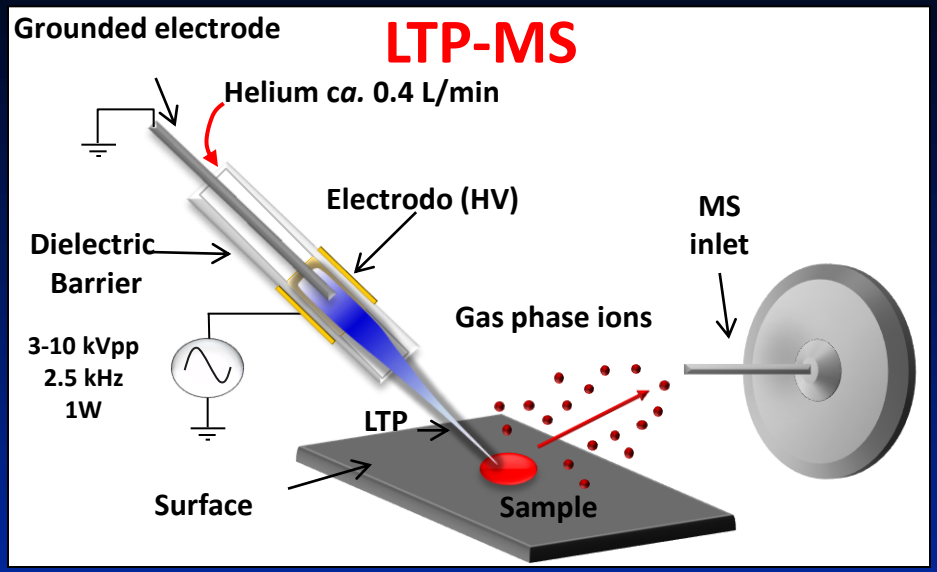
HIgh speed
Polarity switching



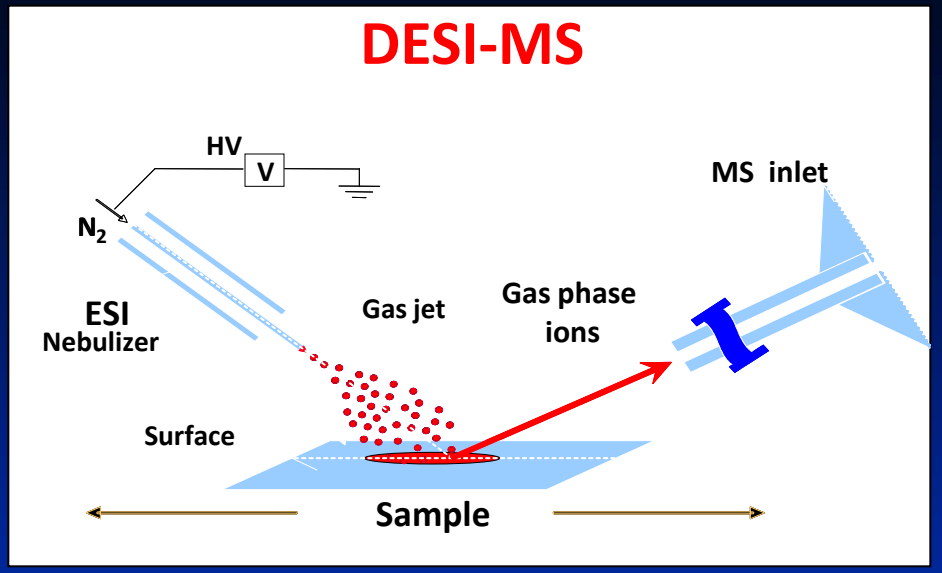
EIC from a pesticide mixture of compounds showing variable polarity en extracto de aceite de oliva (100 ppb) empleando LC-MS de alta resolución con Exactive Orbitrap en modo "polarity switching"

Research Line: Ambient desorption ionization MS

LTP-MS

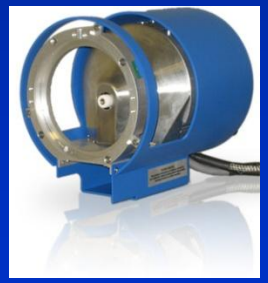


DESI-MS

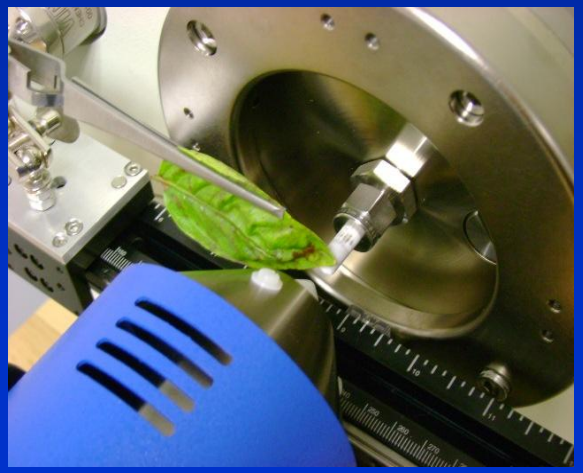


Advantage of (DESI-MS, DART-MS and LTP-MS) ambient MS:

- Analysis in ambient conditions (in different aggregation states)
- High throughput
- No sample treatment
- Variety of analytes and method versatility
- Solvent use elimination (LTP-MS, DART-MS)
- Intrinsic high selectivity and sensitivity (LODs) of MS



DART-MS



Screening of Agrochemicals in Food and Water by Ambient Low-Temperature Plasma Mass Spectrometry

Features of the method:

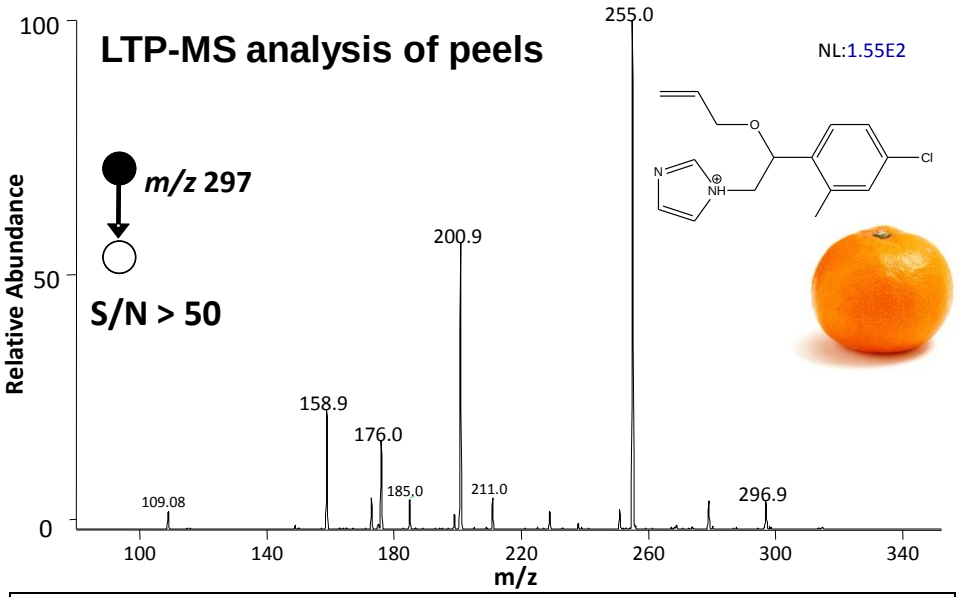
-No need to dilute samples (minor matrix effects) (raw "QuEChERS" extract: 1mL per g)

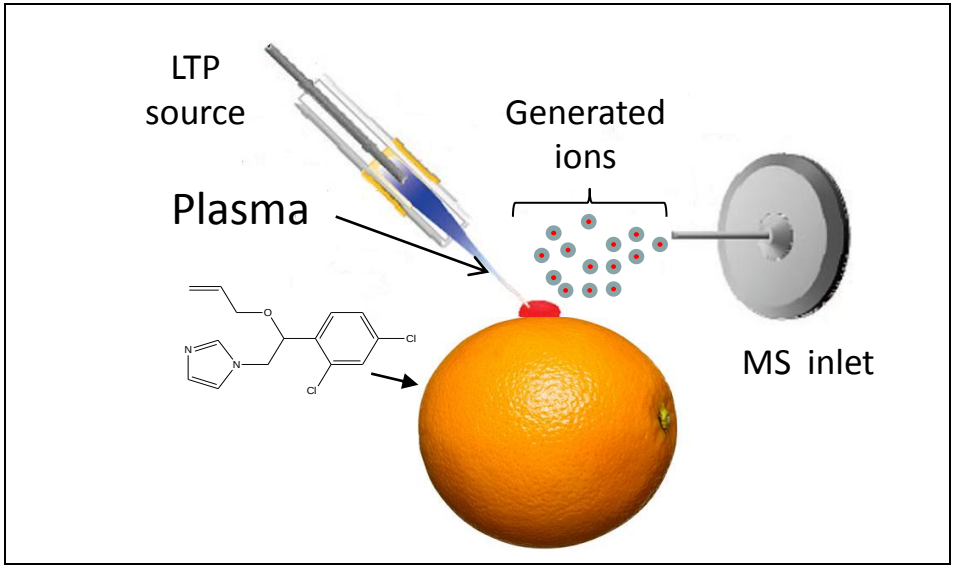
- Non-destructive/invasive detection for fruits and vegetables (no solvents used)

-LODs in the low pg range in matrices and in environmental water samples

Compound	LOD solvent	LOD Tomato Matrix	LOD Orange Matrix
Ametryn	0.3 pg	0.6 pg	1.2 pg
Amitraz	5 pg	60 pg	20 pg
Atrazine	0.6 pg	1.2 pg	4.5 pg
Buprofezin	10 pg	10 pg	10 pg
Diphenylamine	25 pg	45 pg	25 pg
Ethoxyquin	25 pg	60 pg	60 pg
Imazalil	15 pg	30 pg	30 pg
Isofenphos-Met	25 pg	60 pg	40 pg
Malathion	6 pg	15 pg	60 pg
Terbuthylazine	0.3 pg	0.6 pg	2 pg

Substrate used: glass slide heated @ 120 ºC





The Analyst 135 (2010) 971-979

Amadeo R. Fernández-Alba

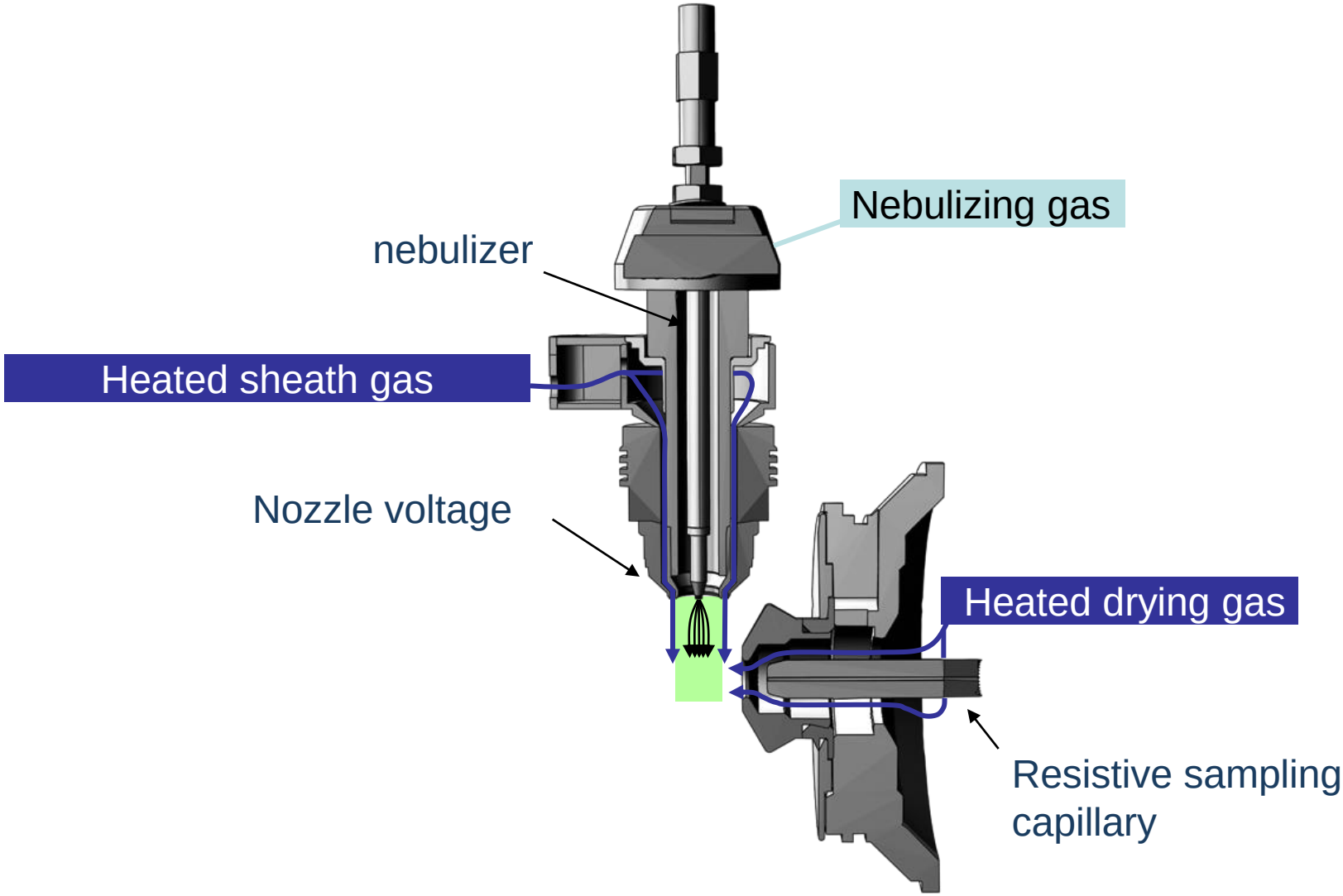
LC-ESI-MS
(APCI)

LC-ESI-TQ-MS/MS
LC-ESI-QLiT-MS/MS
LC-ESI-QTOF-MS/MS

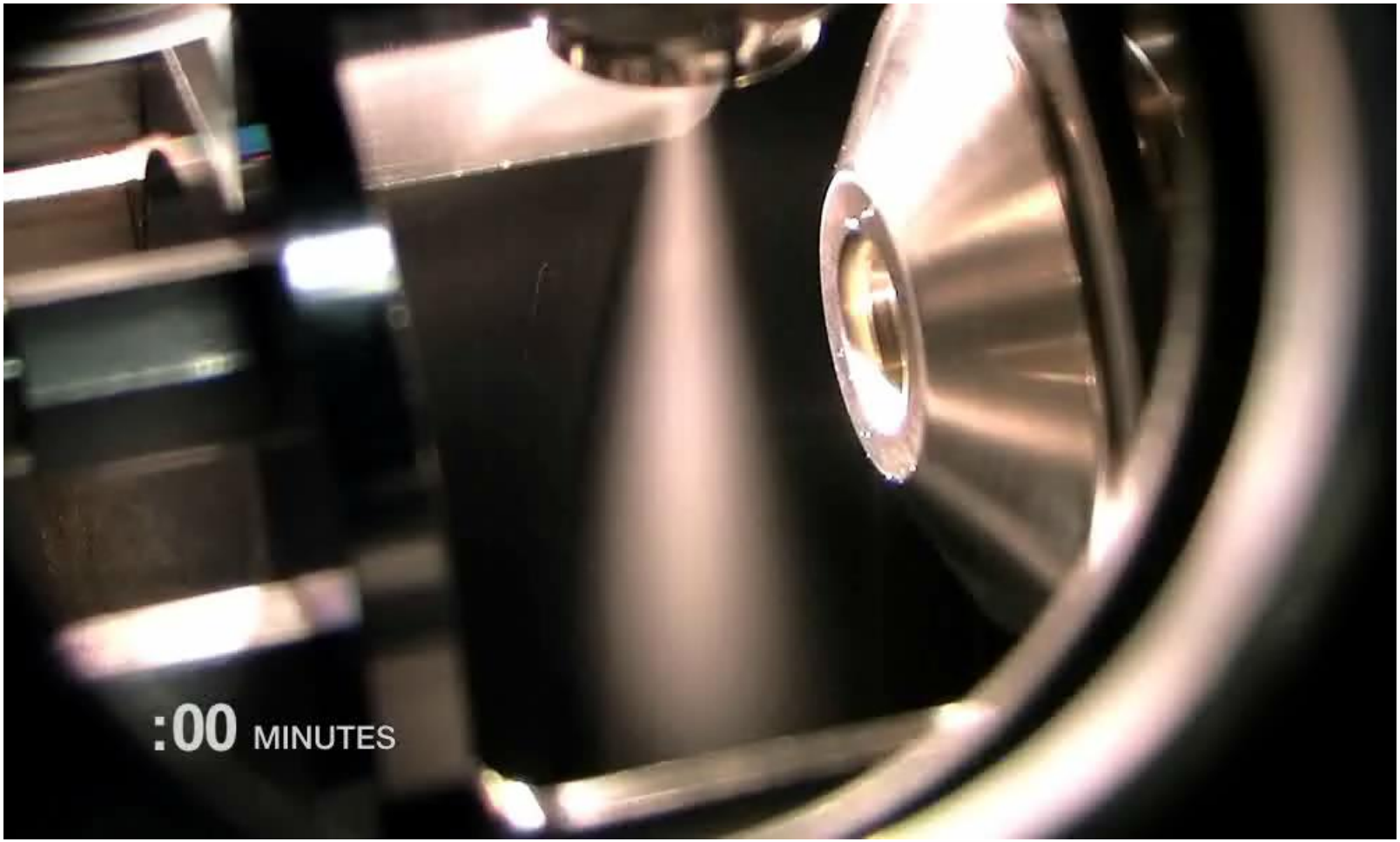
OTHERS

Speed ⟺ Sensitivity

- Introduced Ions
- Ion Transmission
- Ions Detectability


Nebulizing gas
nebulizer
Heated sheath gas
Nozzle voltage
Heated drying gas
Resistive sampling capillary

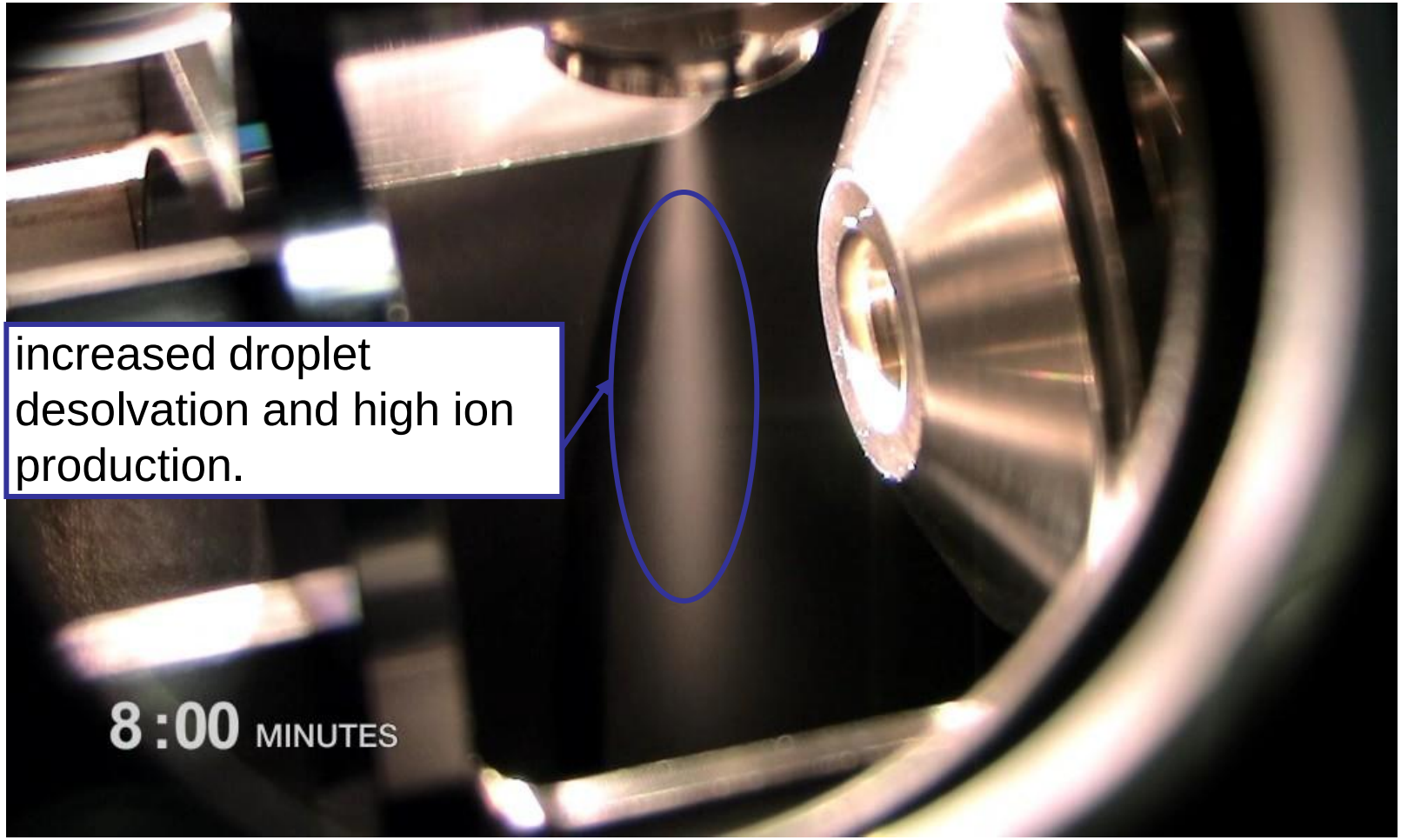
Observing Thermal Focusing



Start temperature = 25 ºC

Stop temperature = 400 ºC

Observing Thermal Focusing

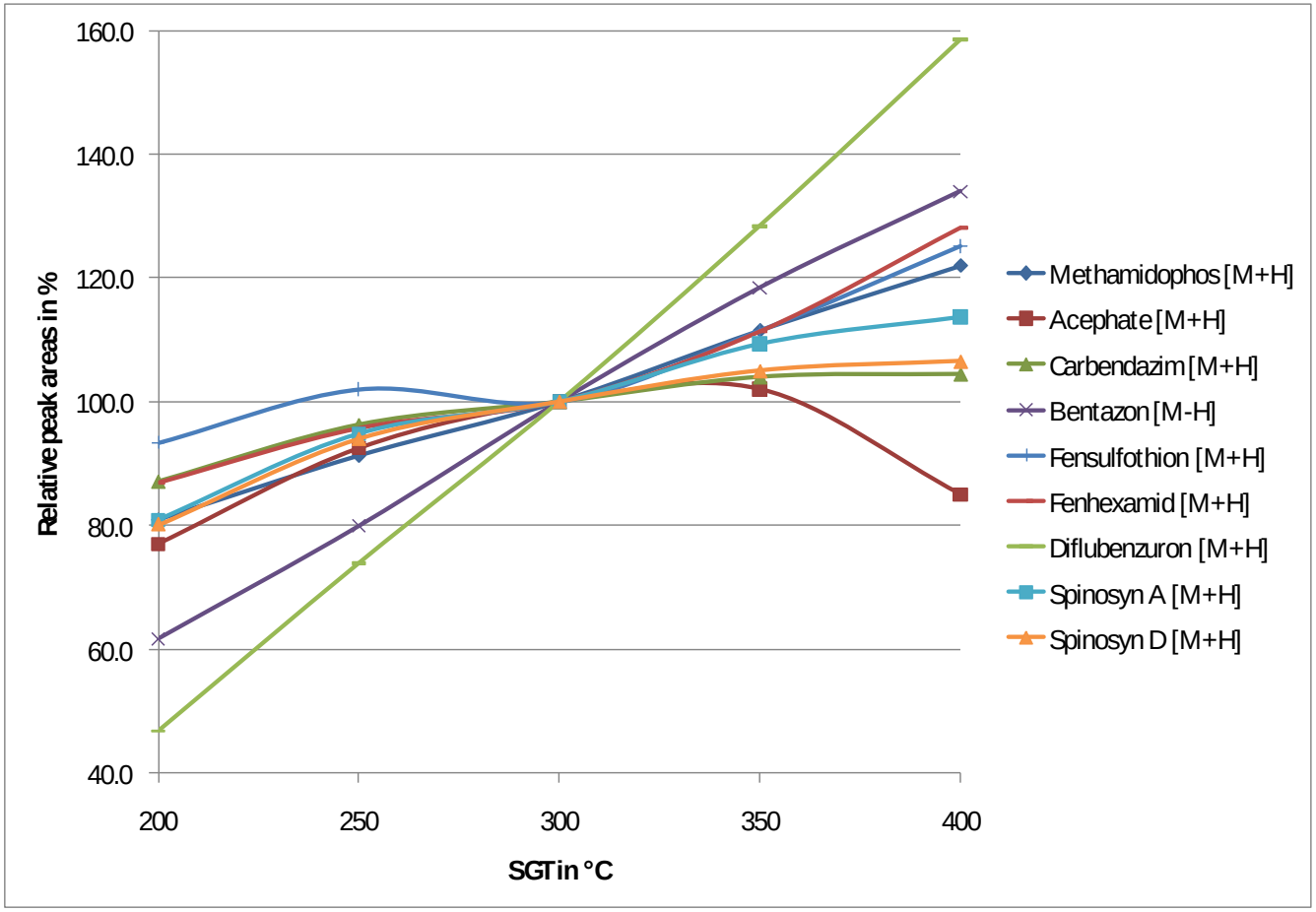


Start temperature = 25 ºC

Stop temperature = 400 ºC

Optimization of ESI Parameters

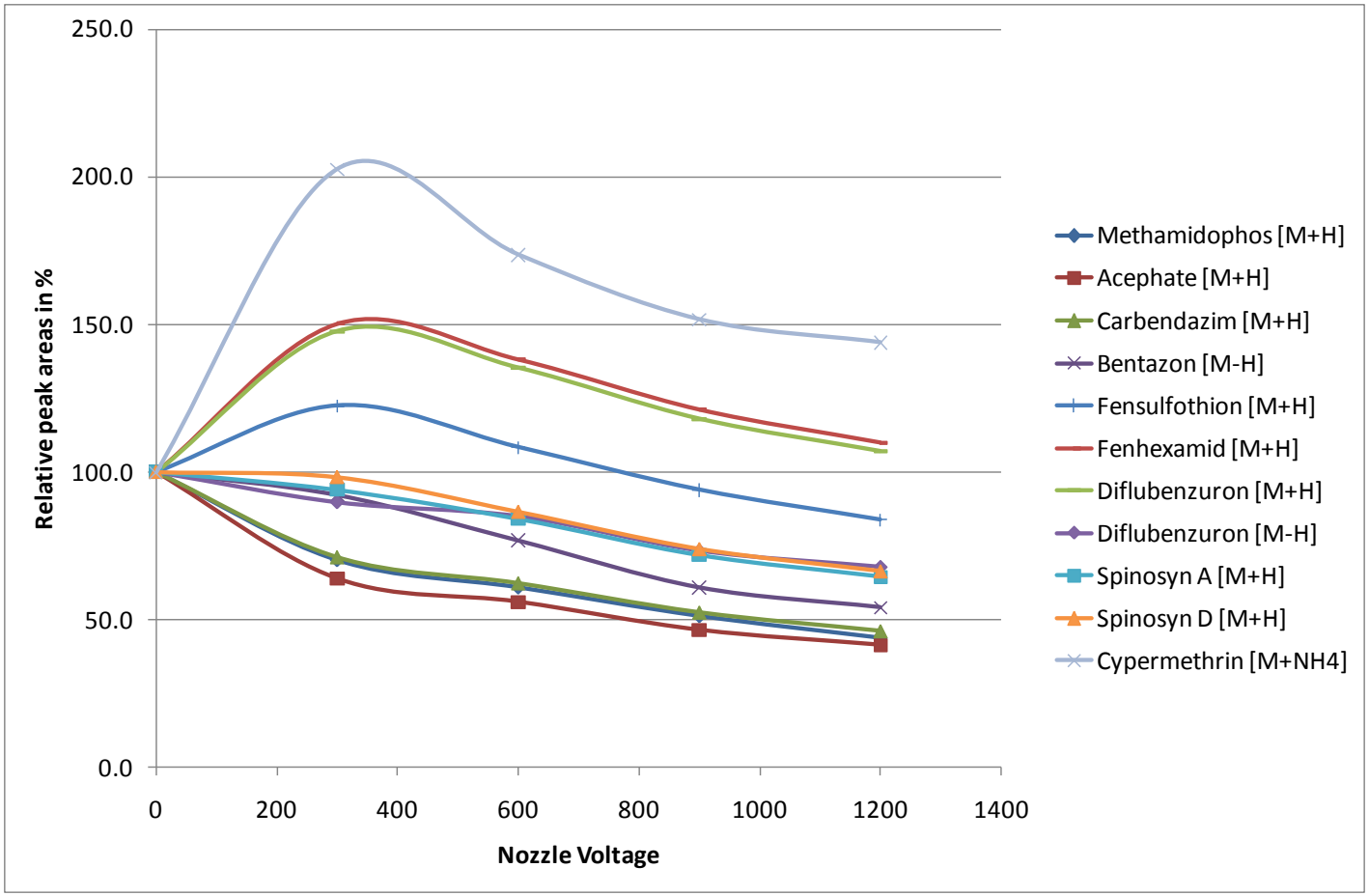
- **Optimization of Sheath Gas Temperature (SGT)**



- Stable compounds forming [M+H] or [M-H] species typically show highest abundance for maximum sheath gas temperature @ 400°C.

Optimization of ESI Parameters

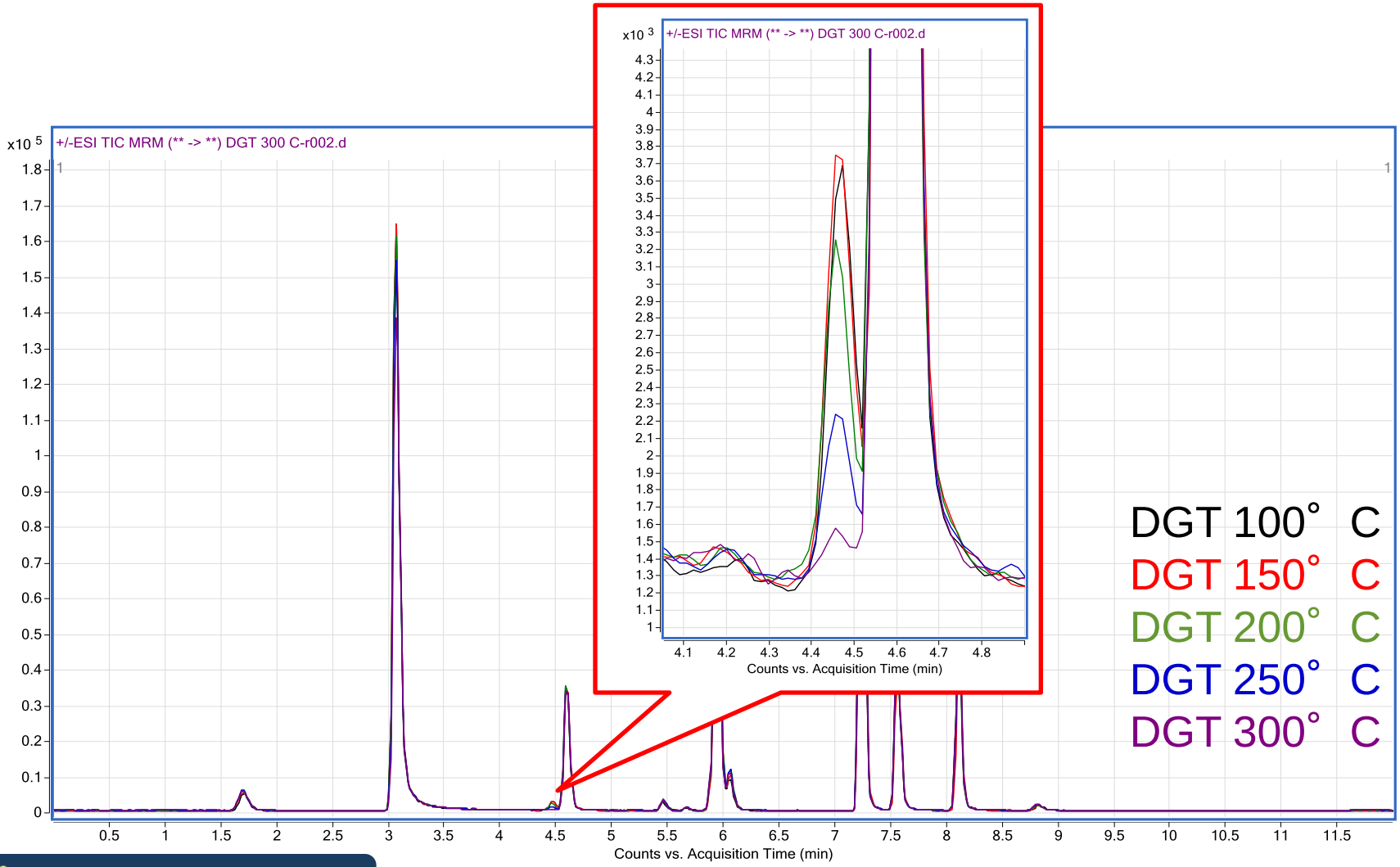
- **Optimization of Nozzle Voltage**



- Fensulfothion, Diflubenzuron, Fenhexamid, and Cypermethrin show optimum for Nozzle Voltage at 300 V, other compounds show optimum at 0 V

Optimization of ESI Parameters

- **Optimization of Drying gas temperature for Dicamba (heat labile compound)**

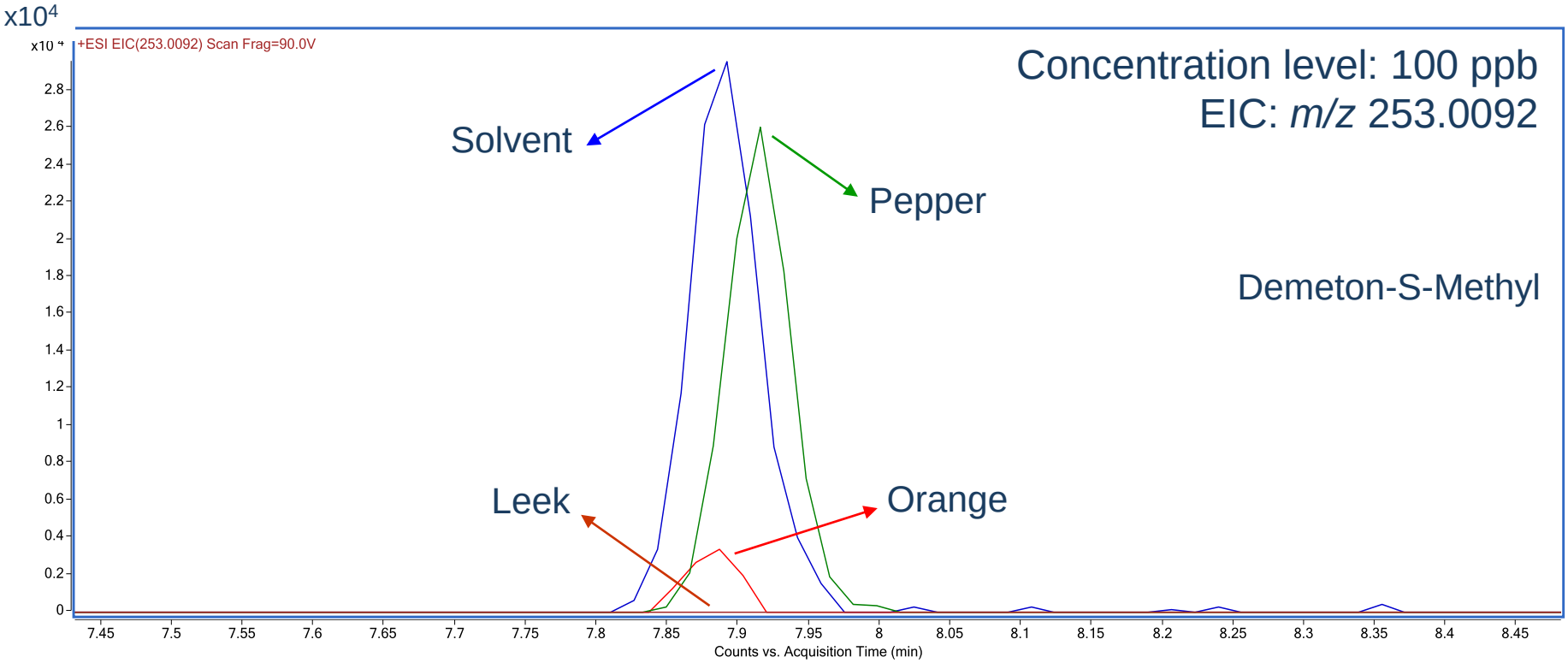


Speed ⟺ Sensitivity

- Introduced Ions
- Ion Transmission
- Ion Detectability

Signal supression due to matrix effects

Injection 1g/ml

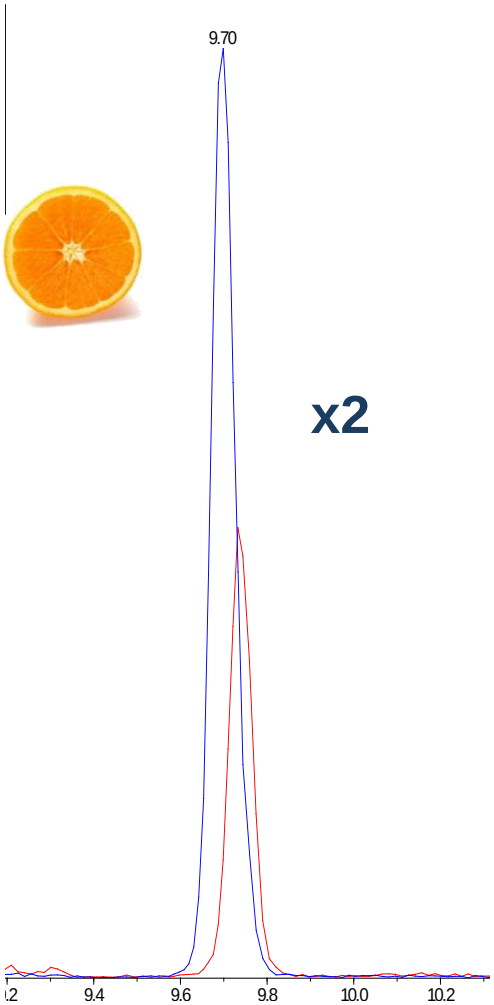


Matrix effect

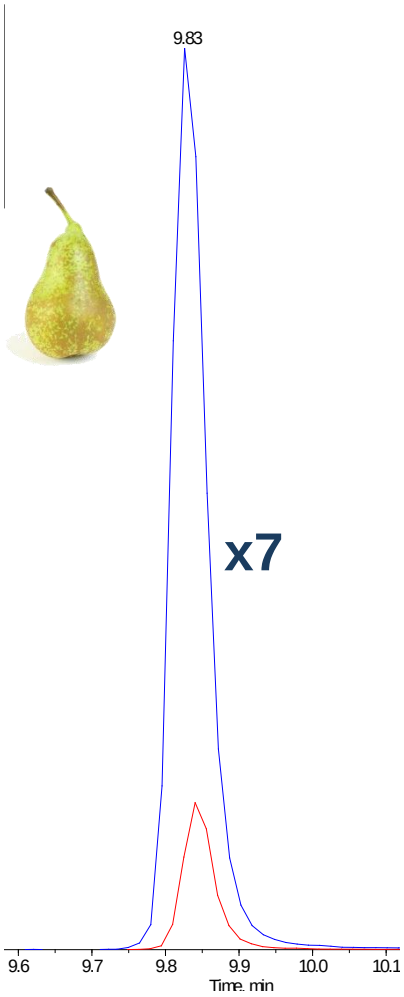
Matrix Dil.5x

Matrix no dilution

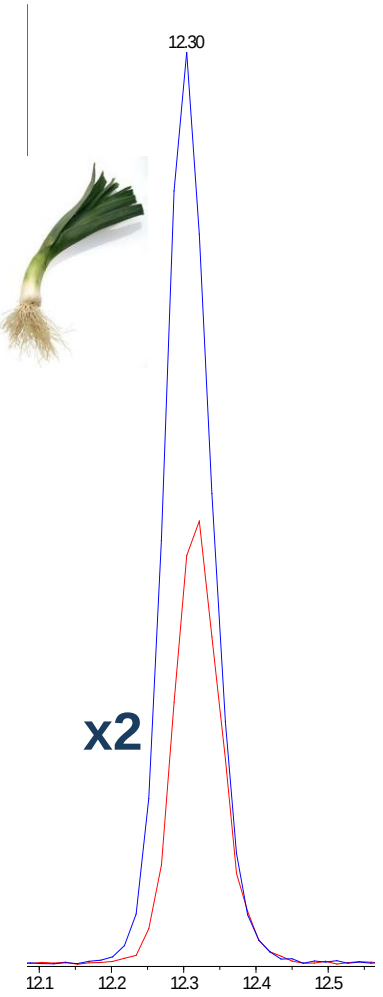
Standard 1 µg/l



Acetamiprid

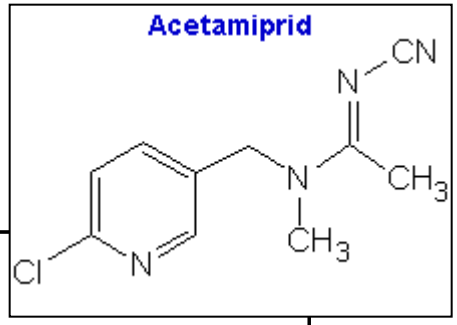


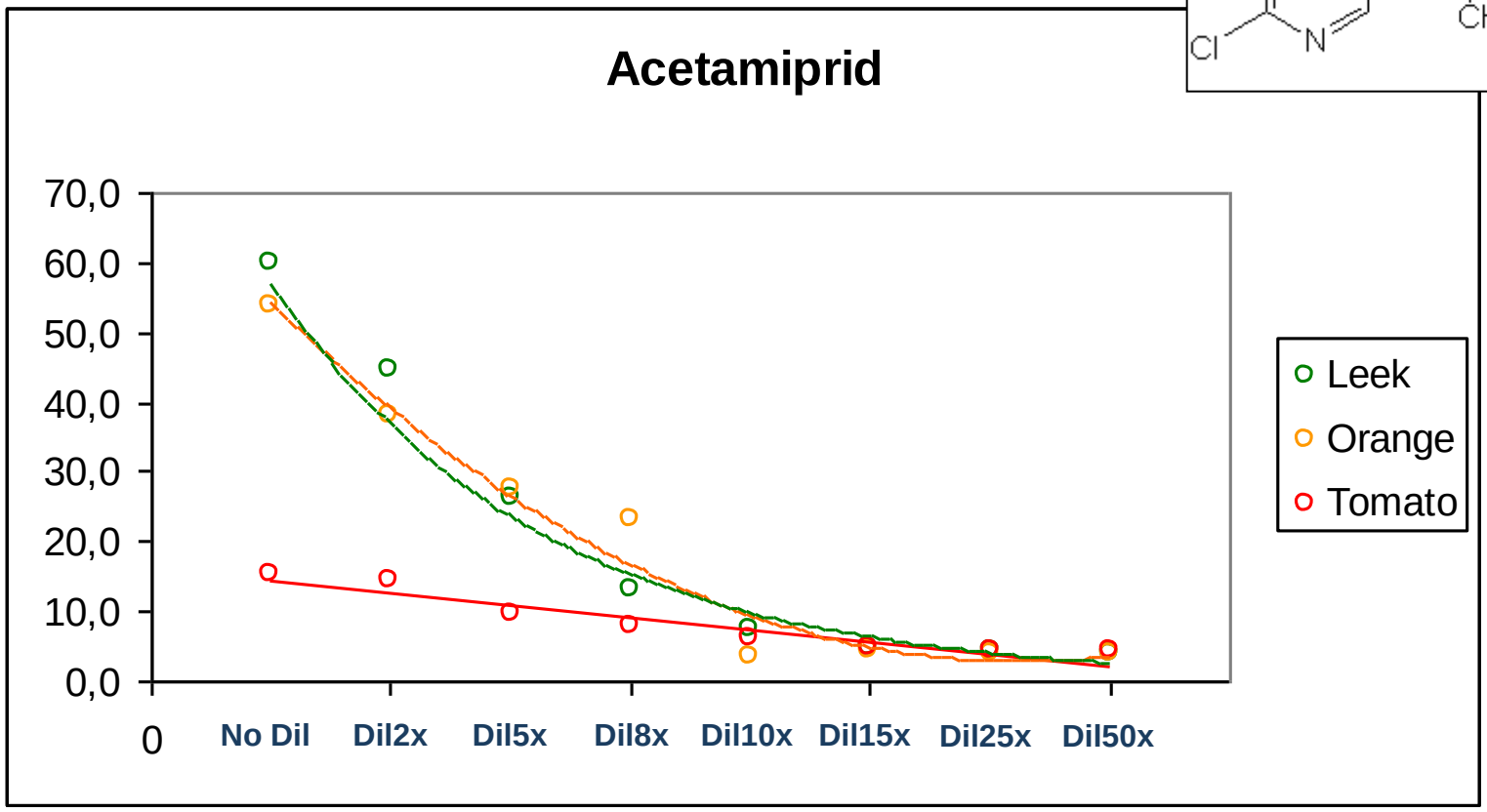
Imazalil



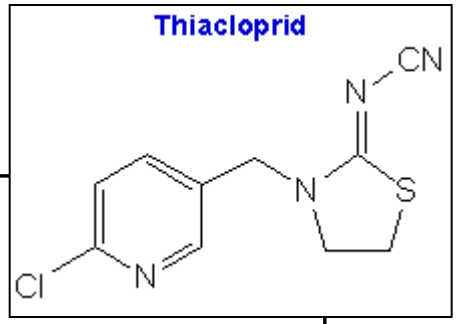
Carbofuran

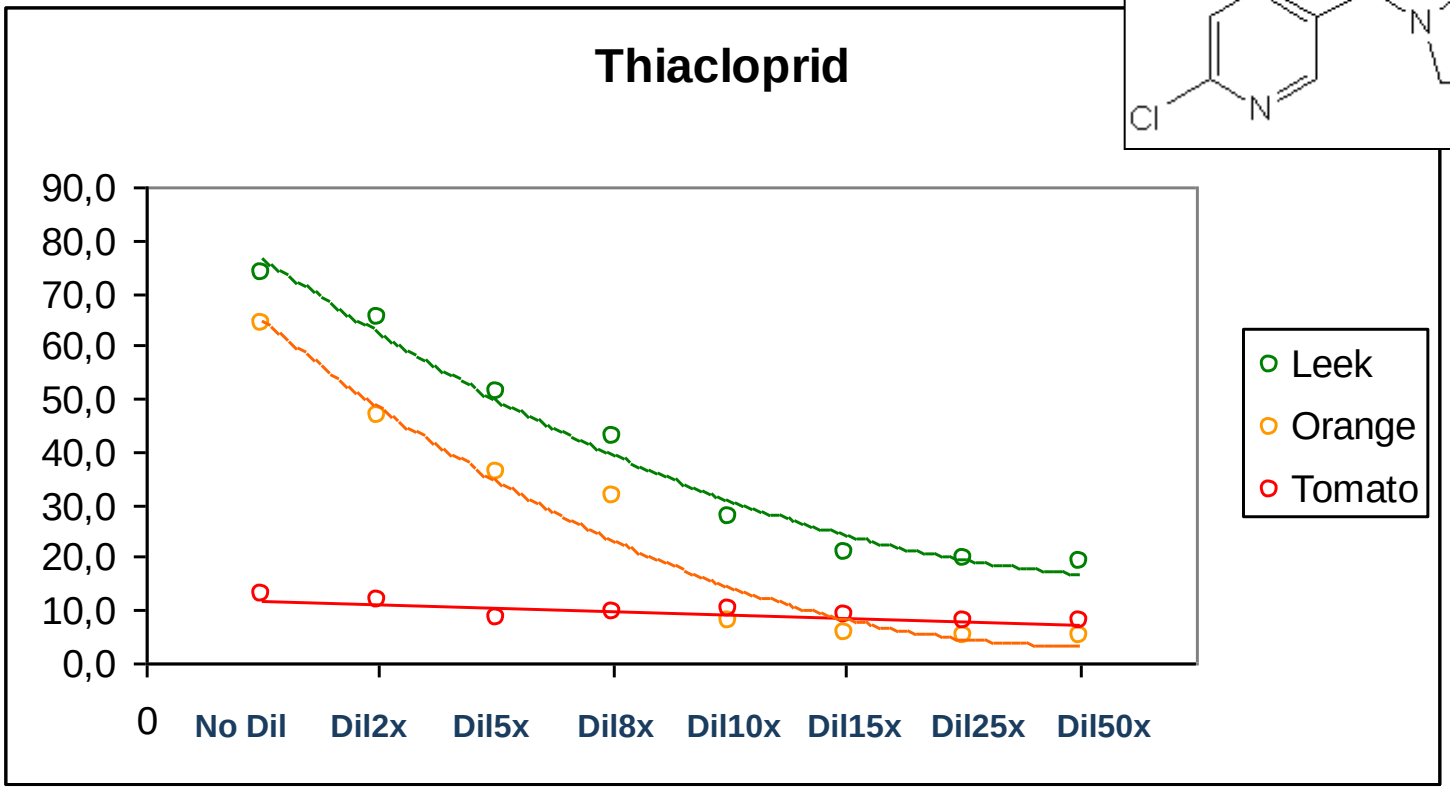
Matrix effect

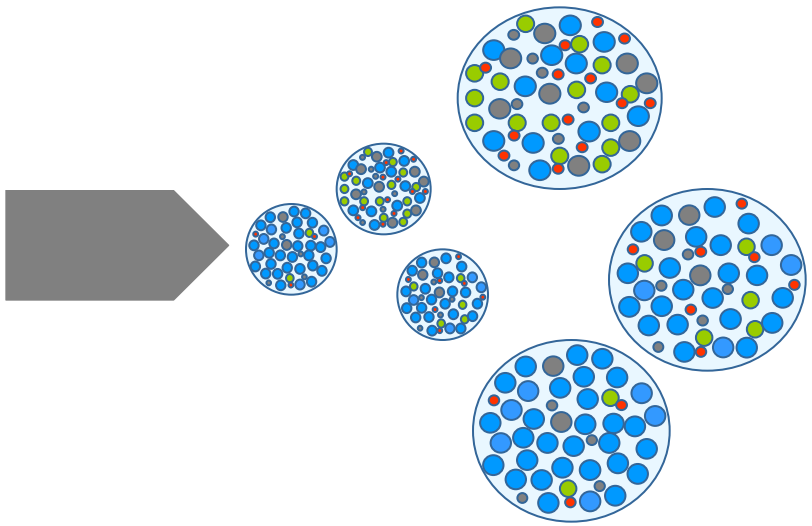


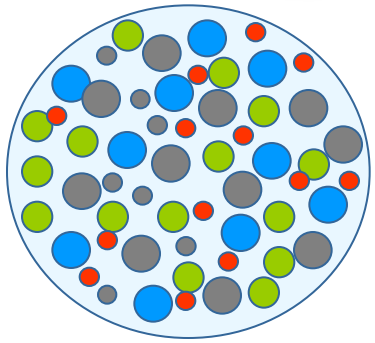


Matrix effect

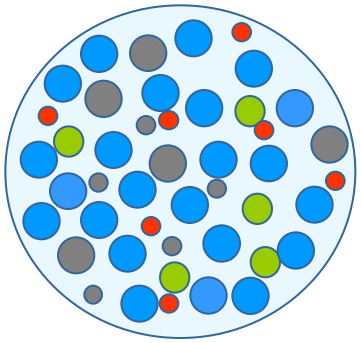




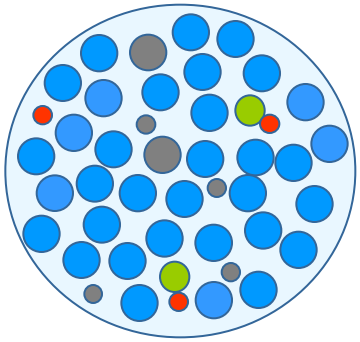




Without dilution



10x Dilution



50x Dilution

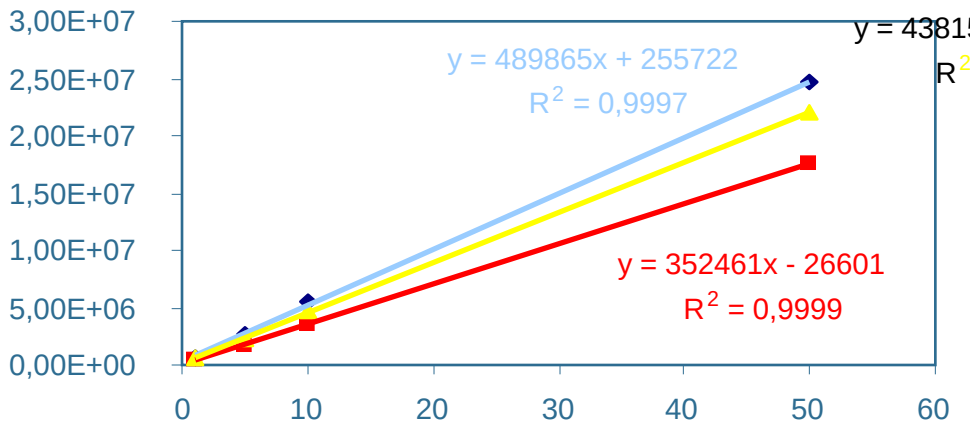
- Solvent
- Pesticide
- Matrix
- Compound that interacts with the pesticide

Signal Supression or Enhancement

Ratio Slope matrix / Slope solvent

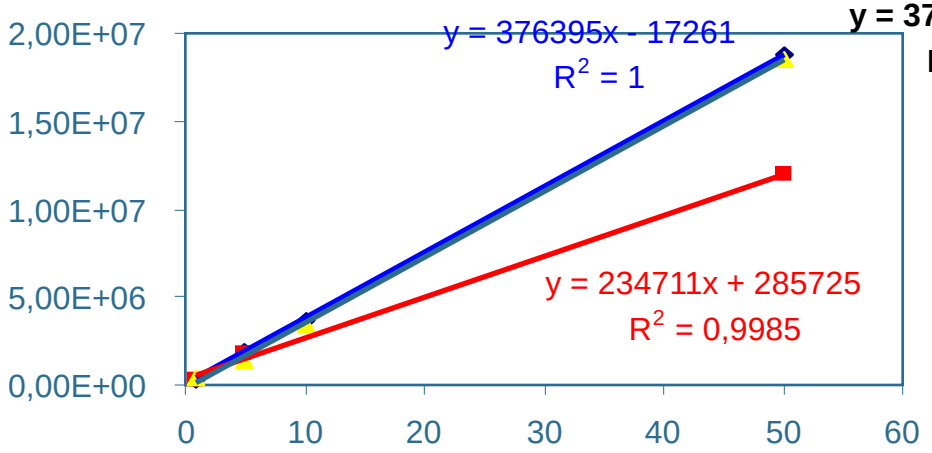
	Orange	Orange Dil5x	Orange Dil10x	
Chloroxuron	0,56	0,90	0,98	
Diuron	0,15	0,30	0,55	✗
Ethiofencarb	0,18	0,36	0,70	
Fluometuron	0,32	0,49	0,86	✓
Flazasulfuron	0,20	0,55	1,16	✓
Isoprocarb	0,57	0,77	1,06	✓

Monurón

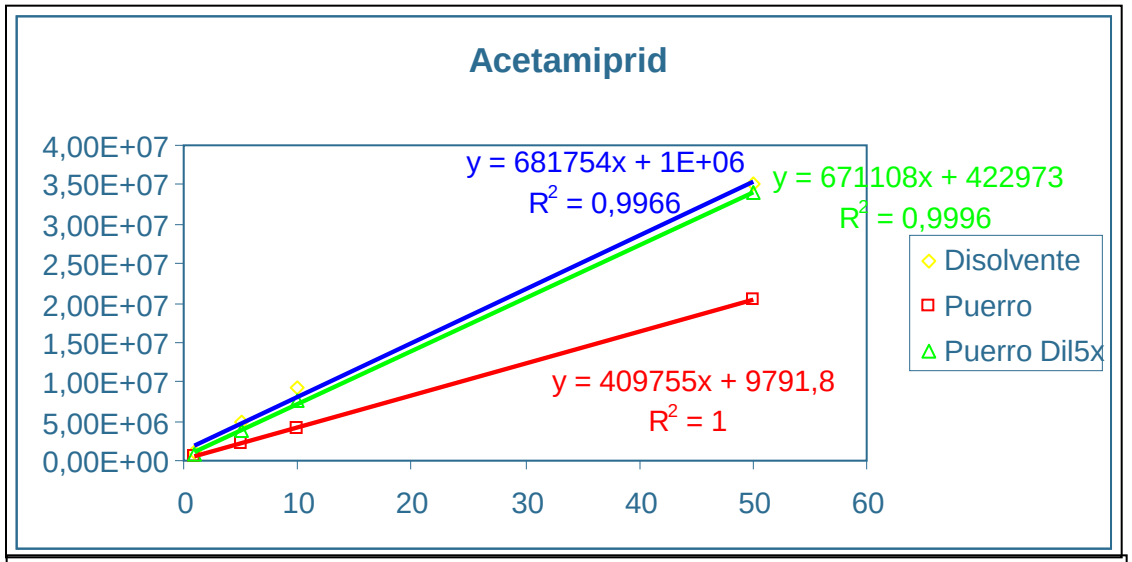


Tomato

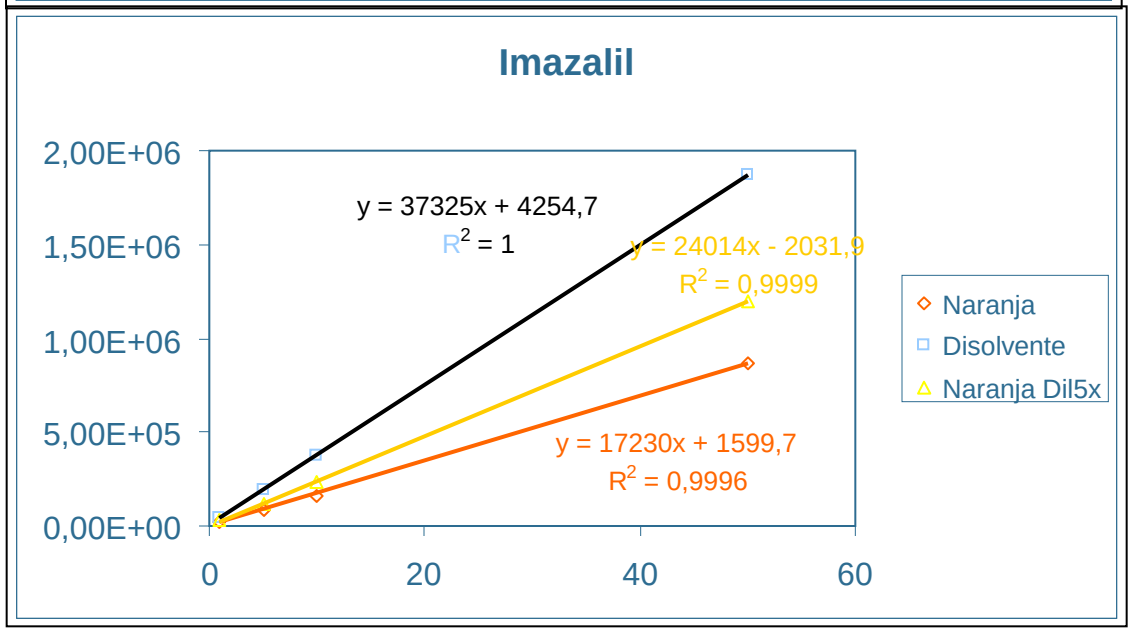
Flazasulfurón



Apple

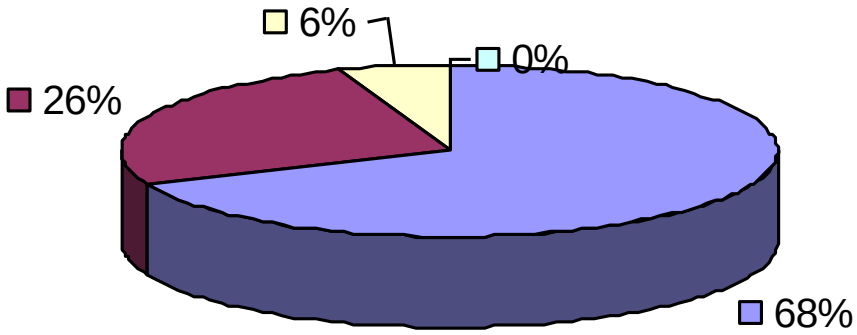

Acetamiprid
4,00E+07
3,50E+07
3,00E+07
2,50E+07
2,00E+07
1,50E+07
1,00E+07
5,00E+06
0,00E+00
0
10
20
30
40
50
60
y = 681754x + 1E+06
R2 = 0,9966
y = 671108x + 422973
R2 = 0,9996
y = 409755x + 9791,8
R2 = 1
Disolvente
Puerro
Puerro Dil5x

Leek


Imazalil
2,00E+06
1,50E+06
1,00E+06
5,00E+05
0,00E+00
0
20
40
60
y = 37325x + 4254,7
R2 = 1
y = 24014x - 2031,9
R2 = 0,9999
y = 17230x + 1599,7
R2 = 0,9996
Naranja
Disolvente
Naranja Dil5x

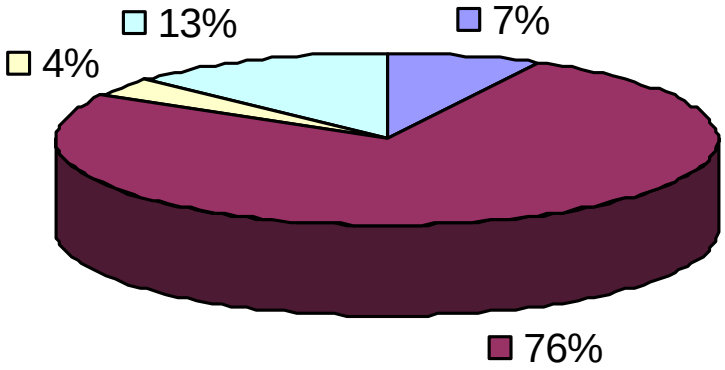
Orange

Tomato

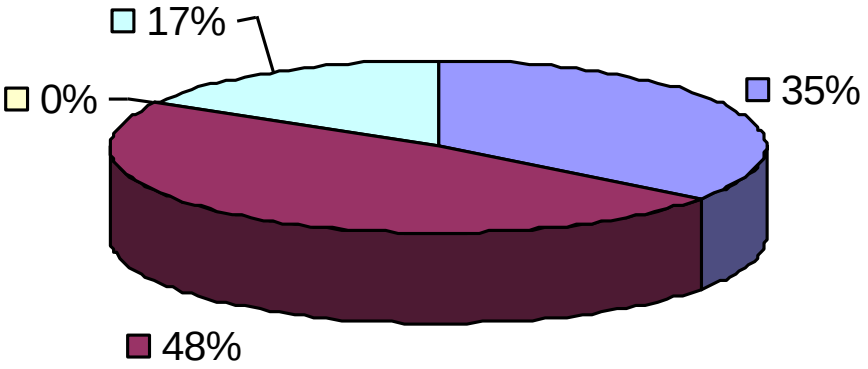


- No matrix effect
- Improves before or with Dil.15x
- Improves at high dilutions (50x-100x)
- Doesn´t improve with dilution

Leek



Orange

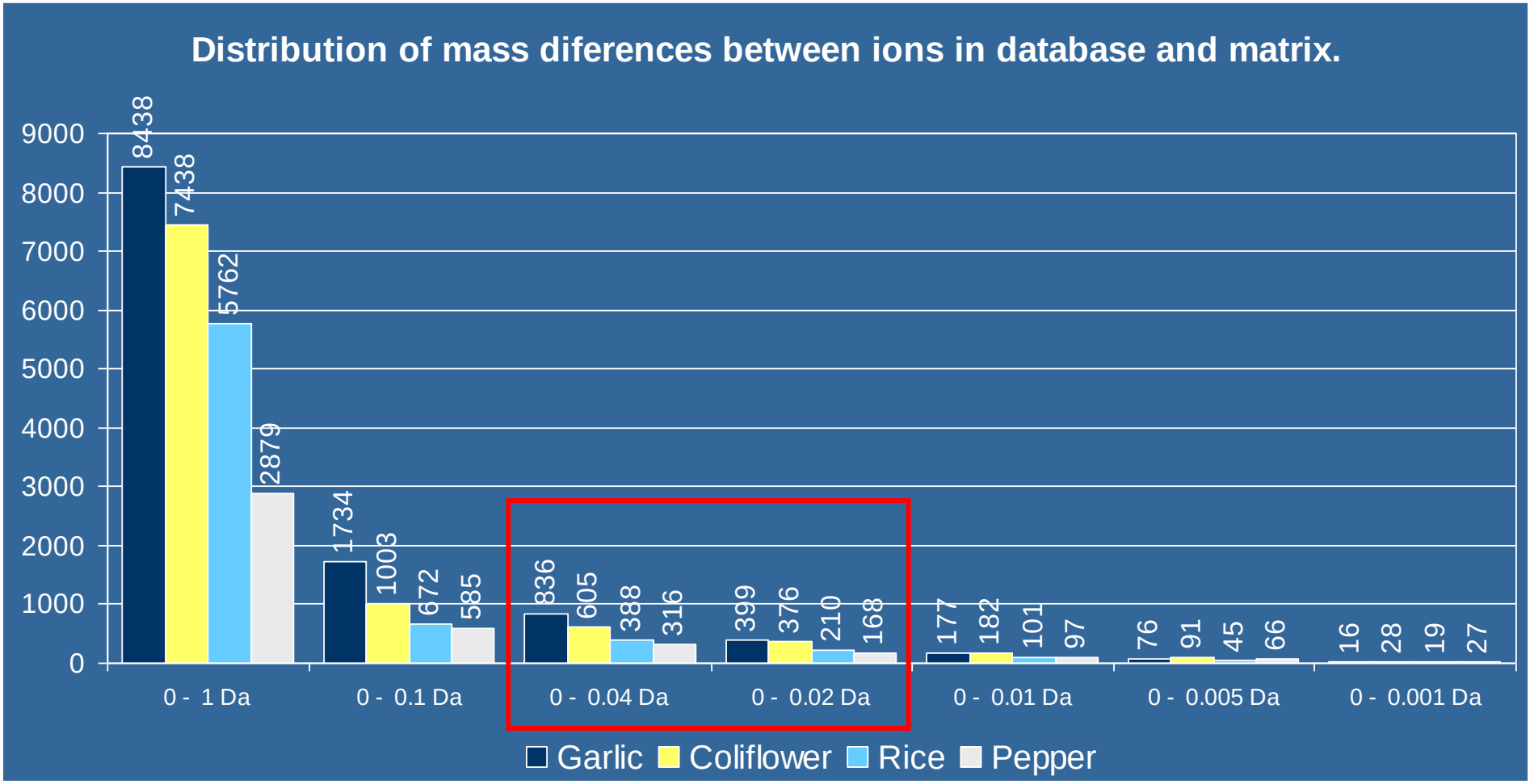


Resolution ⟺ Mass Accuracy

Increasing:

- Frecuency (2MHz-4MHz)
- Path Length
- Calibration

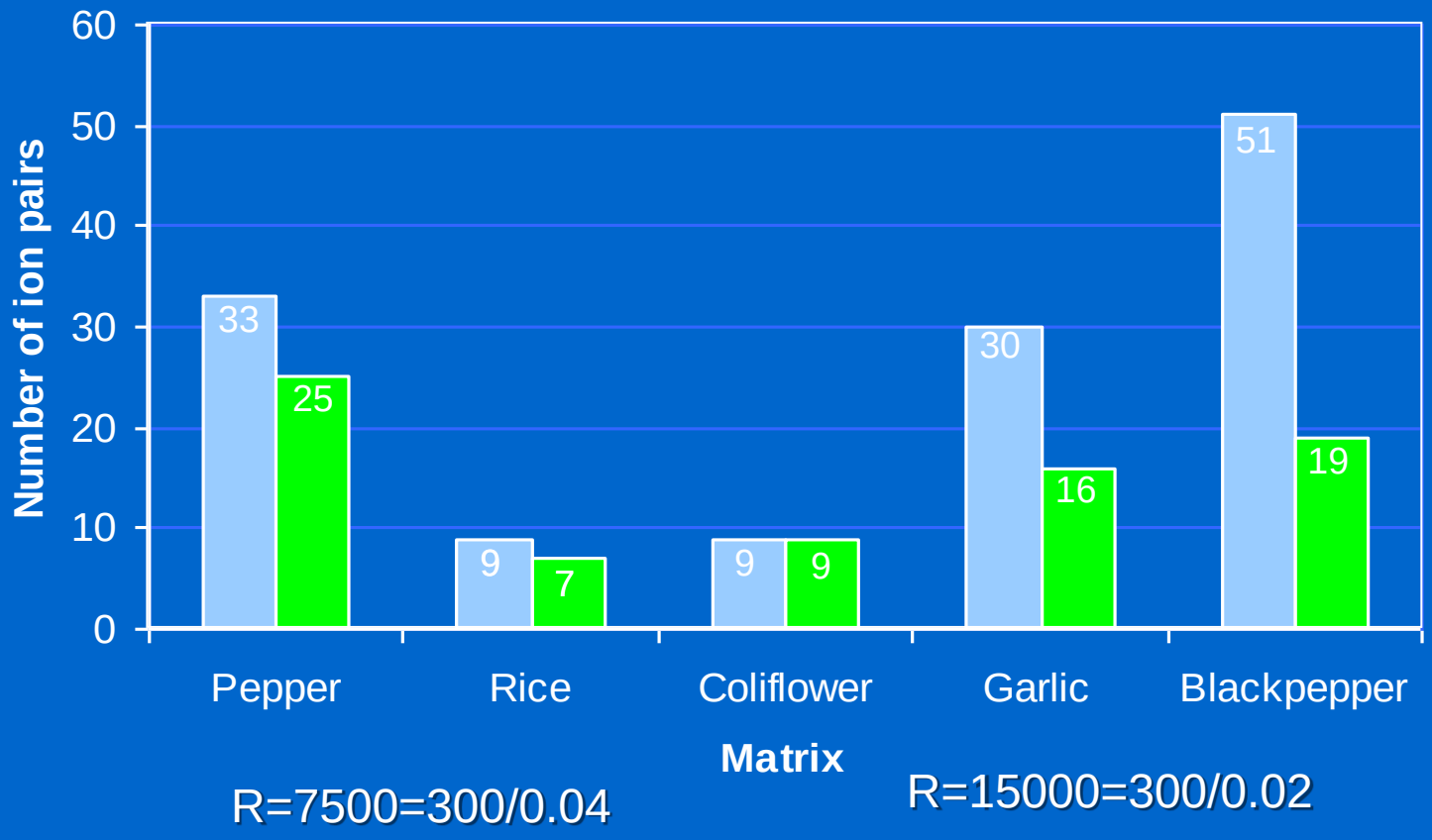
Distribution of mass diferences between ions in database and matrix.



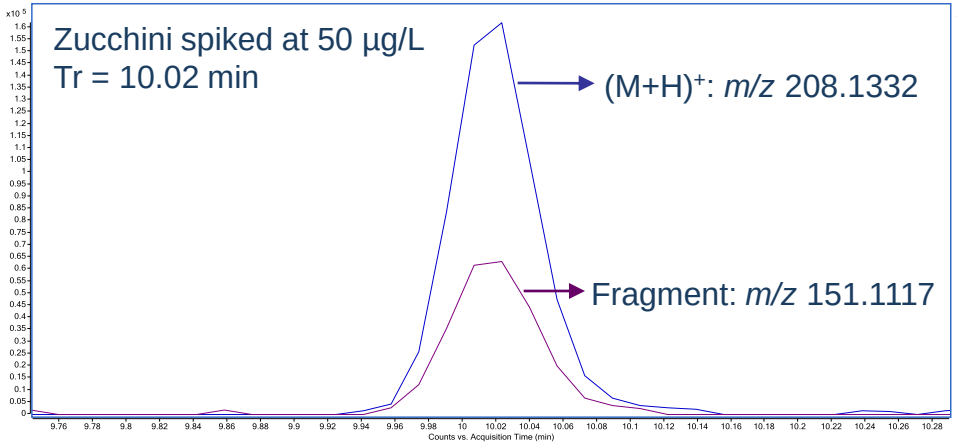
R=15000=300/0.02

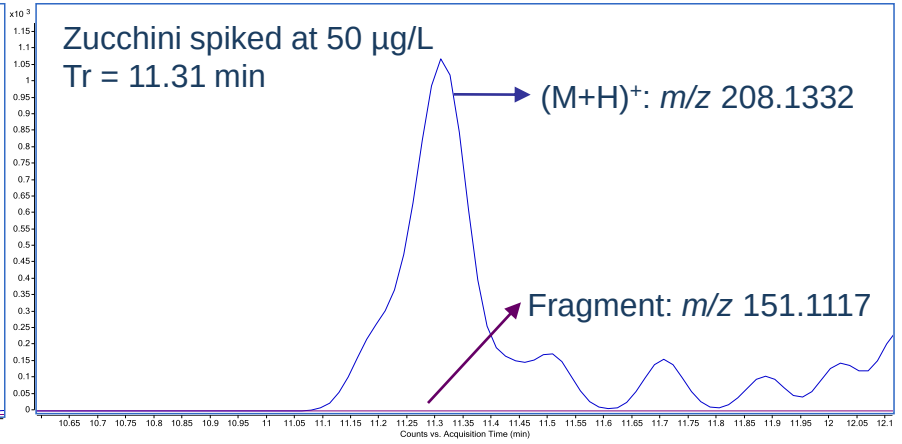
R=7500=300/0.04

Pesticides and interferences with exact mass diferences from 0 to 0.02 Da and from 0 to 0.04 Da and retention time diferences lower than 0.5 min

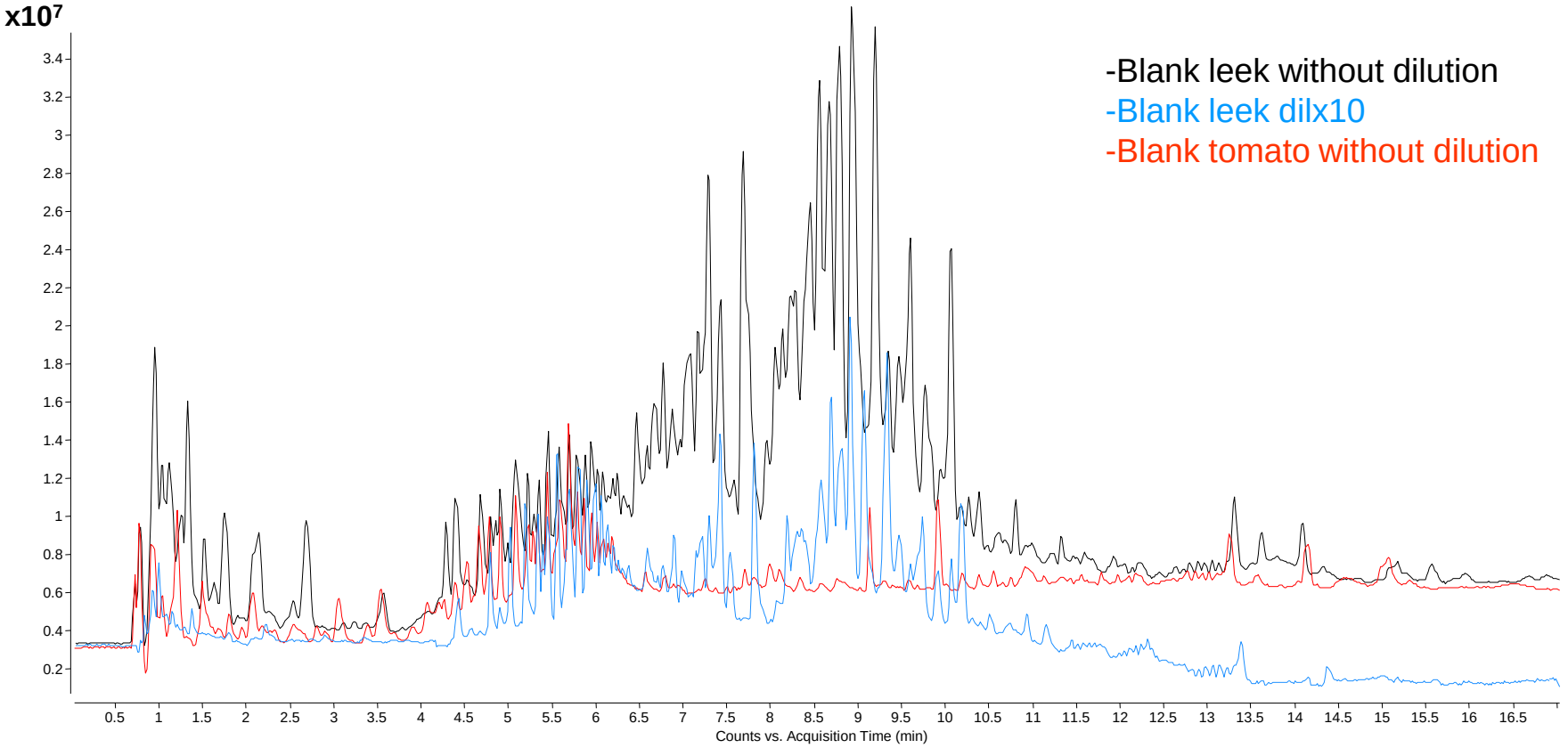


Name	RT	Mass	Mass (DB)	Diff (DB, ppm)	Score (DB)	Formula (Tgt)	Formula (DB)
PROMECARB	10.017	207.126	207.1259	-0.44	99.92	C12H17NO2	C12 H17 N O2
PROMECARB	10.323	207.1263	207.1259	-1.71	98.75	C12H17NO2	C12 H17 N O2
PROMECARB	3.219	207.1255	207.1259	2.03	98.25	C12H17NO2	C12 H17 N O2
PROMECARB	11.315	207.1264	207.1259	-2.37	97.63	C12H17NO2	C12 H17 N O2
PROMECARB F2	7.593	150.1044	150.1045	0.84	99.8	C10H14O	C10 H14 O
PROMECARB F2	10.017	150.1044	150.1045	0.96	99.74	C10H14O	C10 H14 O

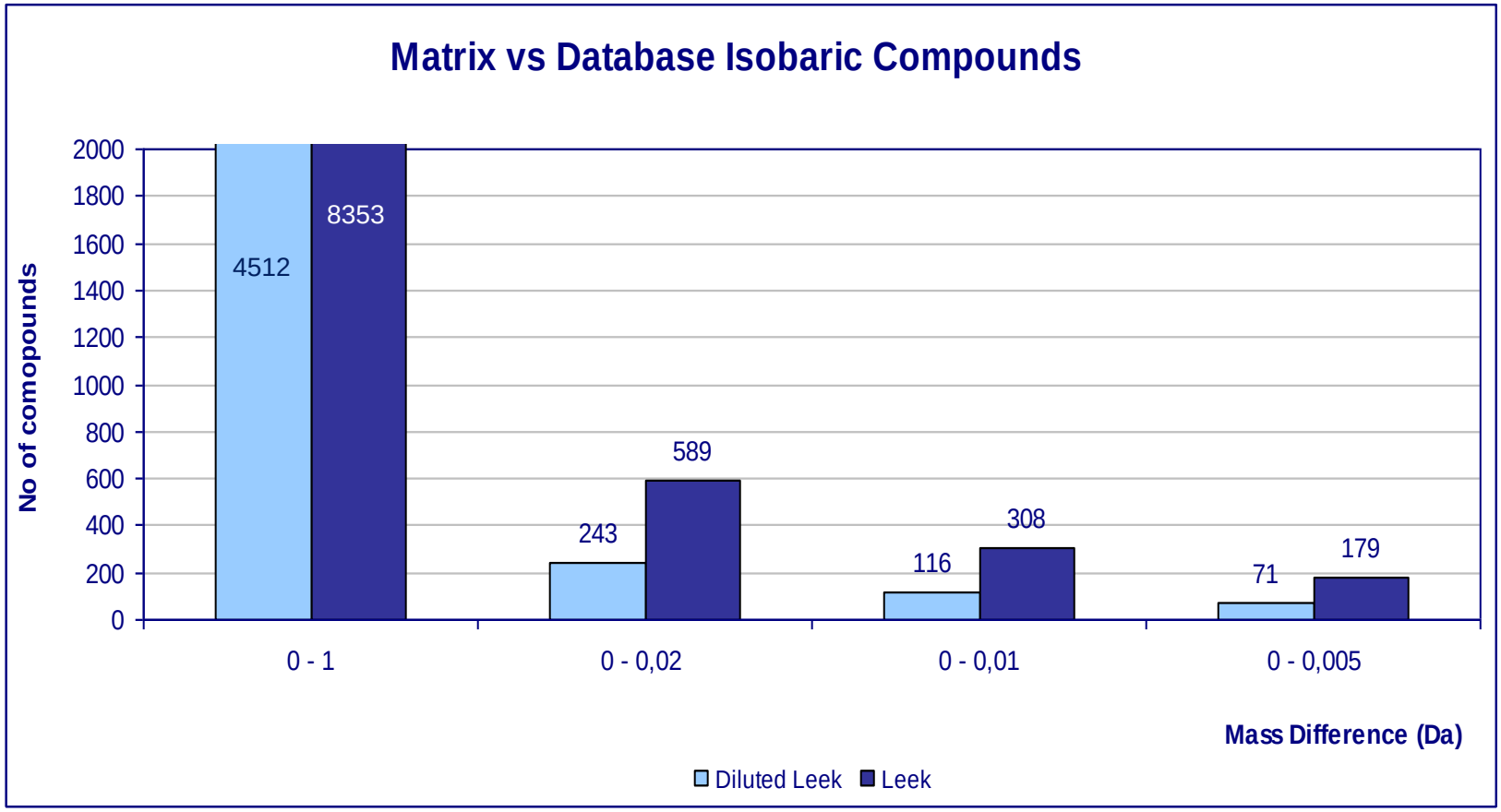




LC-Full scan-MS

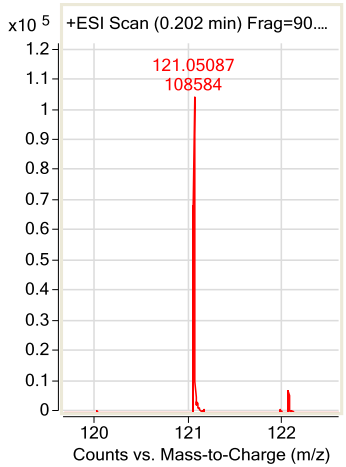


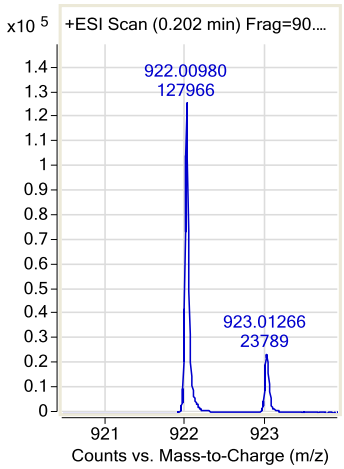
1 g/mL -------- 0.1 g/ml

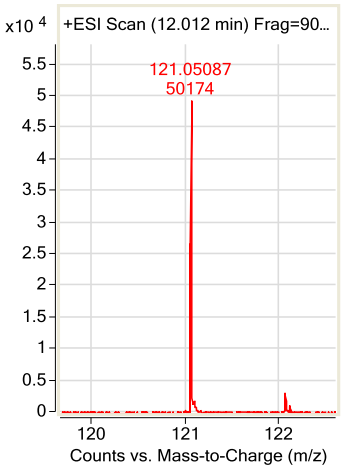

Matrix vs Database Isobaric Compounds
No of comopounds
2000
1800
1600
1400
1200
1000
800
600
400
200
0
4512
8353
243
589
116
308
71
179
0 - 1
0 - 0,02
0 - 0,01
0 - 0,005
Mass Difference (Da)
Diluted Leek
Leek

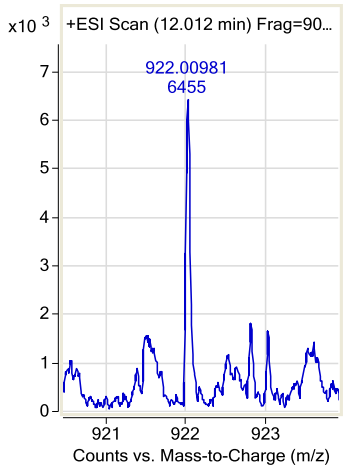
Stability of reference masses

- Intensity of spectral peaks over UHPLC gradient
  - Mobile phase: 10% acetonitrile
  - Mobile phase: 95% acetonitrile

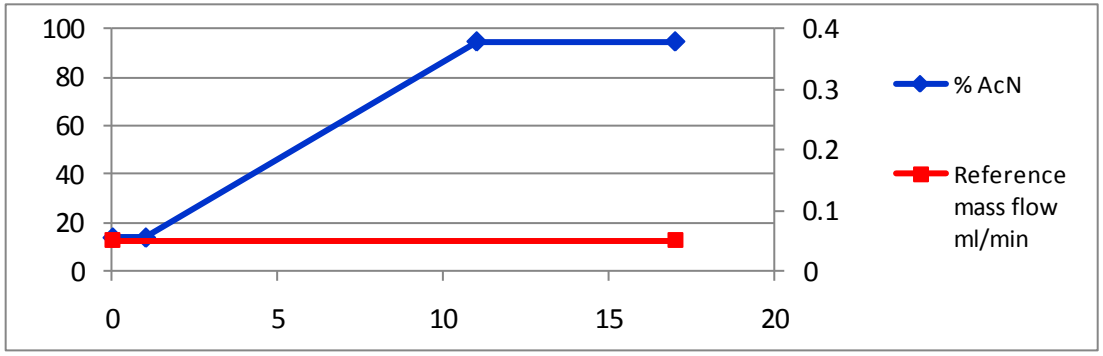








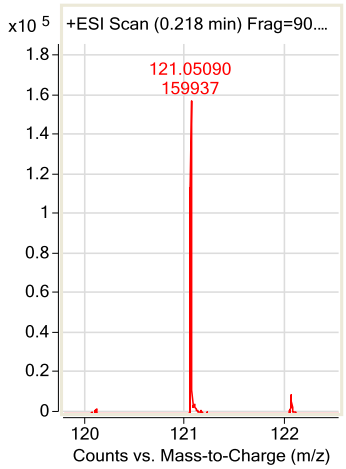
- Reference mass delivery with flow gradient:

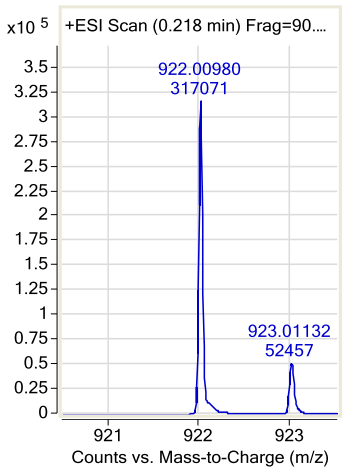


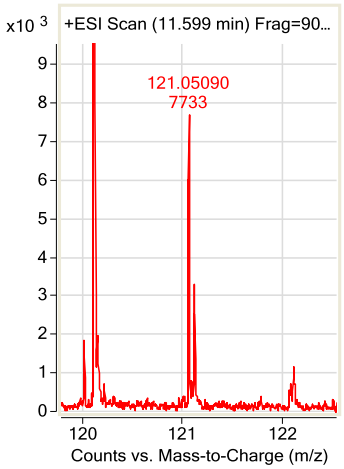
m/z	10% B	100% B
121.05087	110 000	50 000
922.009798	130 000	6 500

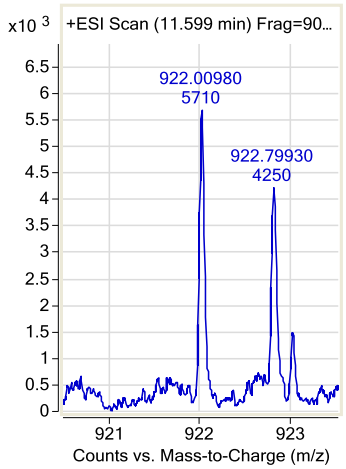
Stability of reference masses

- Intensity of spectral peaks over UHPLC gradient
  - Mobile phase: 10% acetonitrile
  - Mobile phase: 95% acetonitrile

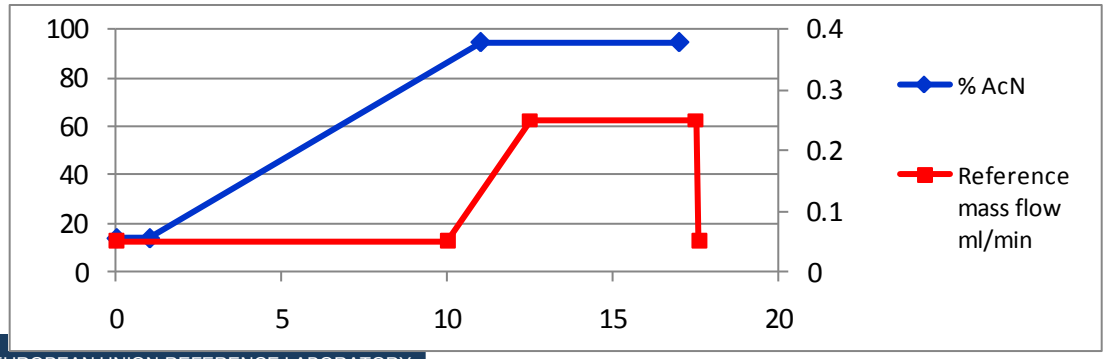








- Reference mass delivery with flow gradient:



SCREENING BASED ON FULL SCAN - MS

LC/GC-TOF – Full scan - MS
GC-Q-Full scan- MS

OR .....

BASED ON MS/MS!

AUTOMATIC SCREENING

FULL SCAN

Additional Advantages

RETROSPECTIVE ANALYSIS

EASY TO IMPLEMENT

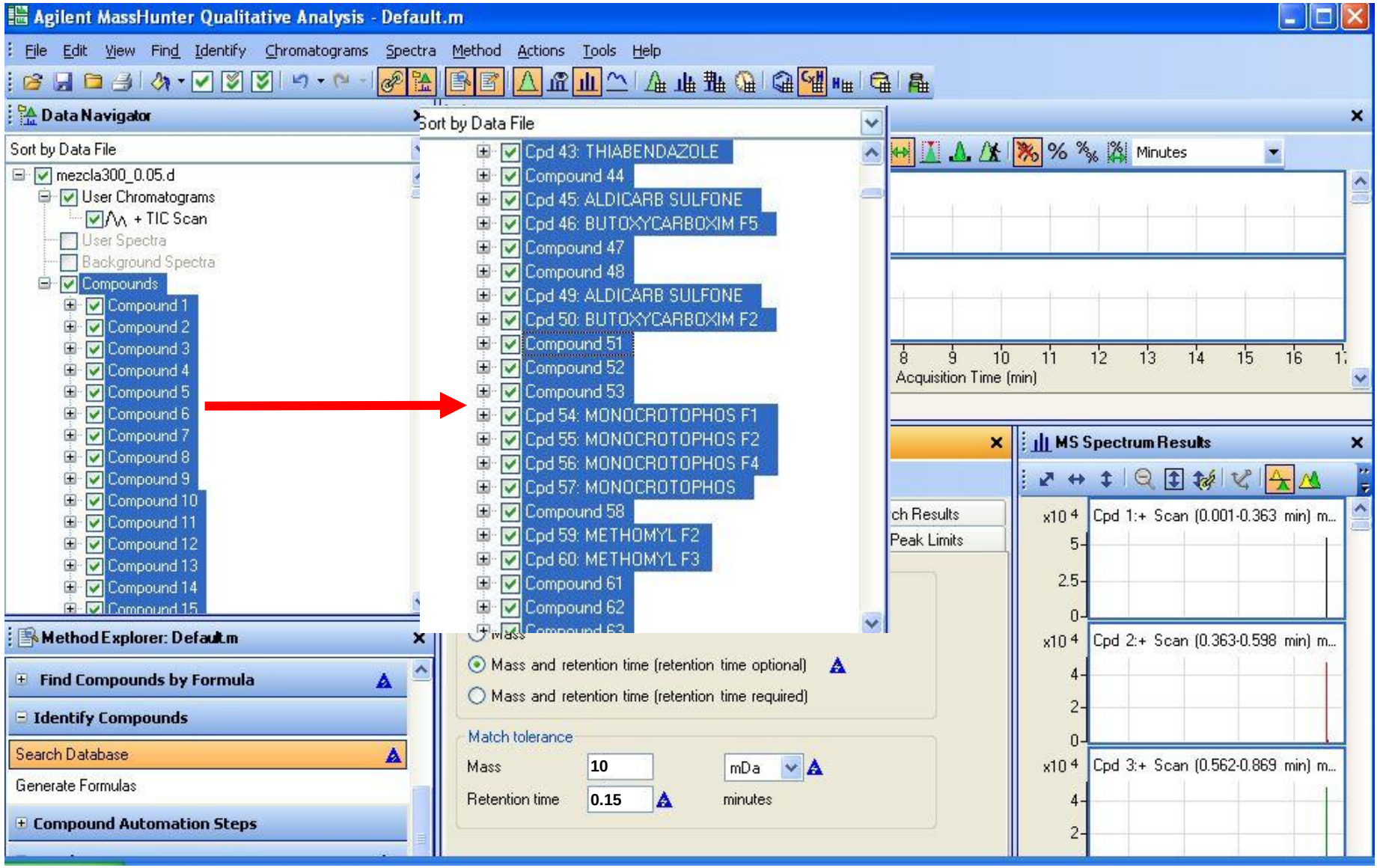
Microsoft Excel - tablafin.xls

G5: 124.9821

	NAME	NAME ion	fig	TR	VOLT	MAIN ION MASS	EXP MASS	error (ppm)	ION DETECTED	ION	ION FORMULA	FORMULA pest
2	ACEPHATE	ACEPHATE	X	1.90	190-230	184.0192	184.0191	-0.4346	[M+H]+	[M+H]+	C4H11NO3PS	C4H10NO3PS
3	ACEPHATE	ACEPHATE F1		1.90	190-230	142.0086	142.0084	5.5258	ACEPHATE F1		C2H9NO2PS	C4H10NO3PS
4	ACEPHATE	ACEPHATE F2		1.90	190-230	136.0158	136.0157	-0.7942	ACEPHATE F2		C3H7NO3P	C4H10NO3PS
5	ACEPHATE	ACEPHATE F3		1.90	190-230	124.9821	124.9821	0.2709	ACEPHATE F3		C2H6O2PS	C4H10NO3PS
6	ACEPHATE	ACEPHATE F4		1.90	190-230	110.9664	110.9667	2.5587	ACEPHATE F4		CH4O2PS	C4H10NO3PS
7	ACEPHATE	ACEPHATE Na	X	1.90	190-230	206.0011	206.0012	0.3657	[M+Na]+	[M+Na]+	C4H10NO3PSNa	C4H10NO3PS
8	ACETAMIPRID	ACETAMIPRID	X	6.69	190-230	223.0745	223.0746	0.4453	[M+H]+	[M+H]+	C10H12ClN4	C10H11ClN4
9	ACETAMIPRID	ACETAMIPRID F1		6.69	190-230	126.0105	126.0100	2.3540	ACETAMIPRID F1		C6H5ClN	C10H11ClN4
10	ACETOCHLOR	ACETOCHLOR	X	10.94	190-230	270.1269	270.1269	1.3575	[M+H]+	[M+H]+	C14H21NO2Cl	C14H20NO2Cl
11	ACETOCHLOR	ACETOCHLOR F1		10.94	190-230	224.0937	224.0940	1.4798	ACETOCHLOR F1		C12H15ClNO	C14H20NO2Cl
12	ACETOCHLOR	ACETOCHLOR F2		10.94	190-230	148.1121	148.1124	2.1876	ACETOCHLOR F2		C10H14N	C14H20NO2Cl
13	ACETOCHLOR	ACETOCHLOR F3		10.94	190-230	132.0808	132.0809	0.9401	ACETOCHLOR F3		C9H10N	C14H20NO2Cl
14	ACETOCHLOR	ACETOCHLOR F4		10.94	190-230	91.0542	91.0543	0.8050	ACETOCHLOR F4		C7H7	C14H20NO2Cl
15	ACLONIFEN	ACLONIFEN	X	11.17	190-230	265.0874	265.0871	-1.3073	[M+H]+	[M+H]+	C12H10ClN2O3	C12H9ClN2O3
16	ACRINATHRIN	ACRINATHRIN F1		13.46	190-230	208.0757	208.0755	-0.9153	ACRINATHRIN F1		C14H10NO	C26H21F6NO5
17	ACRINATHRIN	ACRINATHRIN Na	X	13.46	190-230	564.1216	564.1216	-0.0242	[M+Na]+	[M+Na]+	C26H21F6NO5Na	C26H21F6NO5
18	ALACHLOR	ALACHLOR	X	10.90	190-230	270.1255	270.1253	-0.5635	[M+H]+	[M+H]+	C14H21ClNO2	C14H20ClNO2
19	ALACHLOR	ALACHLOR F1		10.90	190-230	162.1277	162.1276	-0.7775	ALACHLOR F1		C11H16N	C14H20ClNO2
20	ALANYCARB	ALANYCARB	X	10.80	190-230	400.1359	400.1359	0.0665	[M+H]+	[M+H]+	C17H25N3O4S2	C17H24N3O4S2
21	ALANYCARB	ALANYCARB F1		10.80	190-230	236.0696	236.0696	0.1140	ALANYCARB F1		C12H14NO2S	C17H24N3O4S2
22	ALANYCARB	ALANYCARB F2		10.80	190-230	200.1332	200.1334	0.9340	ALANYCARB F2		C12H18NO2	C17H24N3O4S2
412	LINURON	LINURON	X	9.95	190-230	249.0192	249.0191	-0.4401	[M+H]+	[M+H]+	C9H11Cl2N2O2	C9H10Cl2N2O2
413	LINURON	LINURON F1		9.95	190-230	182.0241	182.0239	-4.5262	LINURON F1		C8H7Cl2NO	C9H10Cl2N2O2
414	LINURON	LINURON F2		9.95	190-230	159.9715	159.9727	7.3071	LINURON F2		C8H4Cl2N	C9H10Cl2N2O2
415	LUFENURON	LUFENURON	X	12.29	190-230	510.9957	510.9957	-0.0003	[M+H]+	[M+H]+	C17H9Cl2F8N2O3	C17H8Cl2F8N2O3
416	LUFENURON	LUFENURON F1		12.29	190-230	158.0412	158.0410	-1.2452	LUFENURON F1		C7H6F2NO	C17H8Cl2F8N2O3
417	MALAOXON	MALAOXON	X	8.11	190-230	316.0662	316.0656	-1.8723	[M+H]+	[M+H]+	C10H20O7PS	C10H19O7PS
418	MALATHION	MALATHION	X	10.70	190-230	331.0433	331.0435	0.4619	[M+H]+	[M+H]+	C10H20O6PS2	C10H19O6PS2
419	MALATHION	MALATHION F1		10.70	190-230	285.0015	285.0017	0.7642	MALATHION F1		C8H14O5PS2	C10H19O6PS2
420	MALATHION	MALATHION F2		10.70	190-230	257.0066	257.0069	1.2895	MALATHION F2		C7H14O4PS2	C10H19O6PS2
421	MALATHION	MALATHION F3		10.70	190-230	210.9647	210.9653	2.8314	MALATHION F3		C5H8O3PS2	C10H19O6PS2
422	MALATHION	MALATHION F5		10.70	190-230	127.0390	127.0394	3.3798	MALATHION F5		C6H7O3	C10H19O6PS2
423	MALATHION	MALATHION F6		10.70	190-230	124.9821	124.9817	-2.8295	MALATHION F6		C2H6O2PS	C10H19O6PS2
424	MALATHION	MALATHION F7		10.70	190-230	99.0077	99.0082	5.0404	MALATHION F7		C4H3O3	C10H19O6PS2
425	MEBENDAZOLE	MEBENDAZOLE	X	7.47	190-230	296.1030	296.1036	2.1046	[M+H]+	[M+H]+	C16H14N3O3	C16H13N3O3
426	MEBENDAZOLE	MEBENDAZOLE F1		7.47	190-230	264.0769	264.0769	0.5561	MEBENDAZOLE F1		C15H10NO2	C16H13N3O3
427	MECARBAM	MECARBAM	X	11.06	190-230	330.0590	330.0592	-0.3903	[M+H]+	[M+H]+	C10H21NO5PS2	C10H20NO5PS2
428	MECARBAM	MECARBAM F1		11.06	190-230	226.9961	226.9963	1.3091	MECARBAM F1		C8H12O3PS2	C10H20NO5PS2
429	MECARBAM	MECARBAM F2		11.06	190-230	198.9625	198.9621	-1.8009	MECARBAM F2		C4H8O5PS	C10H20NO5PS2
430	MECARBAM	MECARBAM F3		11.06	190-230	153.0134	153.0132	-1.0868	MECARBAM F3		C4H10O2PS	C10H20NO5PS2
431	MECARBAM	MECARBAM F4		11.06	190-230	142.9385	142.9386	0.7845	MECARBAM F4		CH4O2PS2	C10H20NO5PS2
432	MECARBAM	MECARBAM F5		11.06	190-230	128.9228	128.9229	0.4626	MECARBAM F5		H2O2PS2	C10H20NO5PS2
433	MECARBAM	MECARBAM F6		11.06	190-230	124.9821	124.9820	-0.5291	MECARBAM F6		C2H6O2PS	C10H20NO5PS2

DATABASE SEARCH

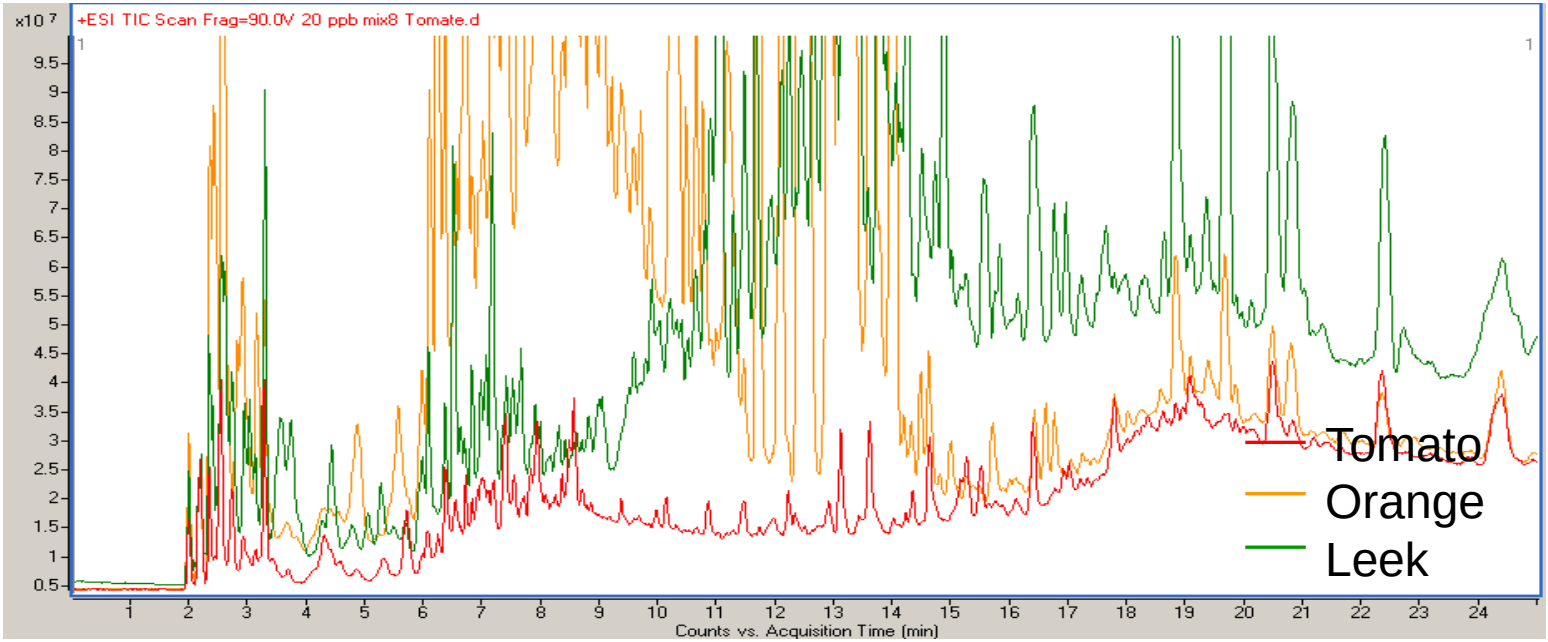
PESTICIDES in solvent (20-500ppb)

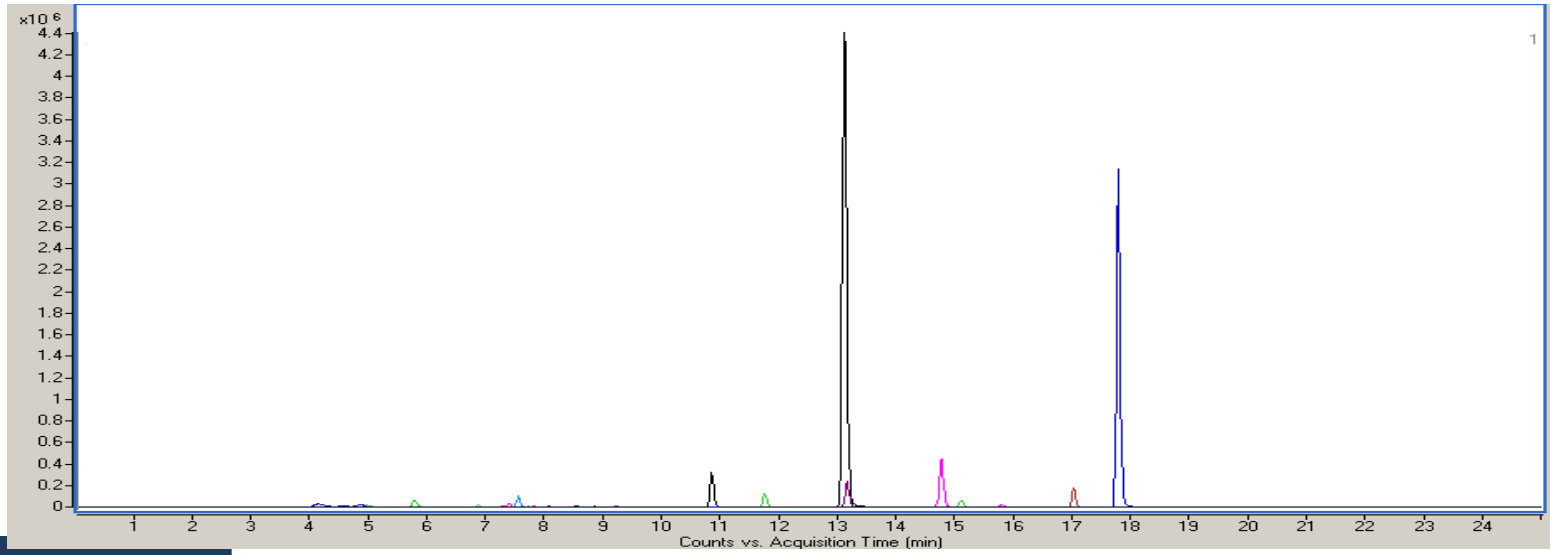


PROBLEMS

Without dilution

1 g/mL





Set up:

5 matrices (Tomato, pepper, Zucchini, Orange and leek).

3 levels (20, 50 and 100 ng/mL).

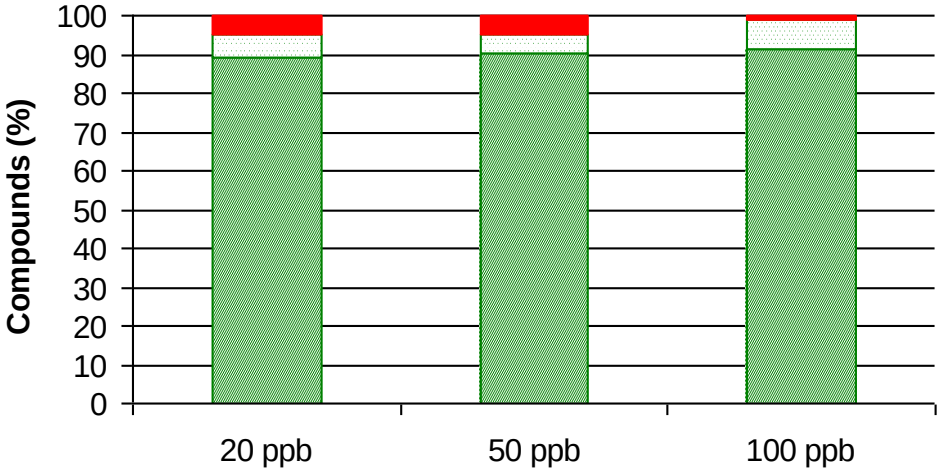
97 compounds (LC and/or GC amenables). 7 were not detected in ESI-QTOF:

- Azocyclotin*
- Carbophenothion (Very low sensitibity)
- Chlozolinate*
- Flubendiamide[1]
- Flucythrinate*
- Halfenprox*
- Terbufos[1]

* Not signal

[1] Not ionize with this source

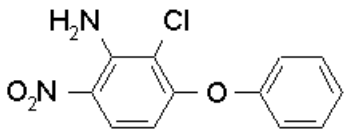
Compounds detected (%) in solvent



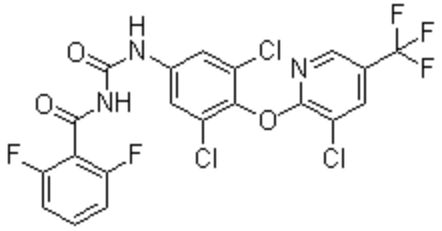
Compounds with low sensitivity (Not detected at 20 ppb in solvent):

- Aclonifen
- Chlorfluazuron
- Clopyralid
- Famoxadone
- Hexaflumuron
- O-Phenylphenol
- Prothiophos

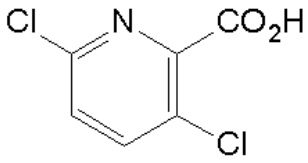
Aclonifen



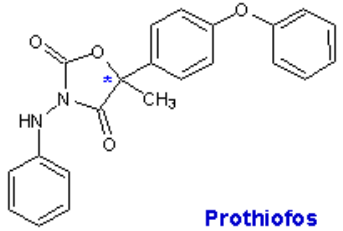
Chlorfluazuron



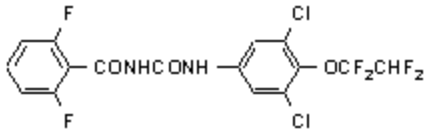
Clopyralid



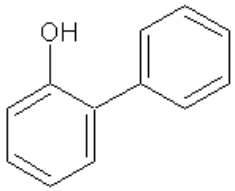
Famoxadone



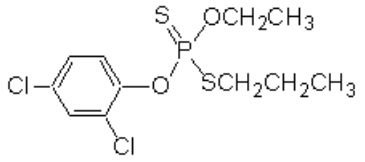
Hexaflumuron



Orthophenylphenol

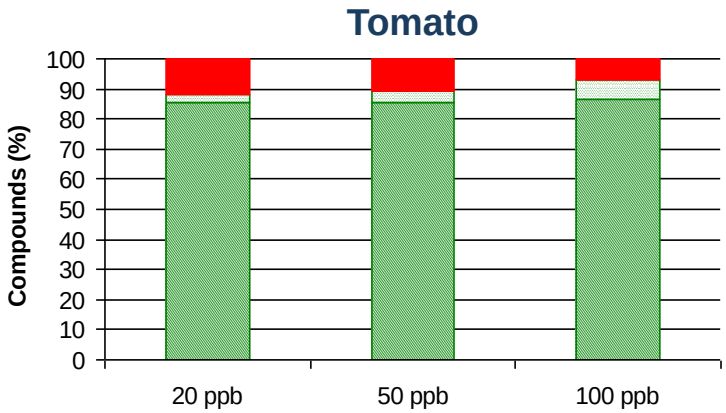


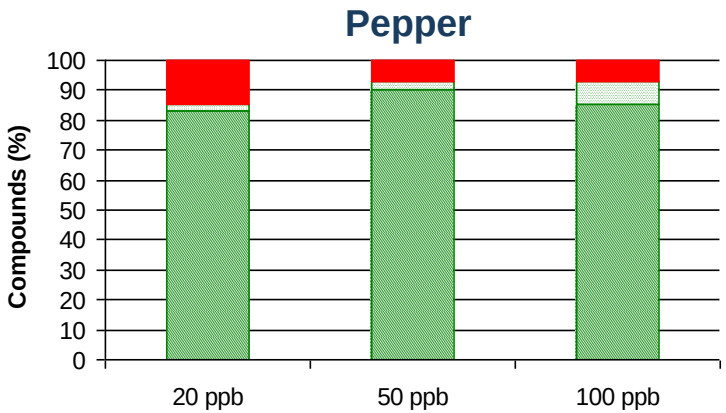
Prothiofos

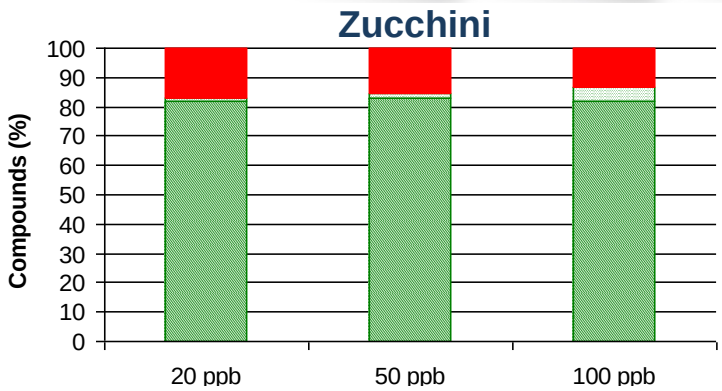


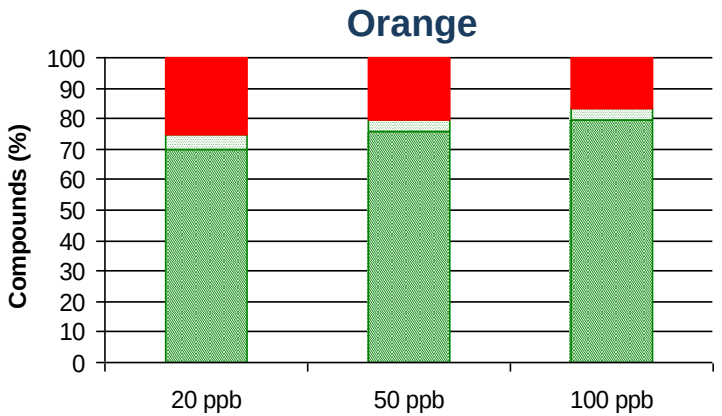
Sensitivity (1g/mL)

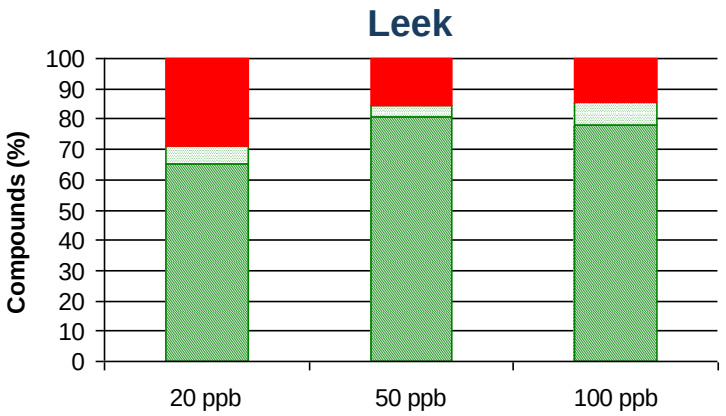
Compounds detected (%) in matrix



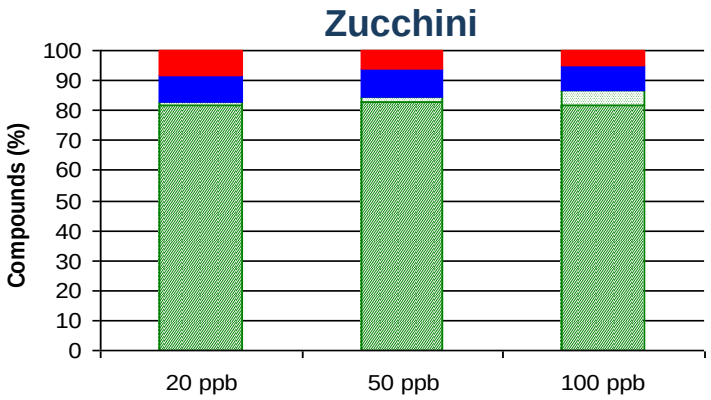


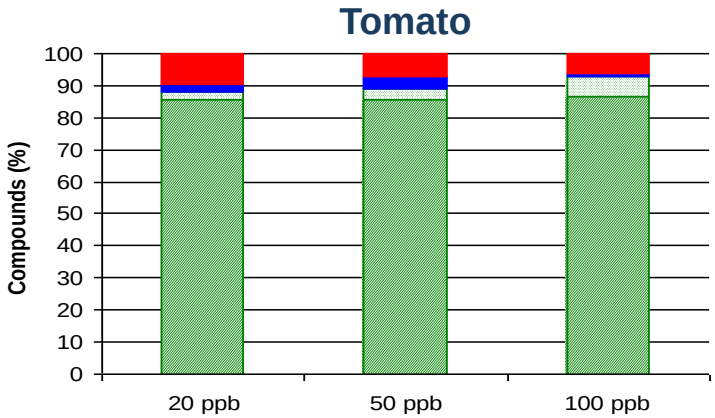


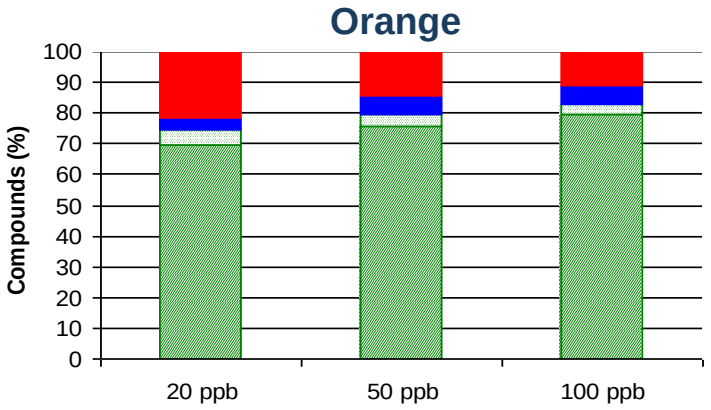


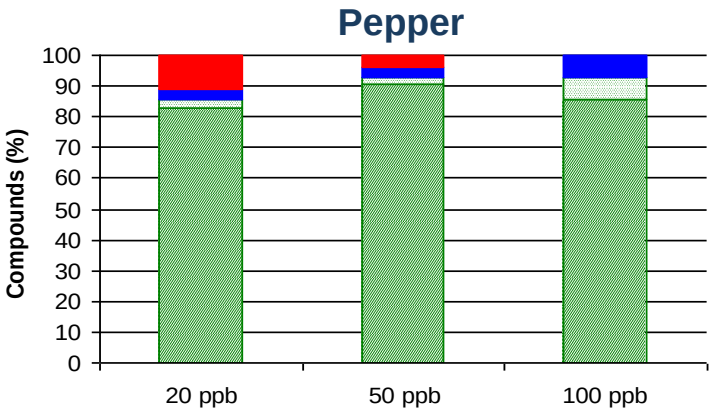


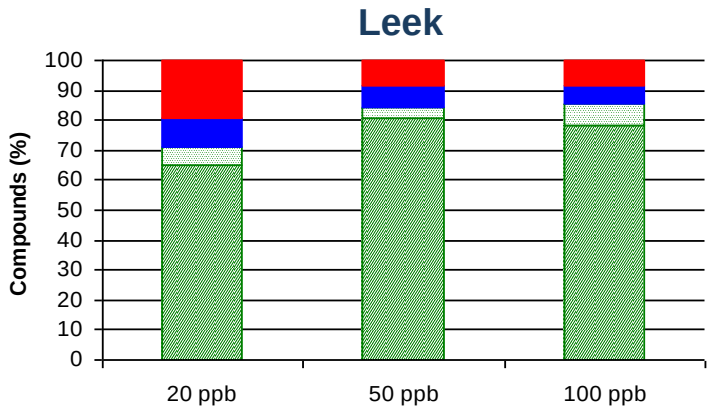
Compounds detected (%) in matrix (LC and GC)



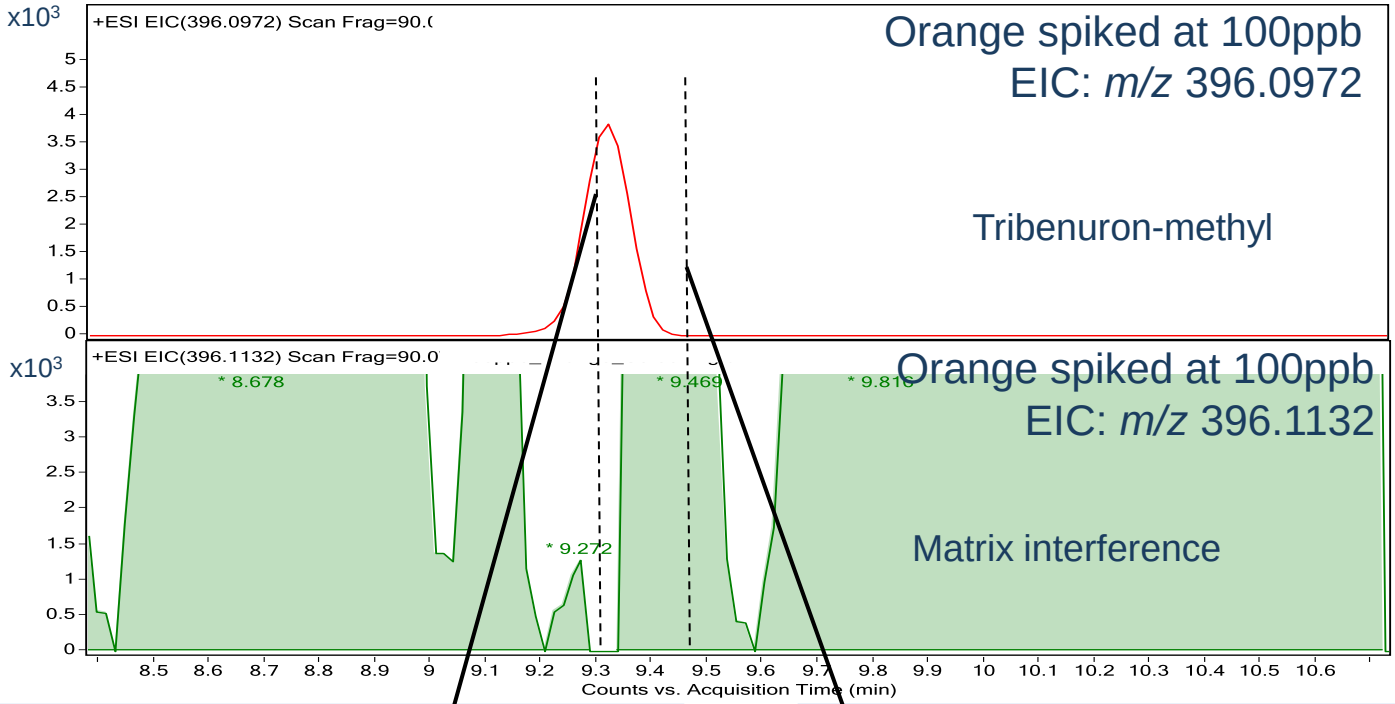


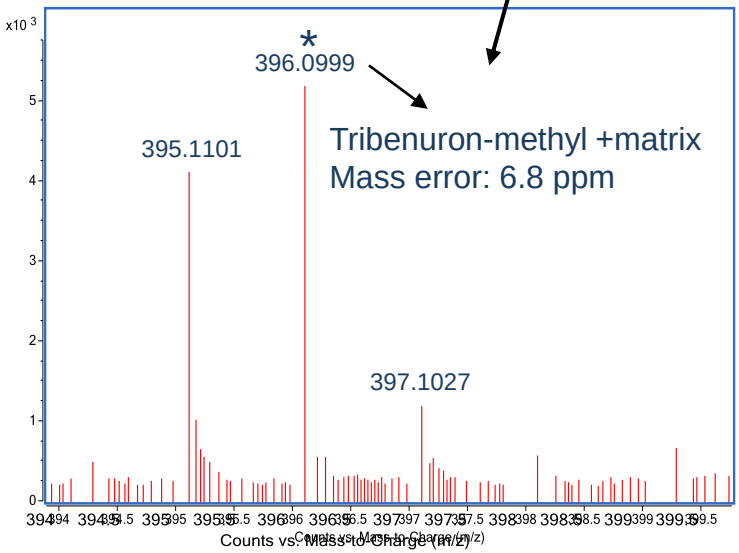


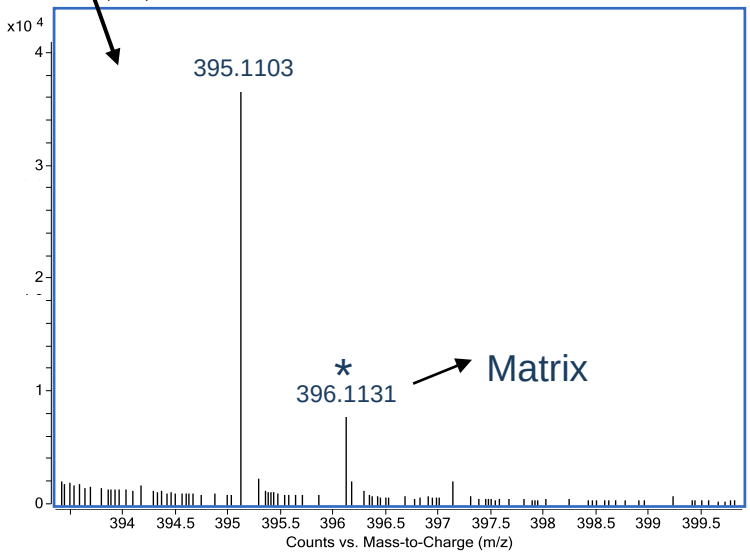




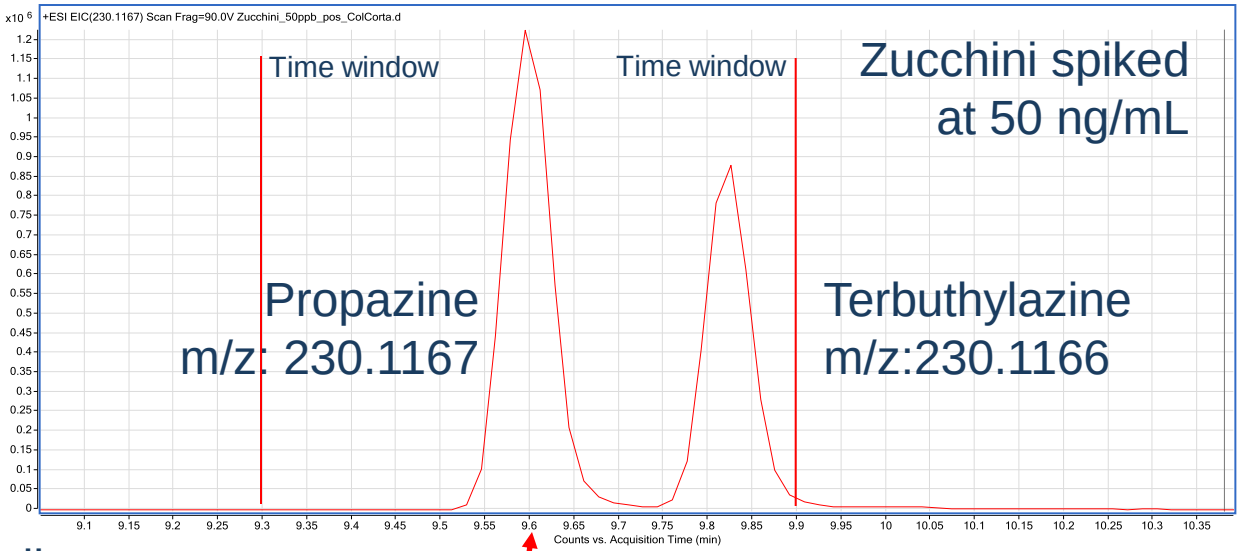
Mass error due to matrix interference (at 15000 resolution)







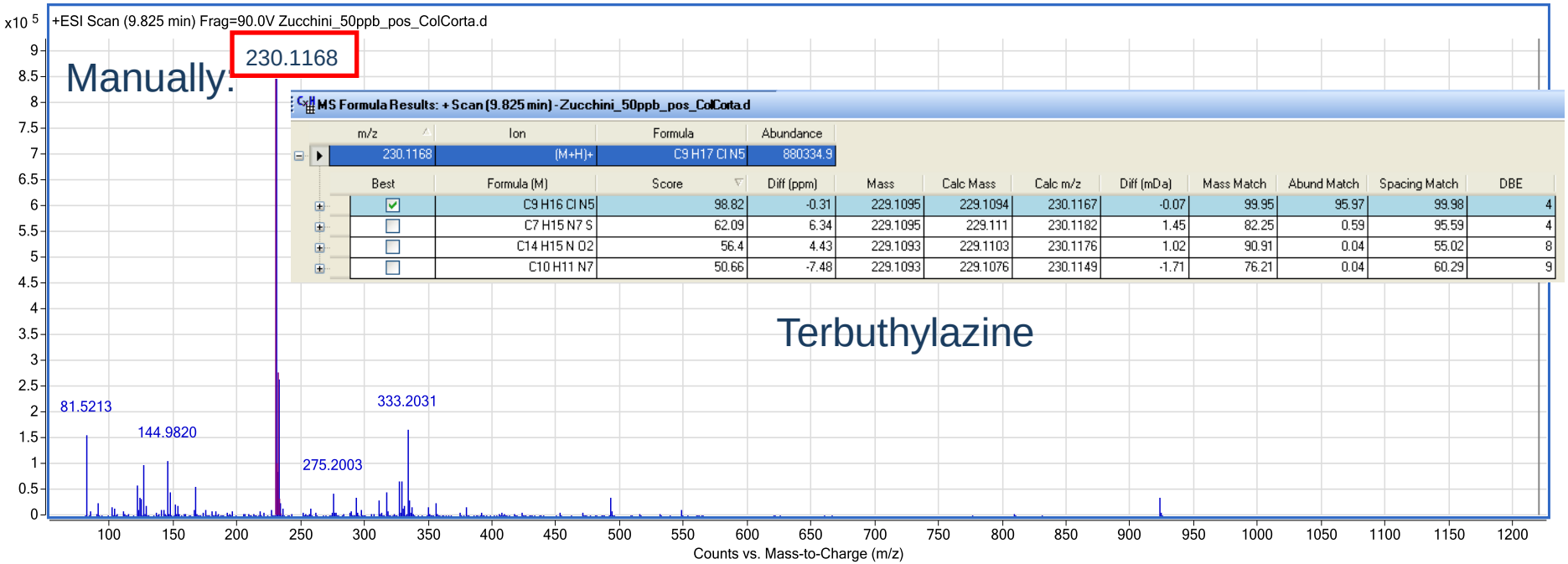
Compound not detected automatically and detected manually



Automatically:

Compound List

Show/Hide	Name	File	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Formula (Tgt)	Score (Tgt)	Score (DB)	Hits (DB)	Ions	Height	Vol %
☑	PROPAZINE	Zucchini_50ppb...	9.619	229.1095	229.1094	0.35	C9H16ClN5	59.43	99.91	2	2	1222938	3.64



MS Formula Results: + Scan (9.825 min) - Zucchini_50ppb_pos_ColCorta.d

m/z	Ion	Formula	Abundance
230.1168	(M+H)+	C9 H17 Cl N5	880334.9

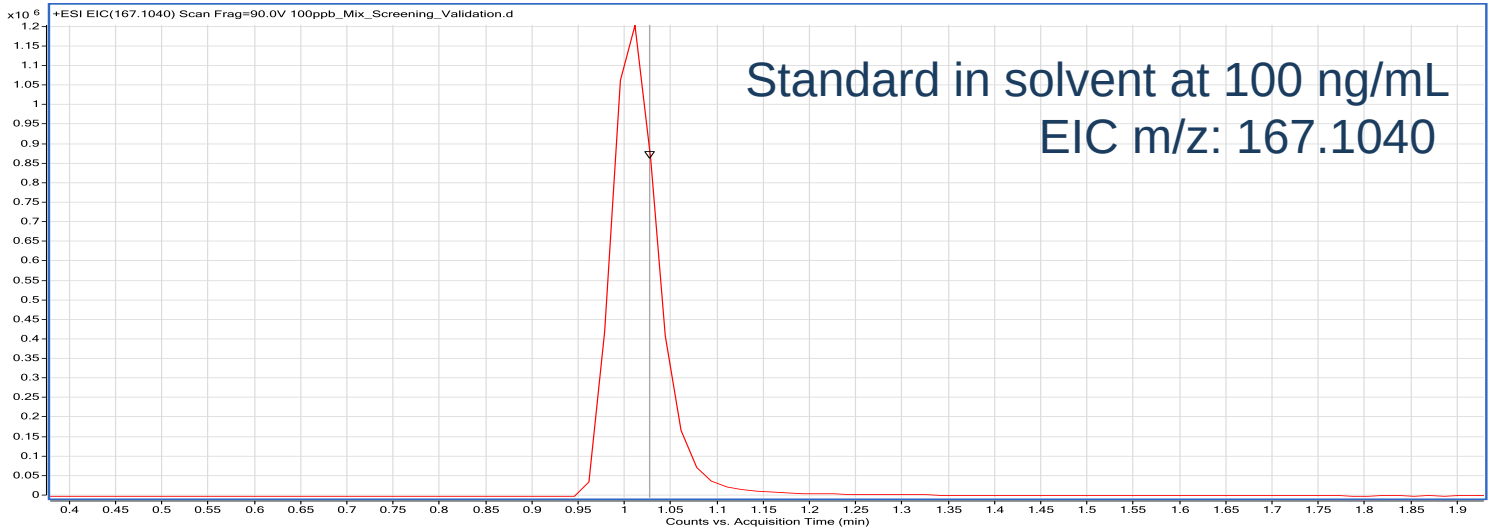
Best	Formula (M)	Score	Diff (ppm)	Mass	Calc Mass	Calc m/z	Diff (mDa)	Mass Match	Abund Match	Spacing Match	DBE
☑	C9 H16 Cl N5	98.82	-0.31	229.1095	229.1094	230.1167	-0.07	99.95	95.97	99.98	4
☐	C7 H15 N7 S	62.09	6.34	229.1095	229.111	230.1182	1.45	82.25	0.59	95.59	4
☐	C14 H15 N O2	56.4	4.43	229.1093	229.1103	230.1176	1.02	90.91	0.04	55.02	8
☐	C10 H11 N7	50.66	-7.48	229.1093	229.1076	230.1149	-1.71	76.21	0.04	60.29	9

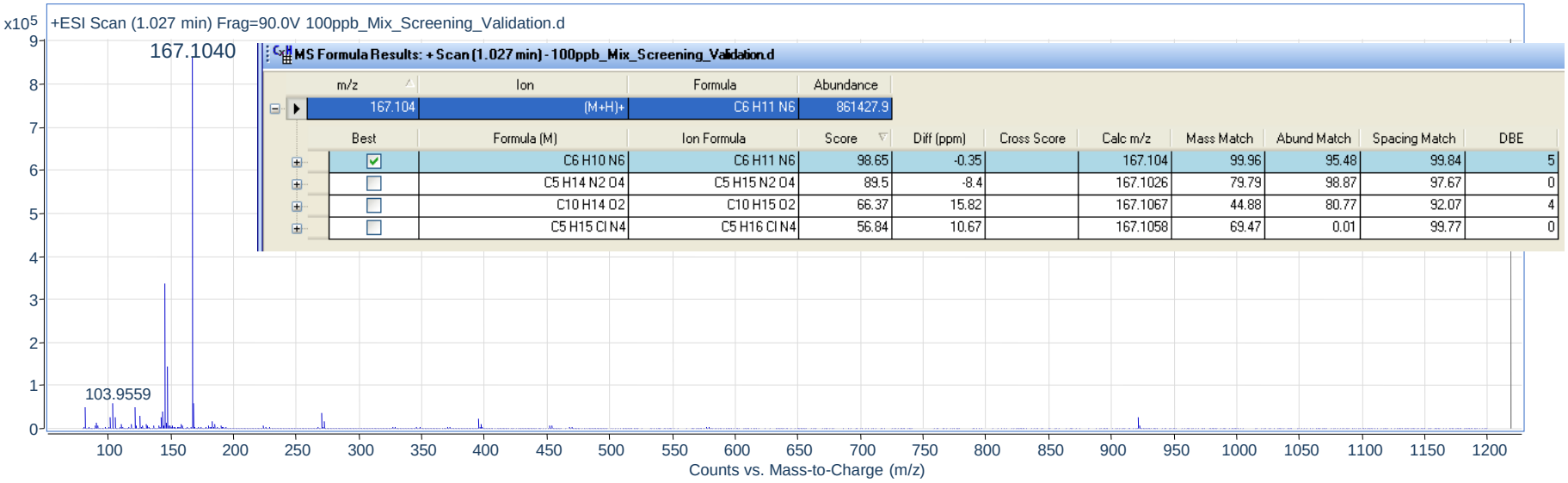
Terbuthylazine

Automatic searching for isotopic patterns

Compound not detected either automatically or manually but spiked

Cyromazine ($C_6H_{10}N_6$) $[M+H]^+$= 167.1040 t_r=1 min

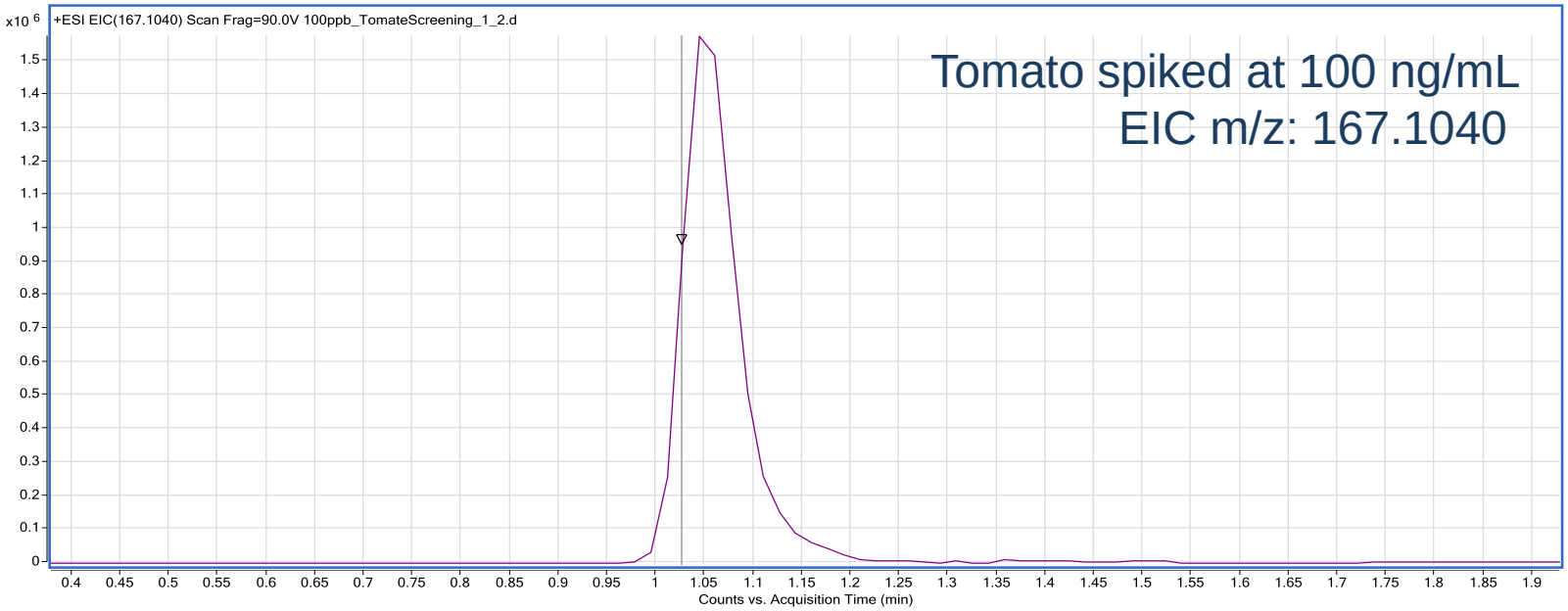




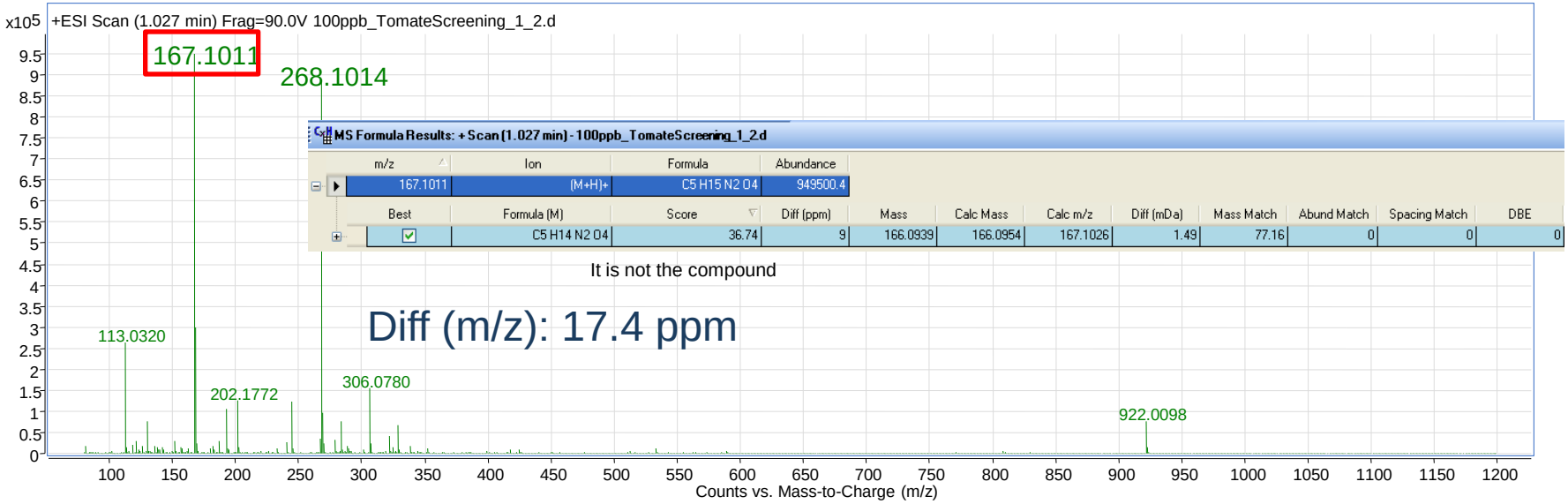
MS Formula Results: +Scan (1.027 min) - 100ppb_Mix_Screening_Validation.d

m/z	Ion	Formula	Abundance
167.104	(M+H)+	C6 H11 N6	861427.9

Best	Formula (M)	Ion Formula	Score	Diff (ppm)	Cross Score	Calc m/z	Mass Match	Abund Match	Spacing Match	DBE
☑	C6 H10 N6	C6 H11 N6	98.65	-0.35		167.104	99.96	95.48	99.84	5
☐	C5 H14 N2 O4	C5 H15 N2 O4	89.5	-8.4		167.1026	79.79	98.87	97.67	0
☐	C10 H14 O2	C10 H15 O2	66.37	15.82		167.1067	44.88	80.77	92.07	4
☐	C5 H15 Cl N4	C5 H16 Cl N4	56.84	10.67		167.1058	69.47	0.01	99.77	0



Tomato spiked at 100 ng/mL
EIC m/z: 167.1040



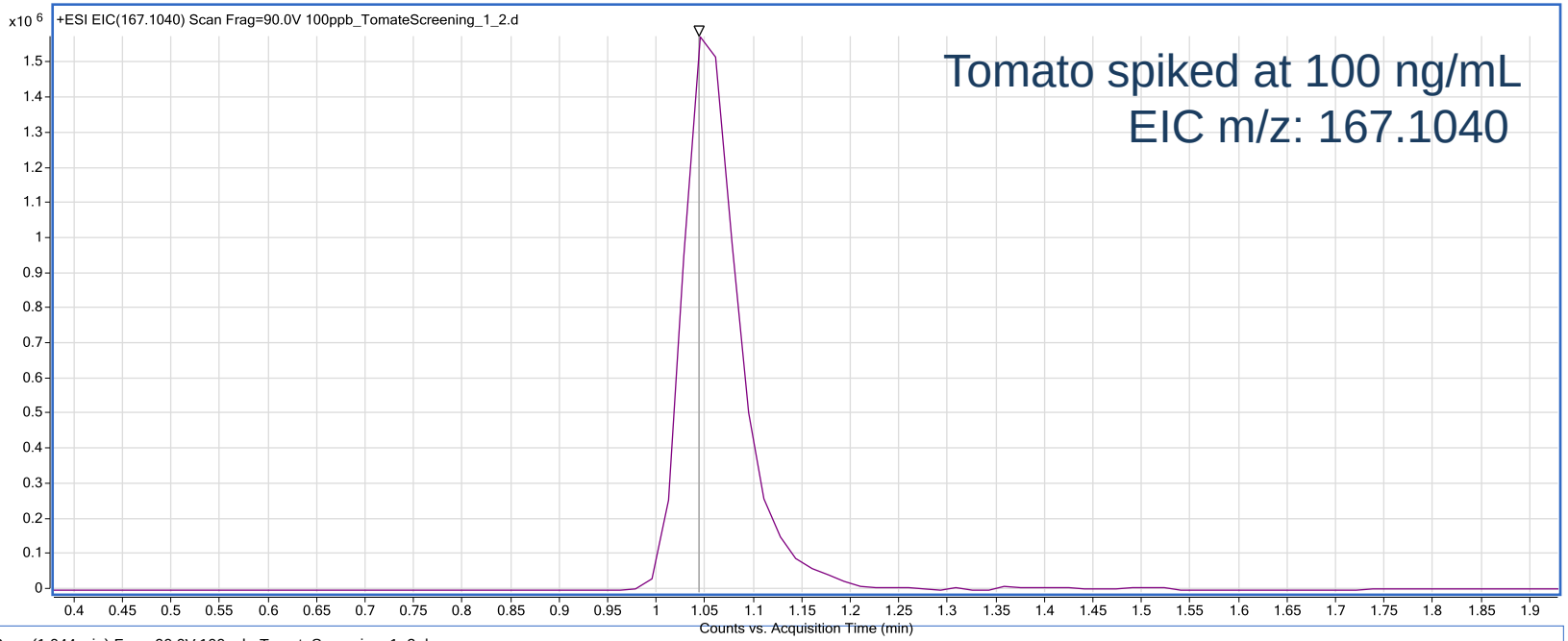
MS Formula Results: +Scan (1.027 min) - 100ppb_TomateScreening_1_2.d

m/z	Ion	Formula	Abundance
167.1011	(M+H)+	C5 H15 N2 O4	949500.4

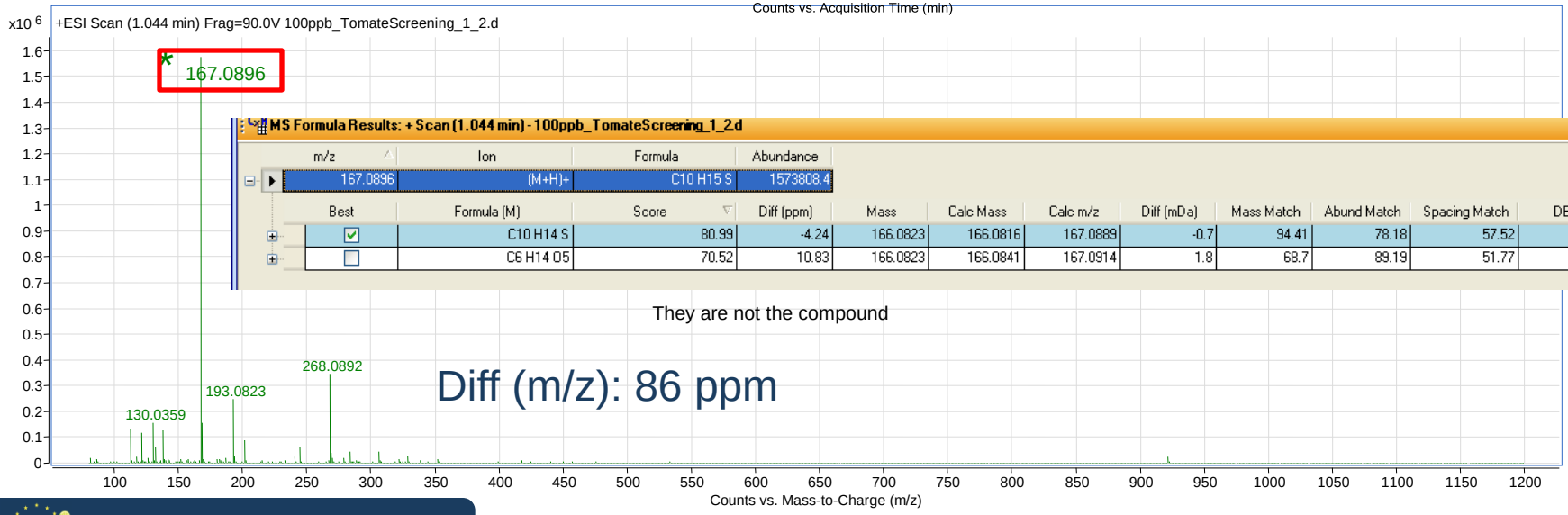
Best	Formula (M)	Score	Diff (ppm)	Mass	Calc Mass	Calc m/z	Diff (mDa)	Mass Match	Abund Match	Spacing Match	DBE
☑	C5 H14 N2 O4	36.74	9	166.0939	166.0954	167.1026	1.49	77.16	0	0	0

It is not the compound

Diff (m/z): 17.4 ppm



Tomato spiked at 100 ng/mL
EIC m/z: 167.1040



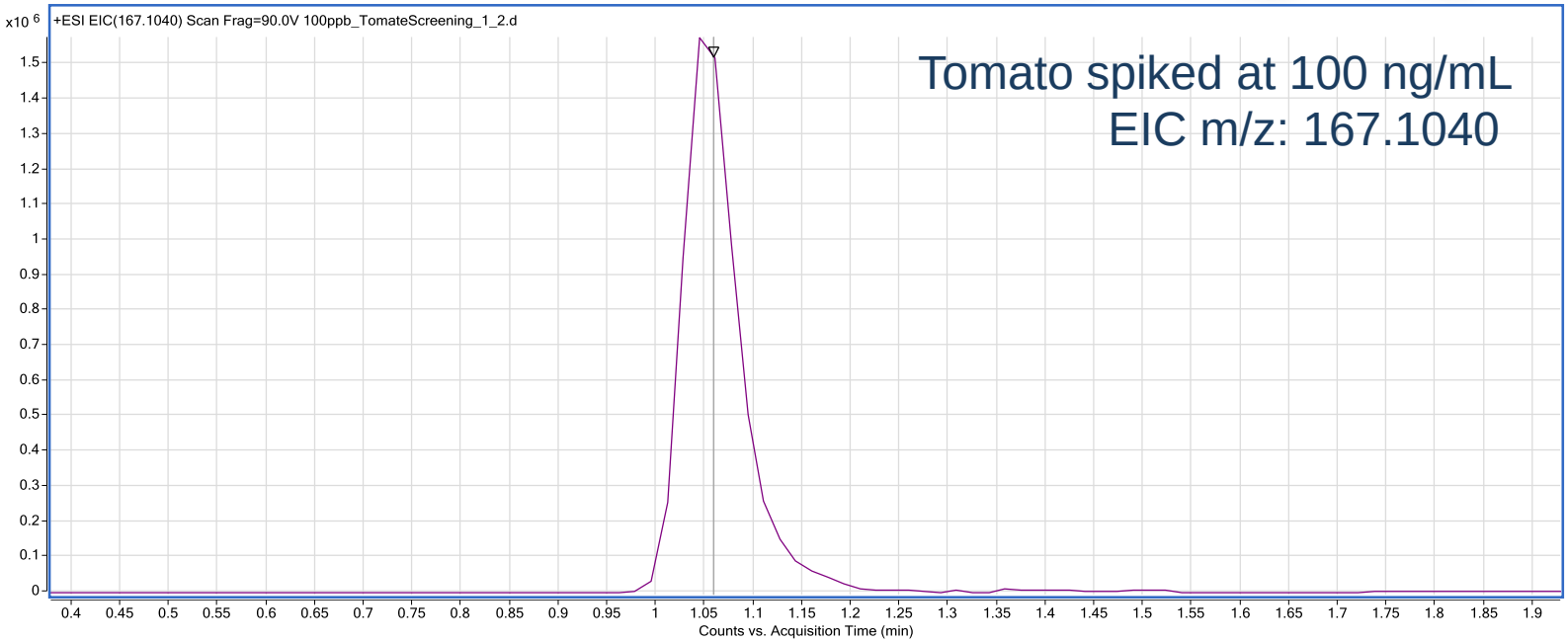
MS Formula Results: +Scan (1.044 min) - 100ppb_TomateScreening_1_2.d

m/z	Ion	Formula	Abundance
167.0896	(M+H)+	C10 H15 S	1573808.4

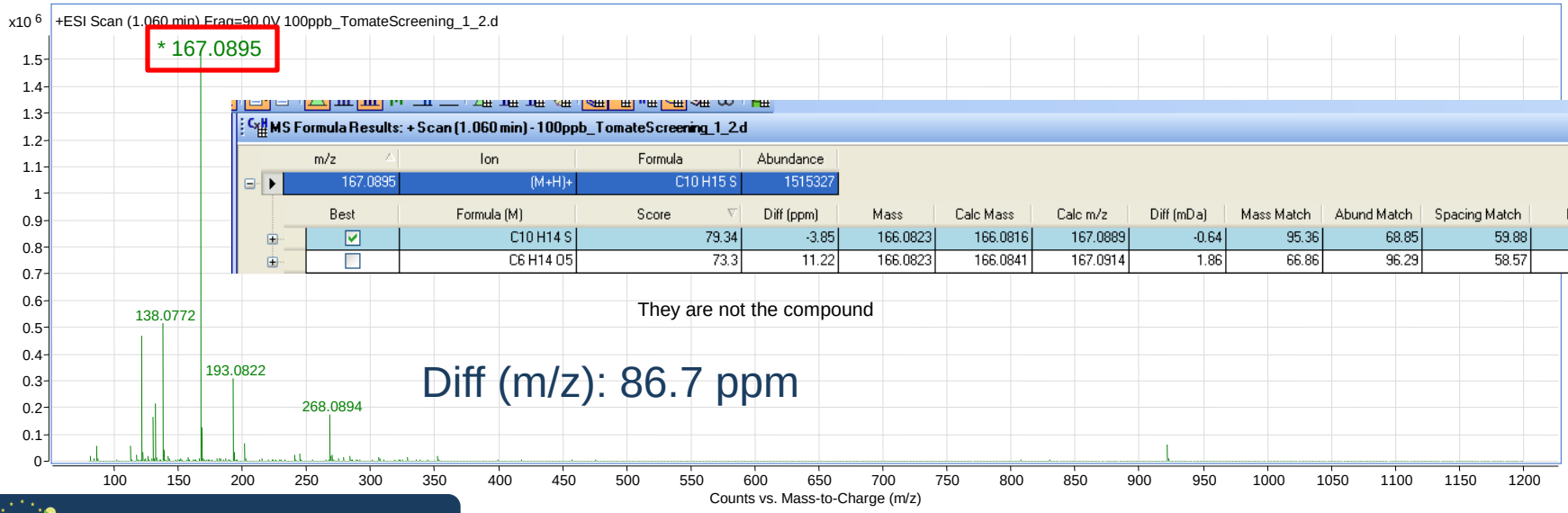
Best	Formula (M)	Score	Diff (ppm)	Mass	Calc Mass	Calc m/z	Diff (mDa)	Mass Match	Abund Match	Spacing Match	DBE
☑	C10 H14 S	80.99	-4.24	166.0823	166.0816	167.0889	-0.7	94.41	78.18	57.52	4
☐	C6 H14 O5	70.52	10.83	166.0823	166.0841	167.0914	1.8	68.7	89.19	51.77	0

They are not the compound

Diff (m/z): 86 ppm



Tomato spiked at 100 ng/mL
EIC m/z: 167.1040



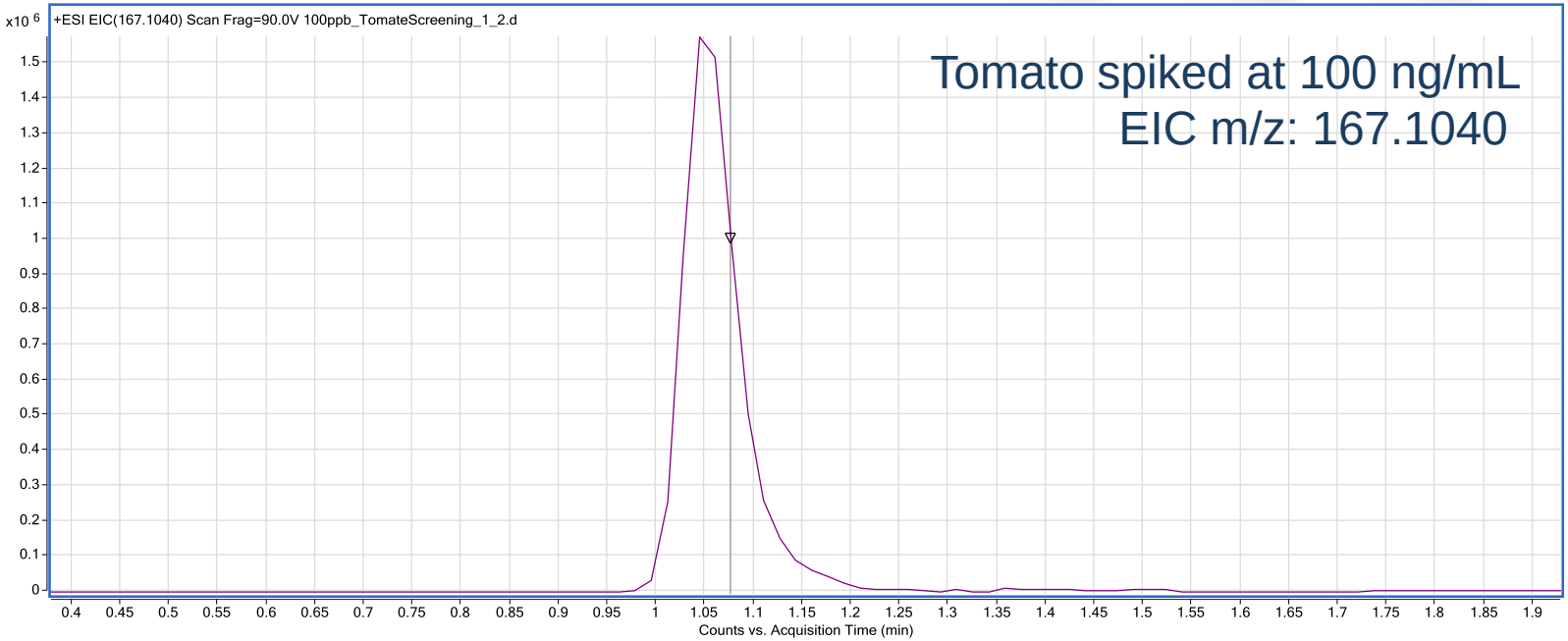
MS Formula Results: + Scan (1.060 min) - 100ppb_TomateScreening_1_2.d

m/z	Ion	Formula	Abundance
167.0895	(M+H)+	C10 H15 S	1515327

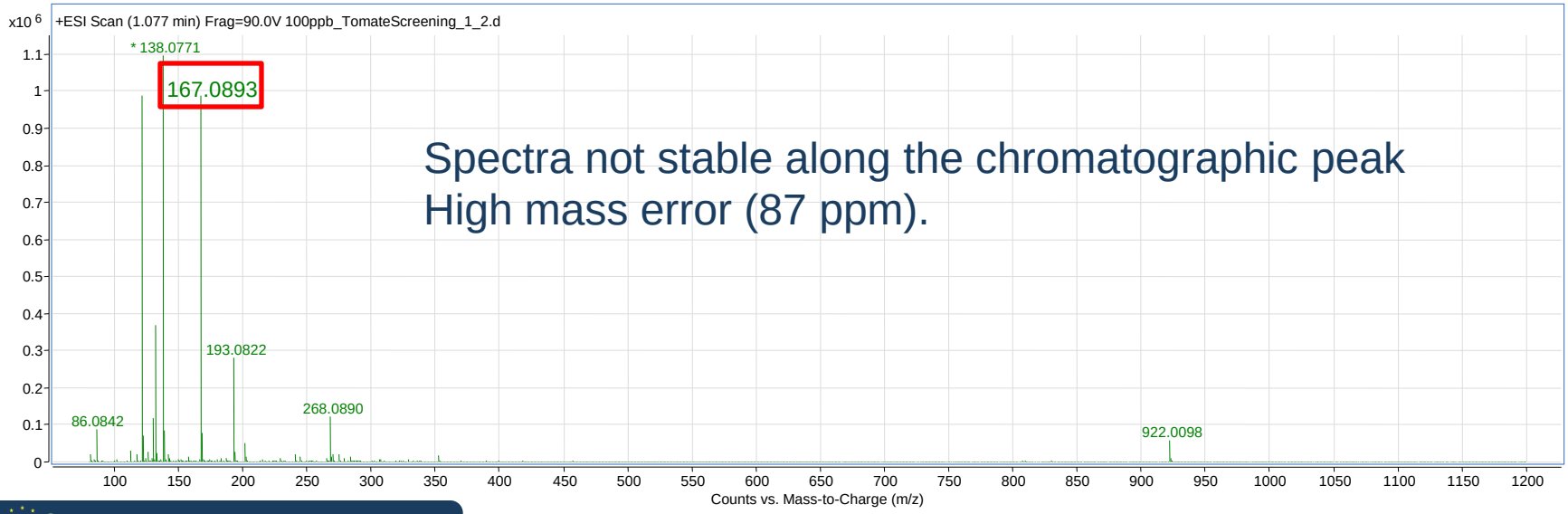
Best	Formula (M)	Score	Diff (ppm)	Mass	Calc Mass	Calc m/z	Diff (mDa)	Mass Match	Abund Match	Spacing Match	DBE
☑	C10 H14 S	79.34	-3.85	166.0823	166.0816	167.0889	-0.64	95.36	68.85	59.88	4
☐	C6 H14 O5	73.3	11.22	166.0823	166.0841	167.0914	1.86	66.86	96.29	58.57	0

They are not the compound

Diff (m/z): 86.7 ppm

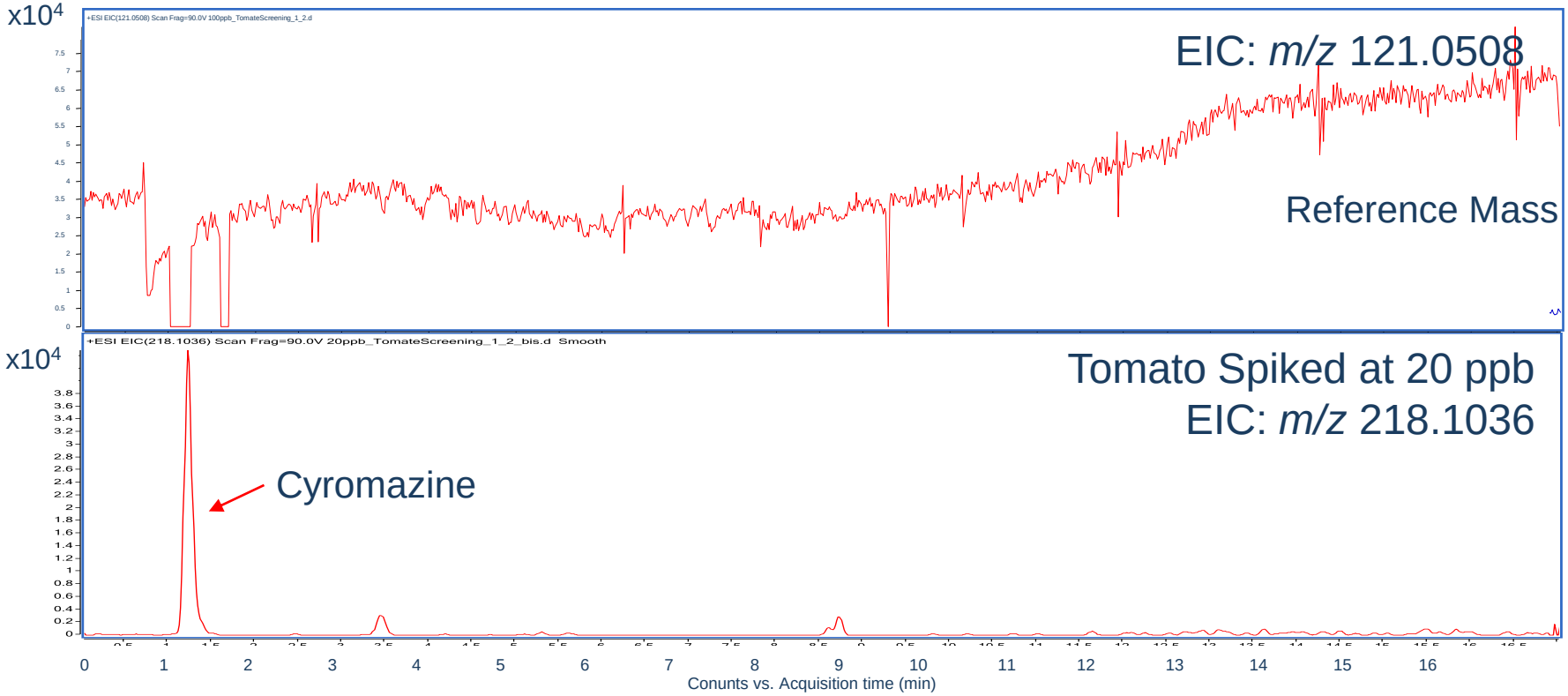


Tomato spiked at 100 ng/mL
EIC m/z: 167.1040

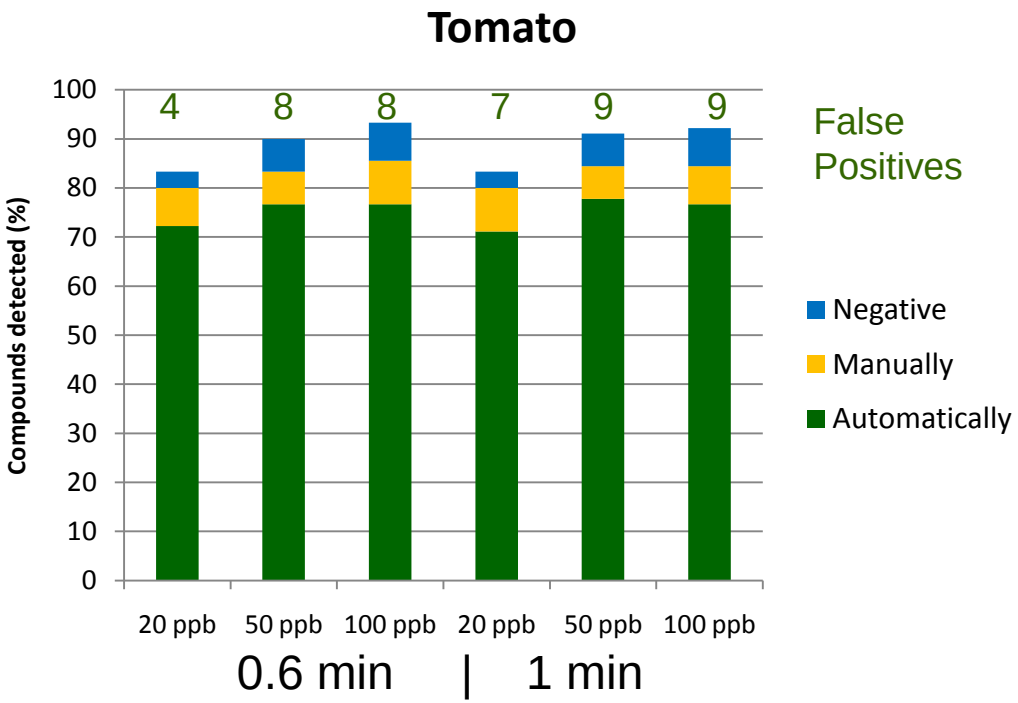


Spectra not stable along the chromatographic peak
High mass error (87 ppm).

Mass error due to supression of calibrant



Comparison of retention time windows in automatic search



Detection
Full Scan
$(M+H)^+$ and $(M-H)^-$

→

Selected
Q-TOF-MS/MS
Automatically

→

Positive Findings
LC-QqQ-MS/MS

Detection
Full Scan
$(M+H)^+$ and $(M-H)^-$

And

Selected
Q-TOF-MS
Automatically

→

Positive Findings
LC-QqQ-MS/MS

Quick scan of LC screening method for pesticides in vegetables/fruits

LC-QTRAP-MS

Set up:

3 matrices (Tomato, Zucchini and Lee

All matrices were injected with a four-fold d ution

3 levels (15, 50 and 100 ng/mL)

97 compounds (LC and/or GC amenables). 4 were not detected in ESI-QTRA

Azocy

Chlozo

Flucyth

Halfer

Databases for use with Analyst Reporter (CES Confirmation Library Search)

Library for pesticides with 512 compounds (possibility of increasing the number of compounds)

* Not signal

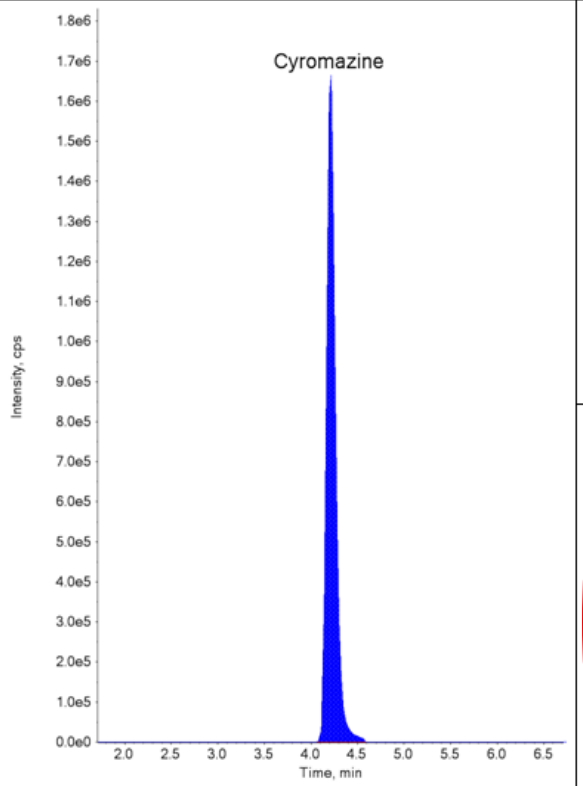
Automatic confirmation by LC-QTRAP-MS

Retention Time: 4.21 minutes
Q1/Q3: 167.100/125.000 Da
Fit (%) 100.0 **RFit (%)** 98.5

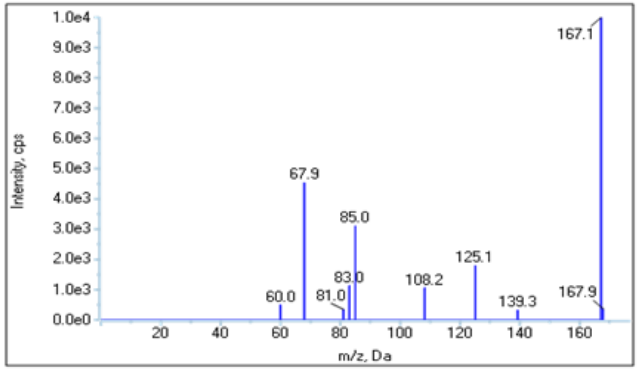
Exp RT: 4.22 minutes
Analyte Peak Name
(MRM Transition): Cyromazine

Date: 2/18/2011 9:52:57 AM

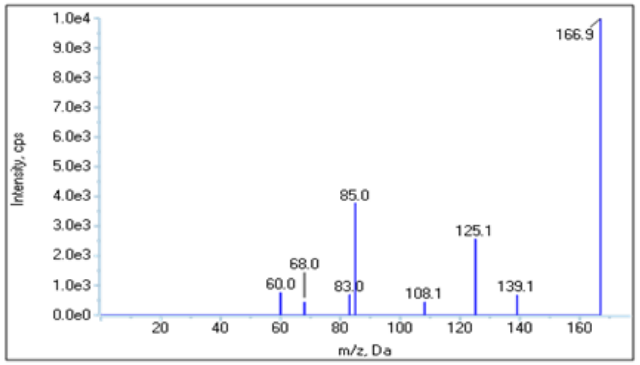
Collision Energy = 35 ± 15 eV



Acquired Spectrum

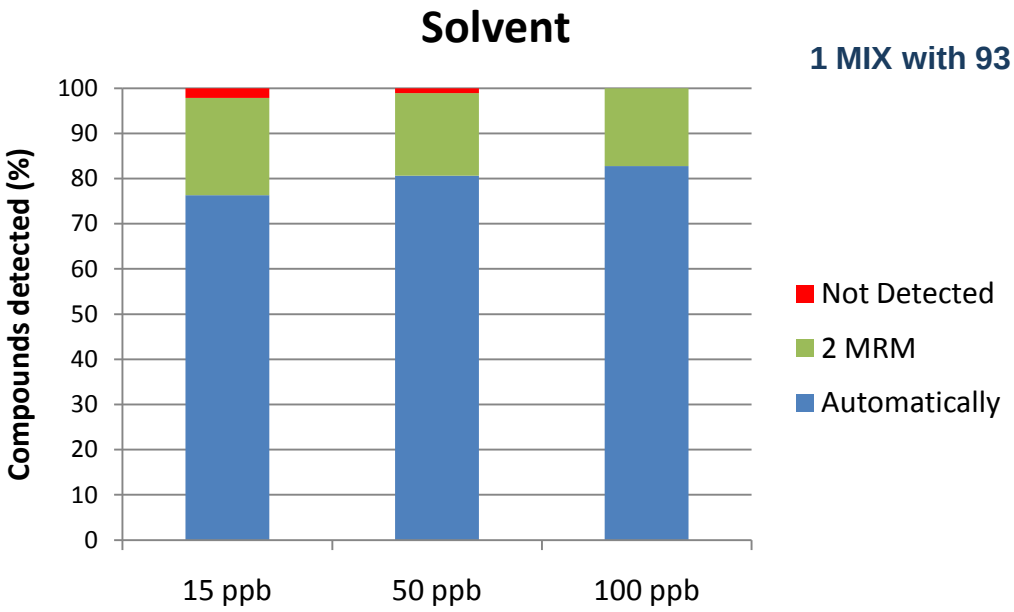


Library Spectrum



	Compound Name	Peak Area	Purity (%)	Visual Check?
1	Cyromazine	1.12e+007	98.5	

Compounds detected (%) in solvent

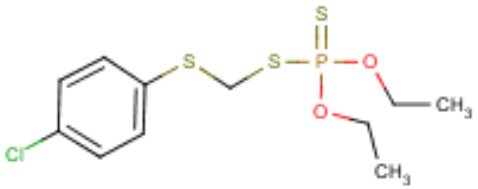


1 MIX with 93 compounds

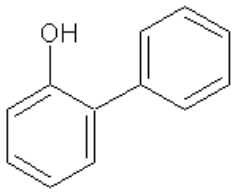
Compounds with low sensitivity (Not detected at 15 ng/mL in solvent):

- Carbophenothion
- Famoxadone
- O-Phenylphenol
- Prothiophos

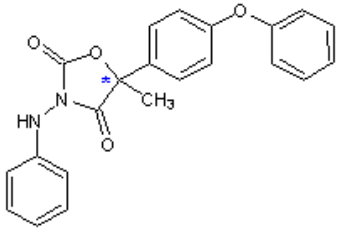
Carbophenothion



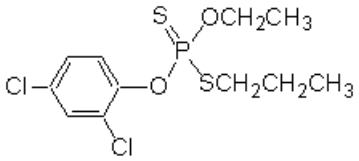
Orthophenylphenol



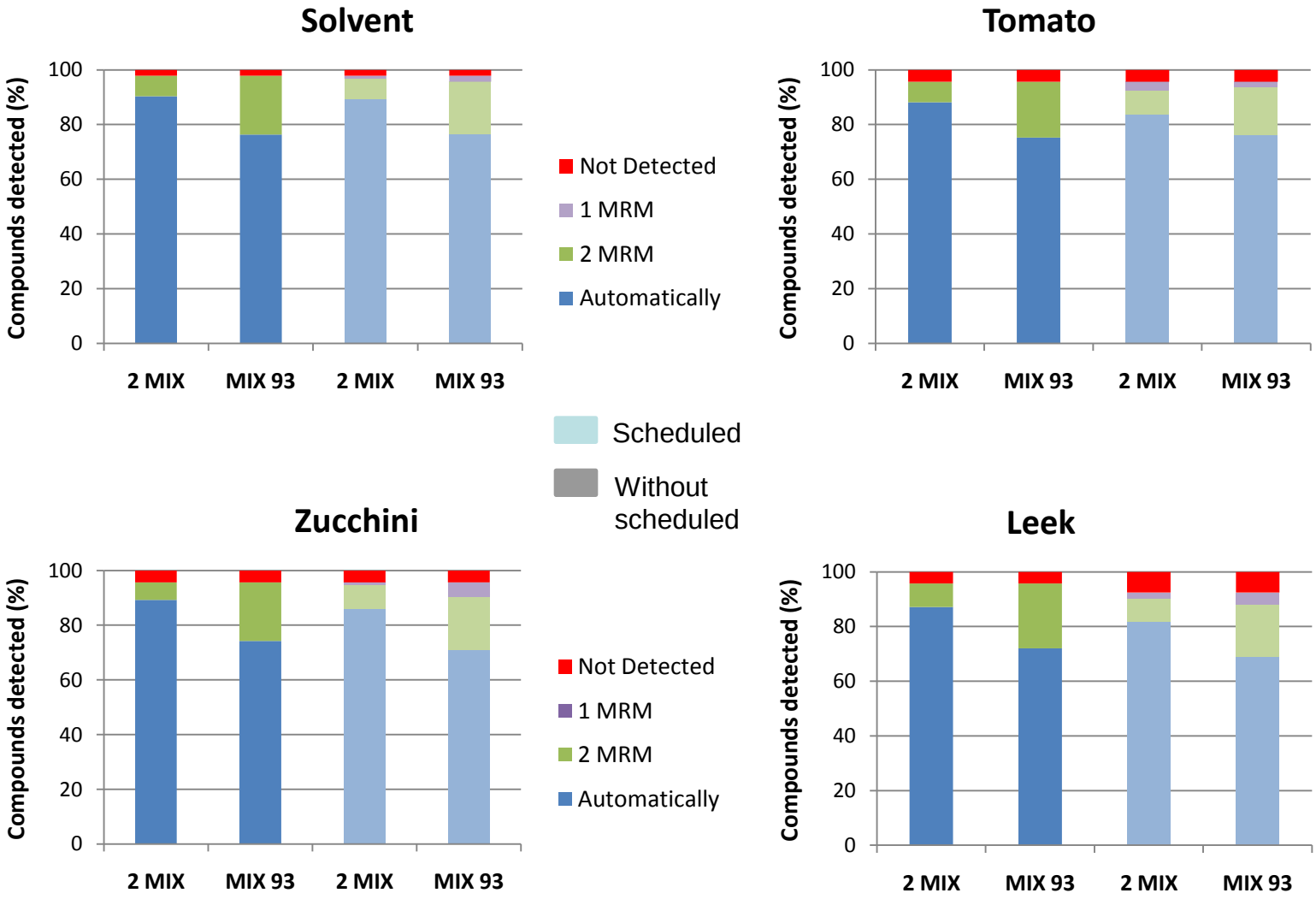
Famoxadone



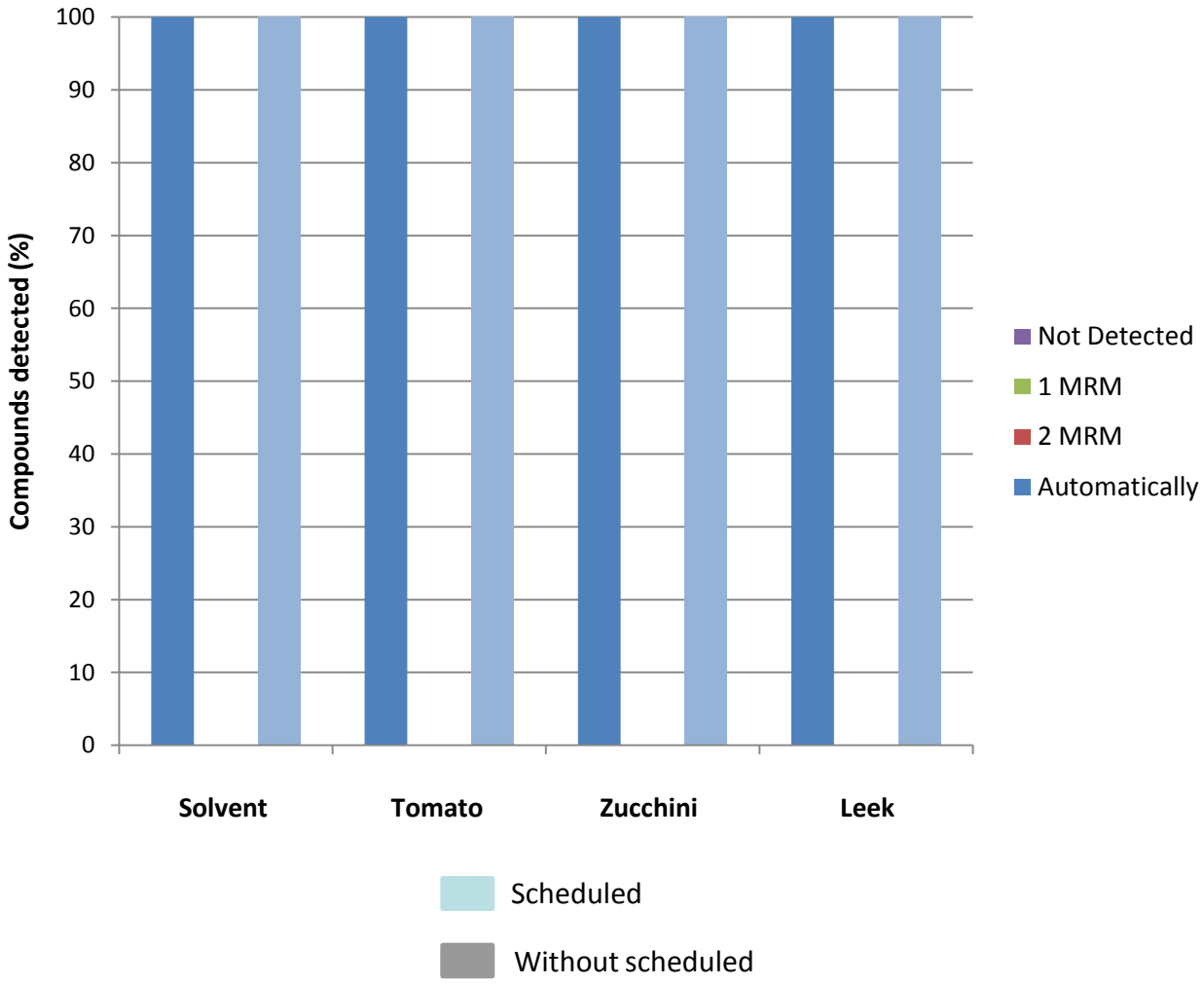
Prothiophos



Comparing different conditions at 15 ng/mL

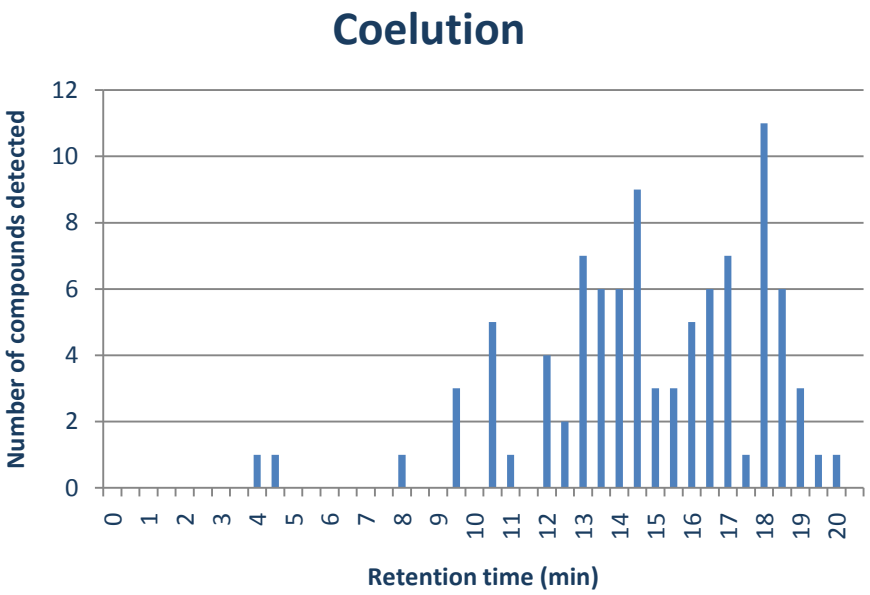


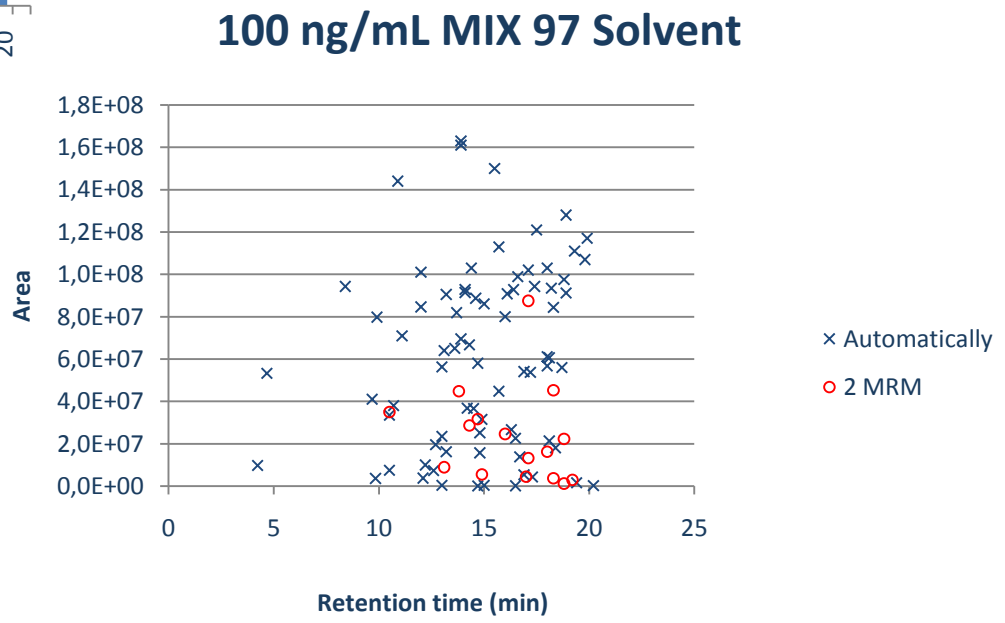
Comparing different conditions in MIX 6 at 15 ng/mL



Coelution problems

Coelution problems



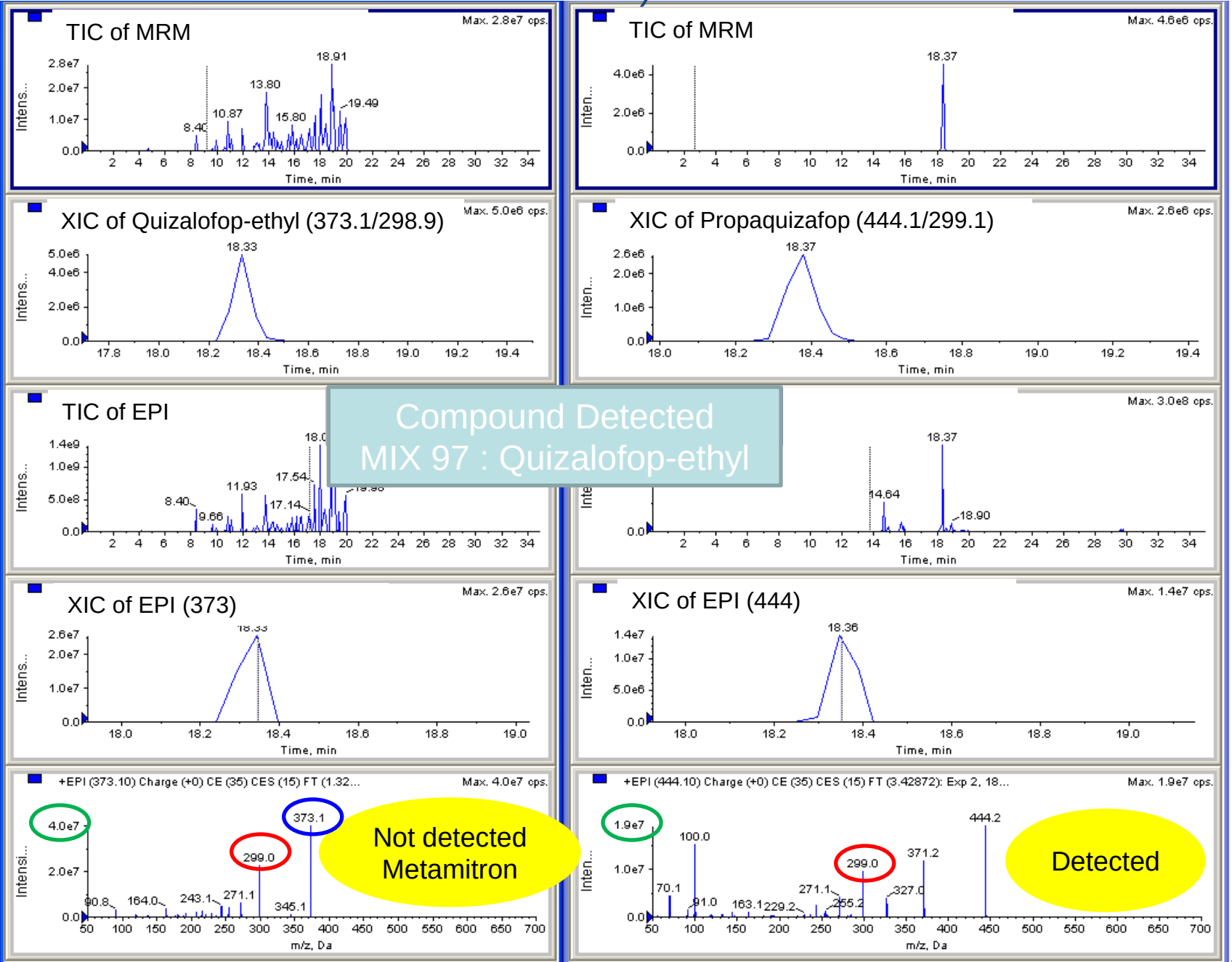


Coelution:
Compounds with common ions

Propaquizafop (tr=18.35 min) // Quizalofop-ethyl (tr=18.35 min)

MIX 97 15 ng/mL Solvent (Quizalofop-ethyl)

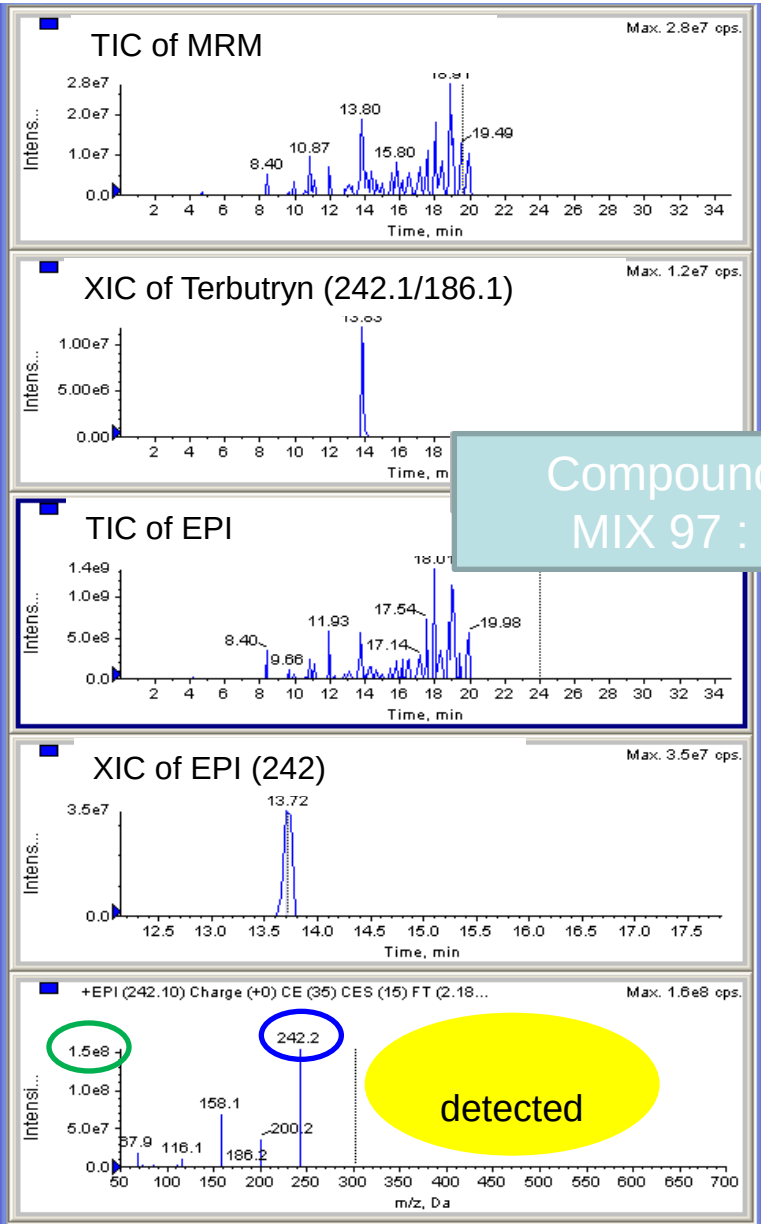
Propaquizafop 15 ng/mL Solvent (Alone)



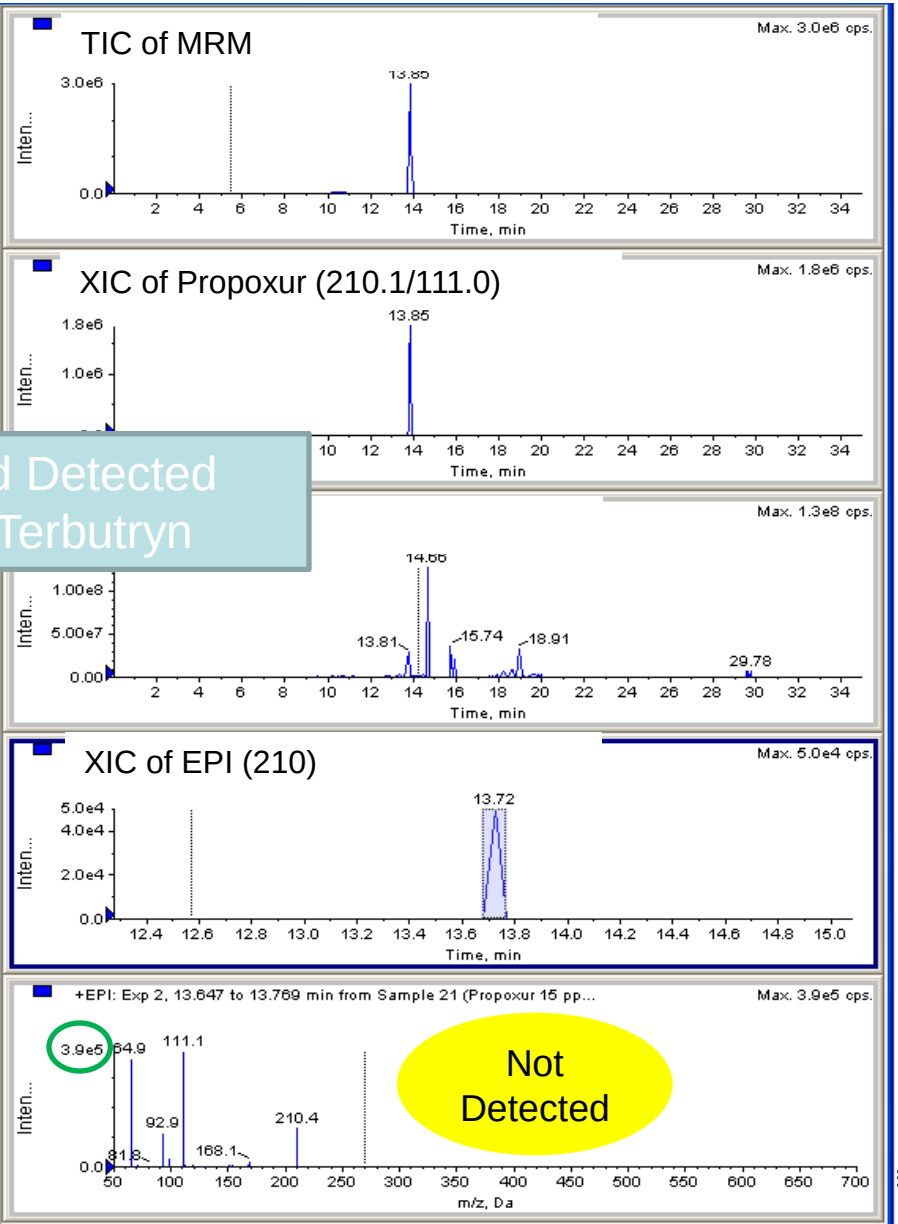
Coelution
with compounds more intense

Propoxur (tr=13.84 min)

MIX 97 15 ng/mL Solvent (Terbutryn)



Propoxur 15 ng/mL Solvent

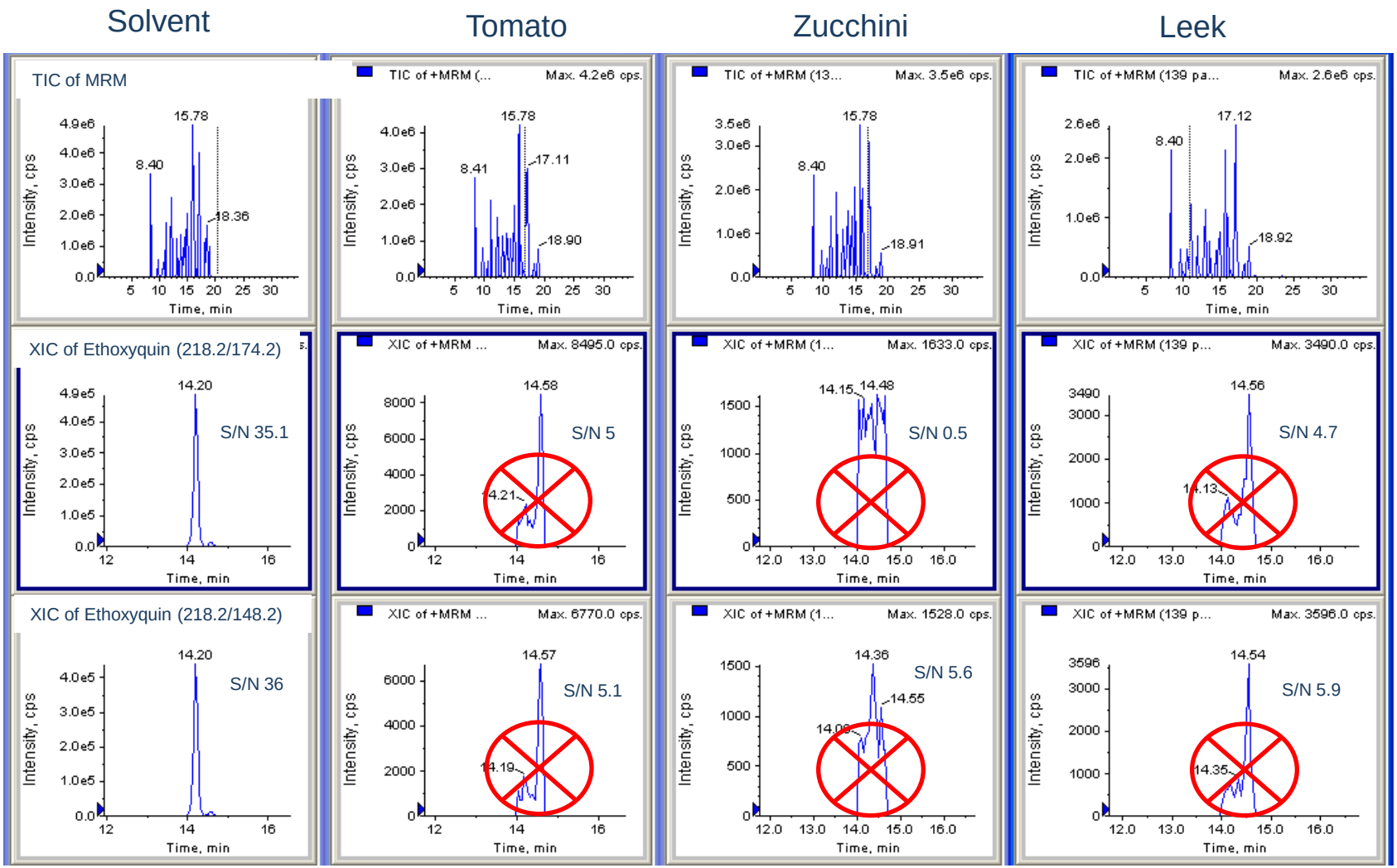


Compound Detected
MIX 97 : Terbutryn

Target analysis

Non target analysis

Ethoxyquin 5 ng/mL



Comparing different conditions with 2 MIX