

**Cutting-edge approach to overcome sensitivity issues
associated with polarity switching employing dual-
channel chromatography**

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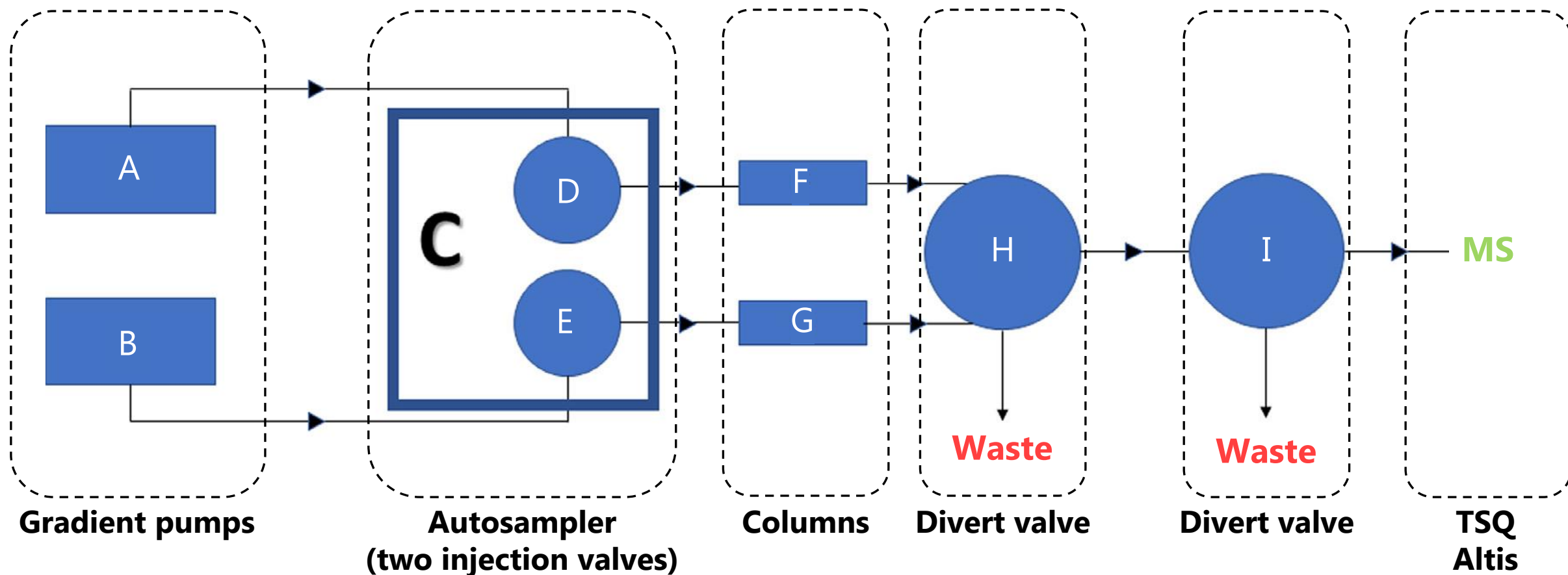
Łukasz Rajski

lr231@ual.es

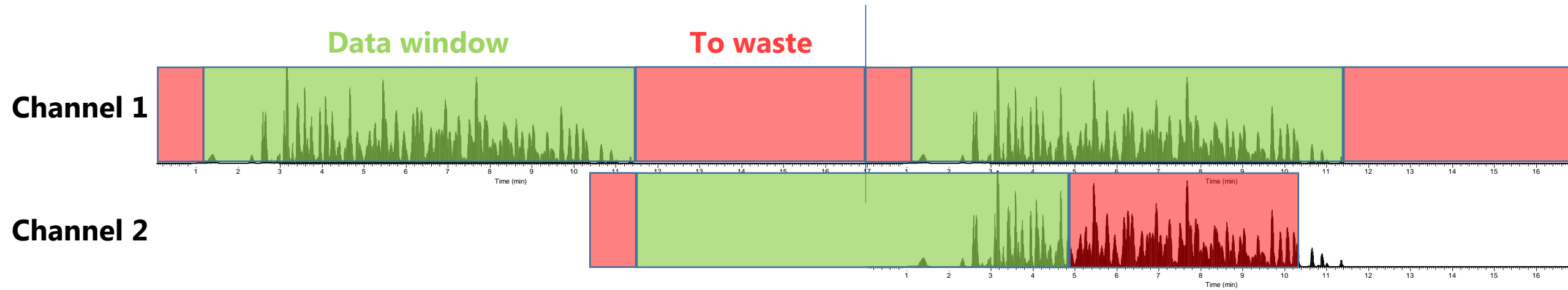
Amadeo R. Fernández-Alba

amadeo@ual.es

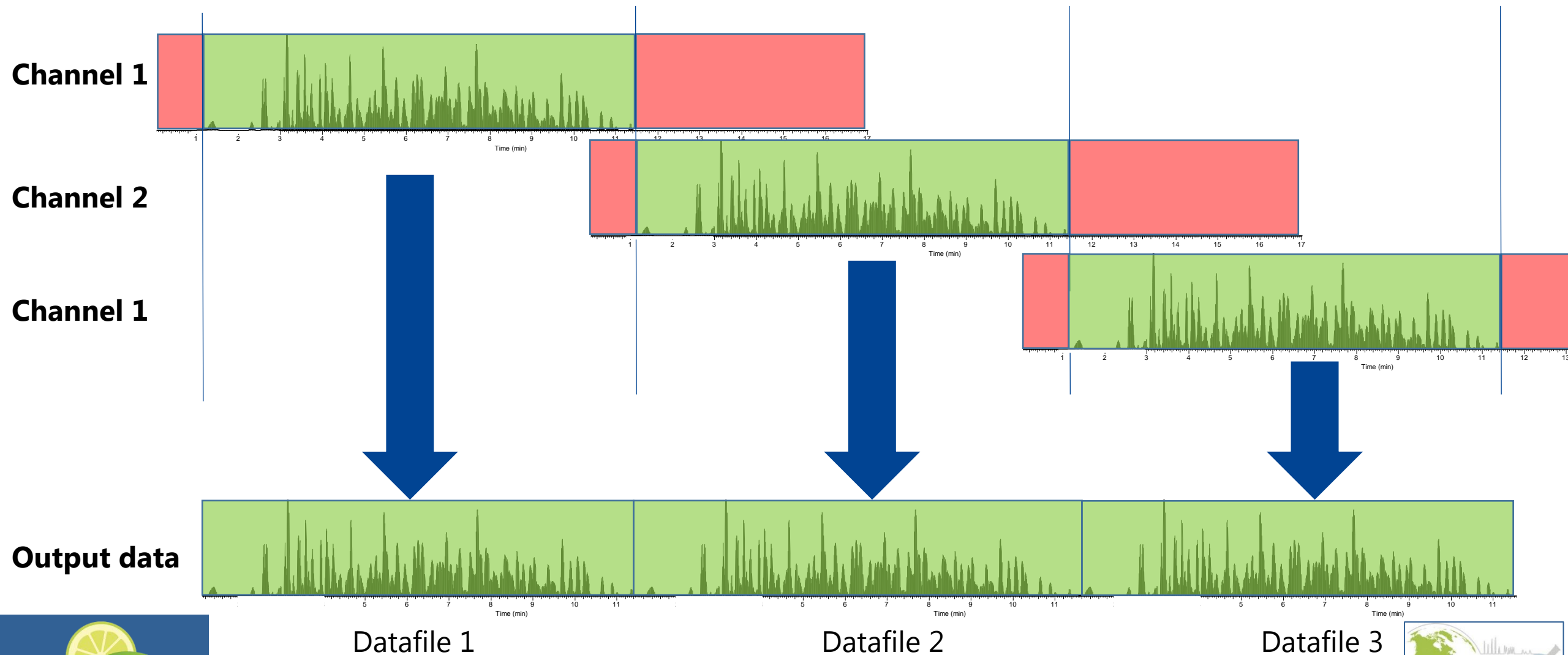
Dual-Channel LC-MS/MS: general diagram



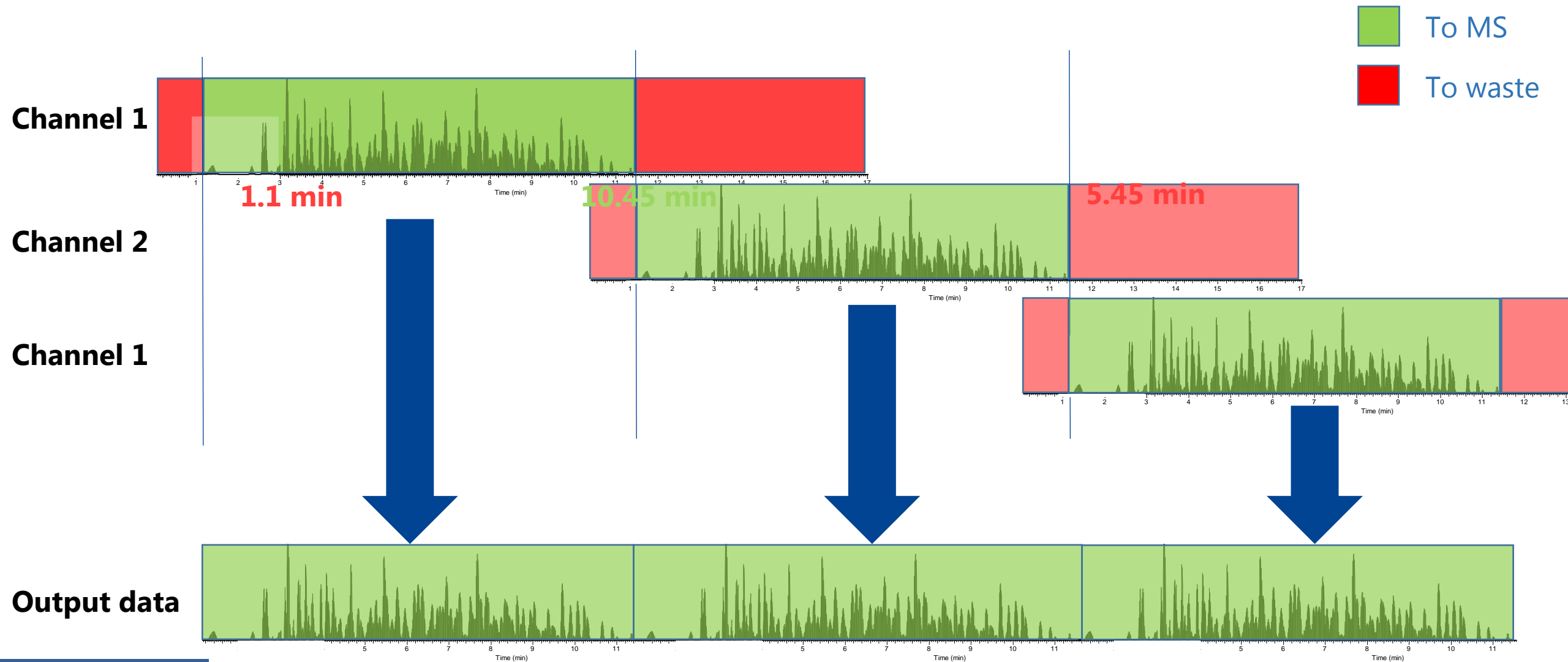
Dual-Channel LC-MS/MS: sample throughput



Dual-Channel LC-MS/MS: sample throughput



Dual-Channel LC-MS/MS: sample throughput



■ To MS
■ To waste

1.1 min

10.45 min

5.45 min

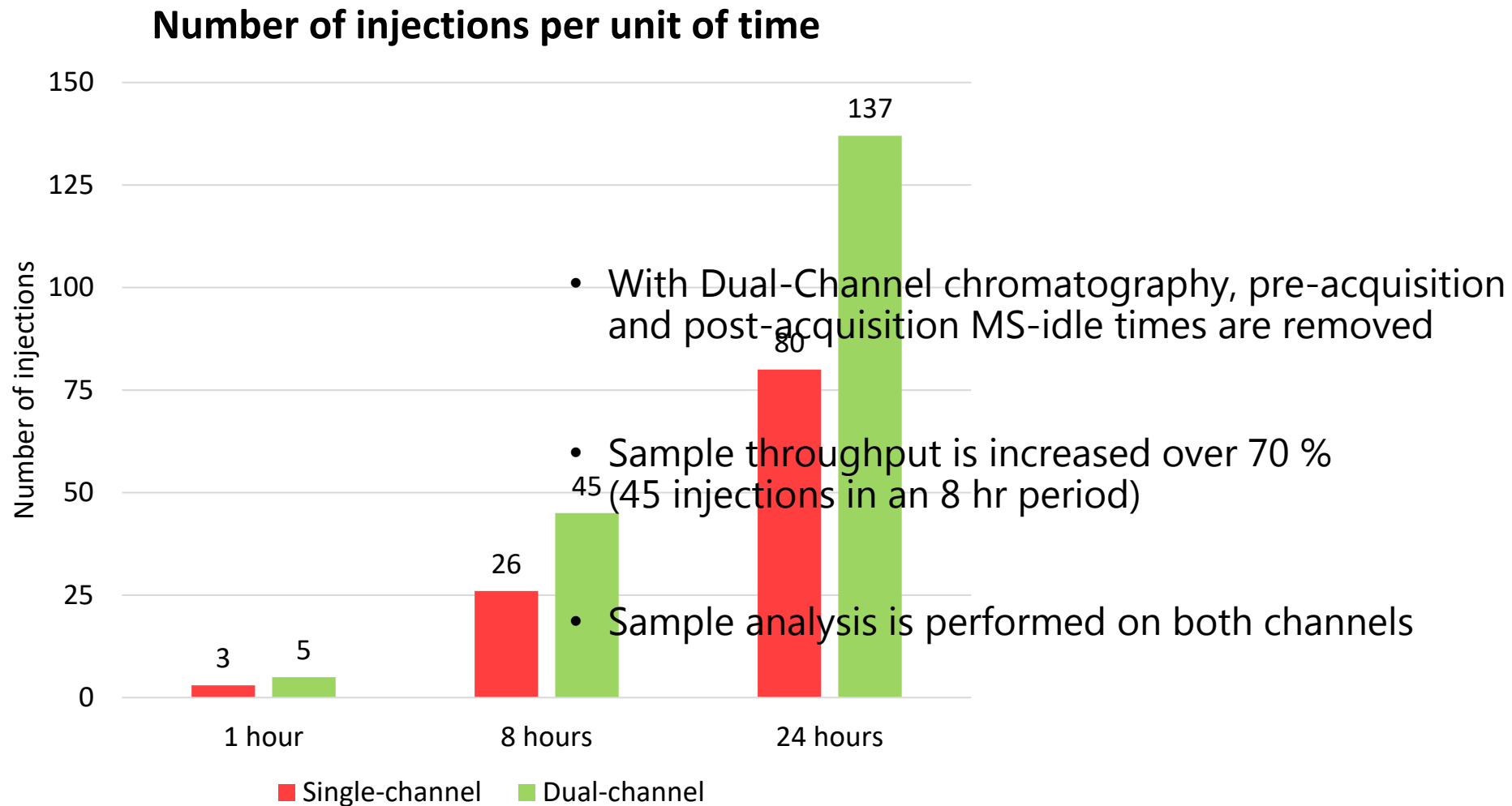
Output data

Datafile 1

Datafile 2

Datafile 3

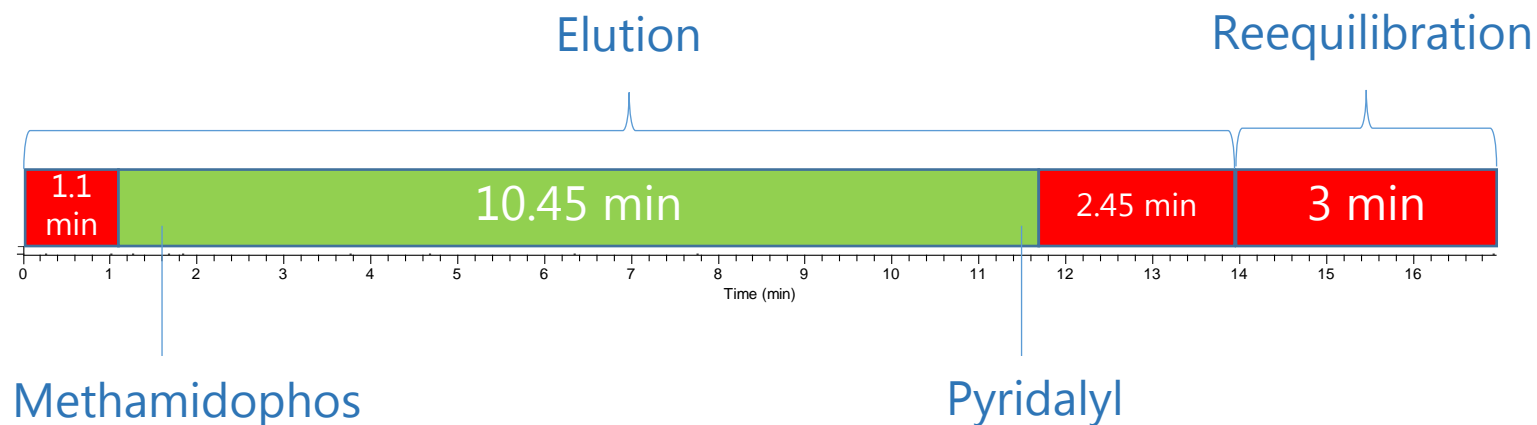
Dual-Channel LC-MS/MS: sample throughput



Dual-Channel LC-MS/MS: independent mobile phases

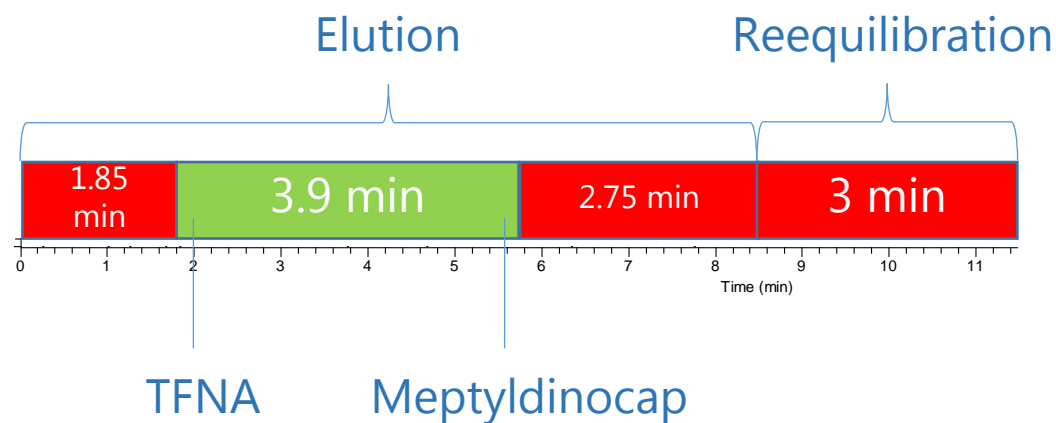
Gradient 1

Water:MeOH
Formic acid (0.1 %)
Ammonium formate (5 mM)



Gradient 2

Water:AcN
Acetic acid (0.05 %)

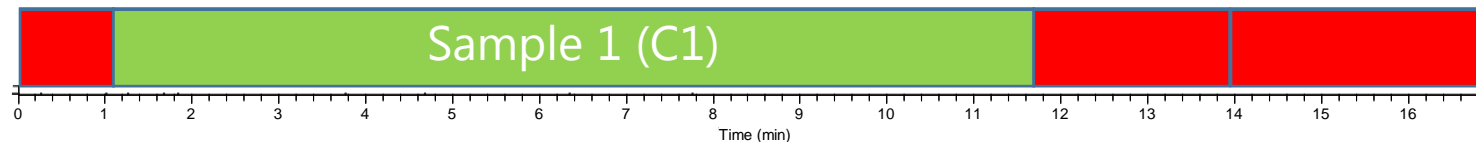


To waste

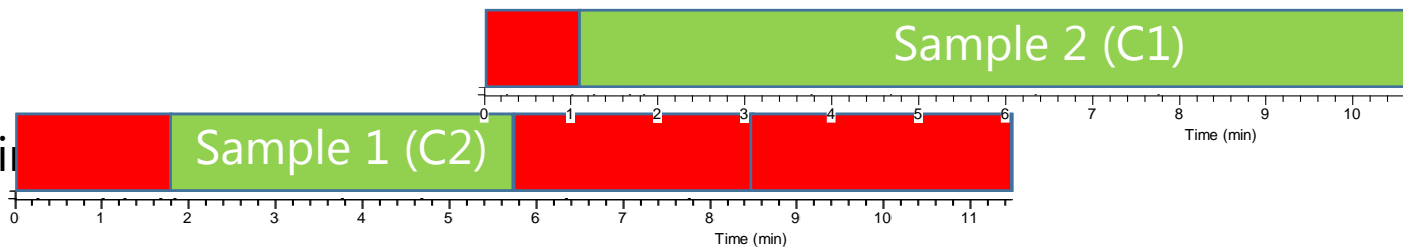


To MS

Dual-Channel LC-MS/MS: independent mobile phases

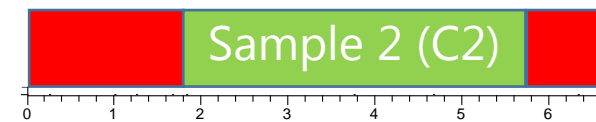


On a single-channel instrument with polarity switching



On a dual-channel instrument with optimized mobile phases, **sample analysis is 18 min**

Improved method efficiency without time loss – no compromises



 To waste

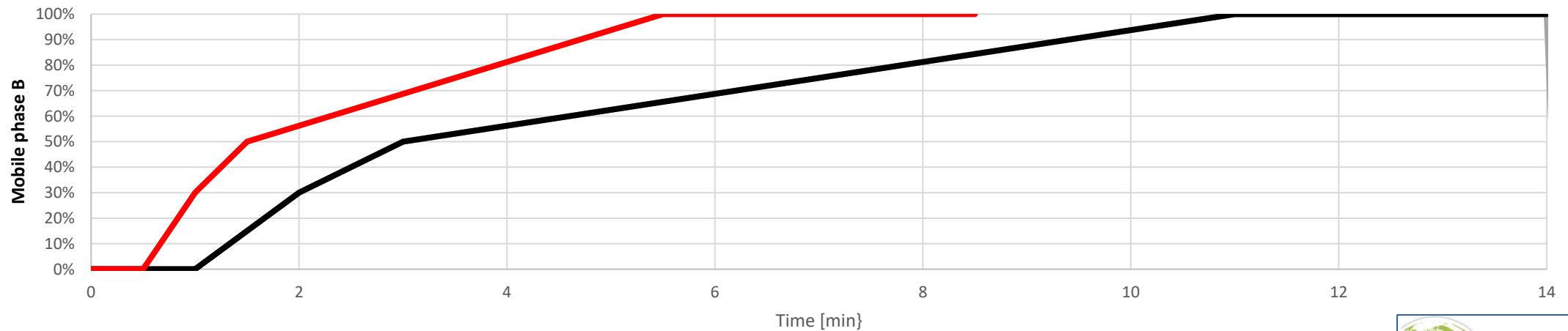
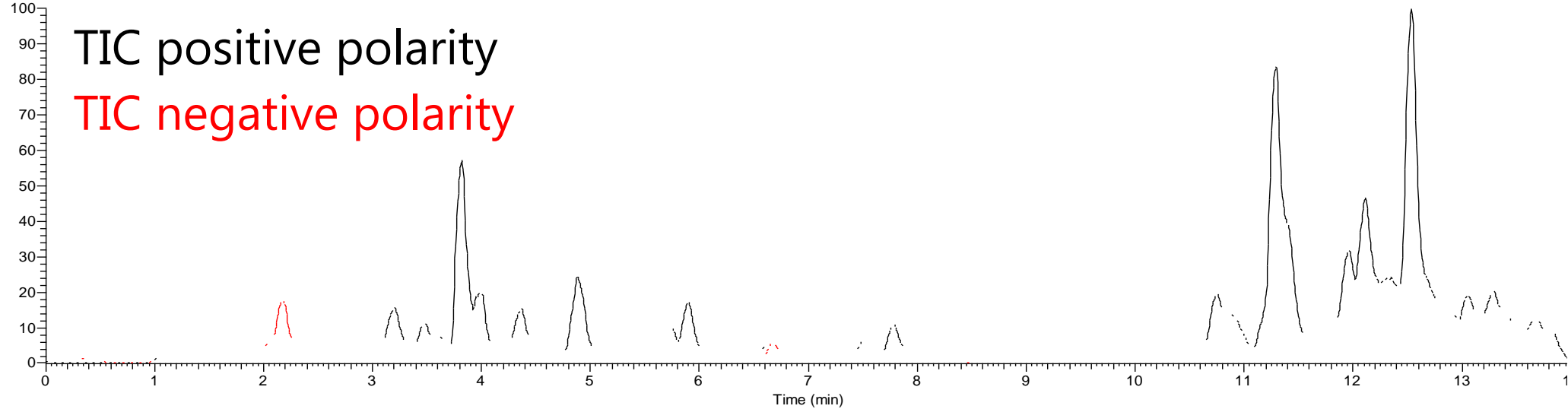
 To MS



Dual-Channel LC-MS/MS: total ion chromatograms

Tomato

RT: 0.00 - 14.01 SM: 15B

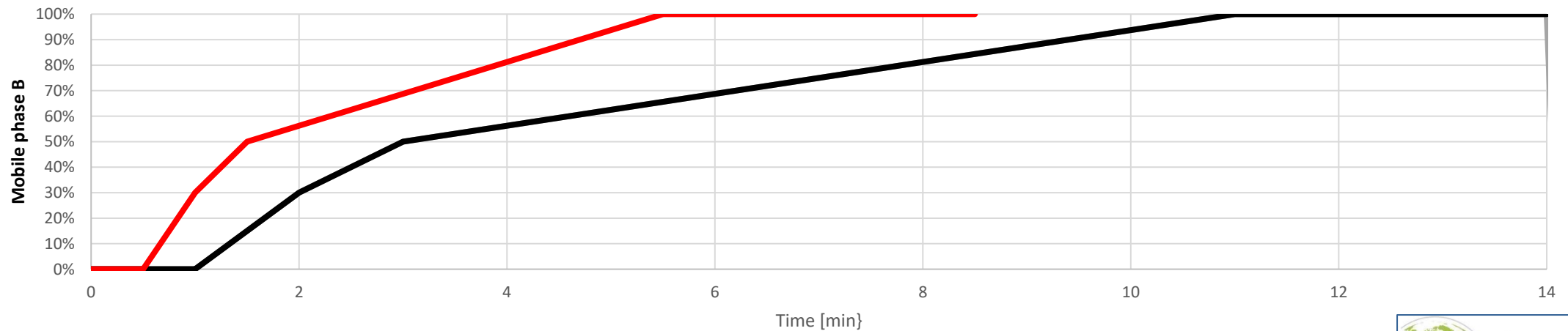
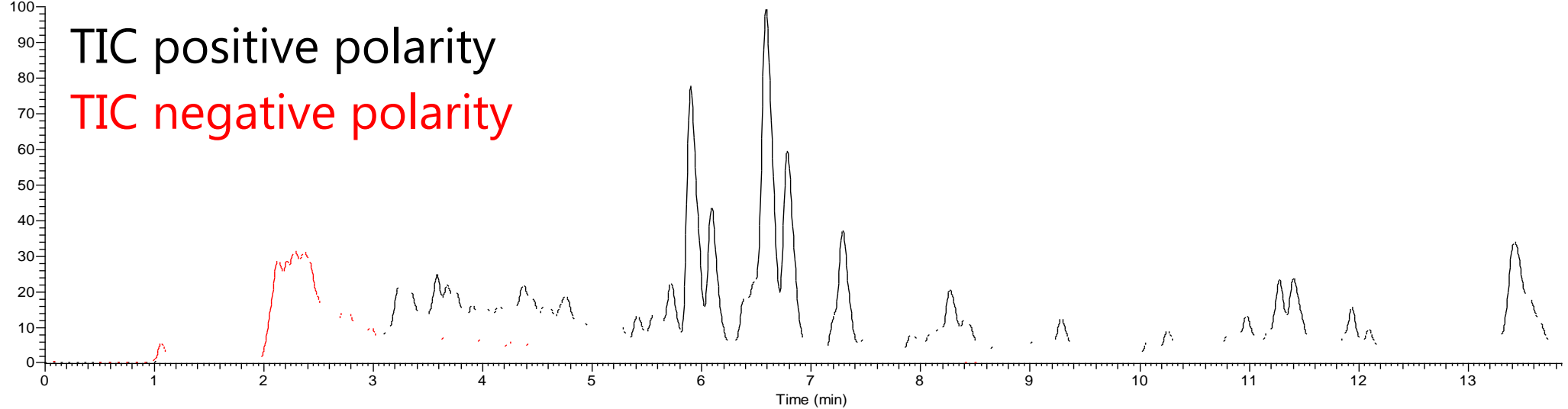




Dual-Channel LC-MS/MS: total ion chromatograms

Orange

RT: 0.00 - 14.00 SM: 15G

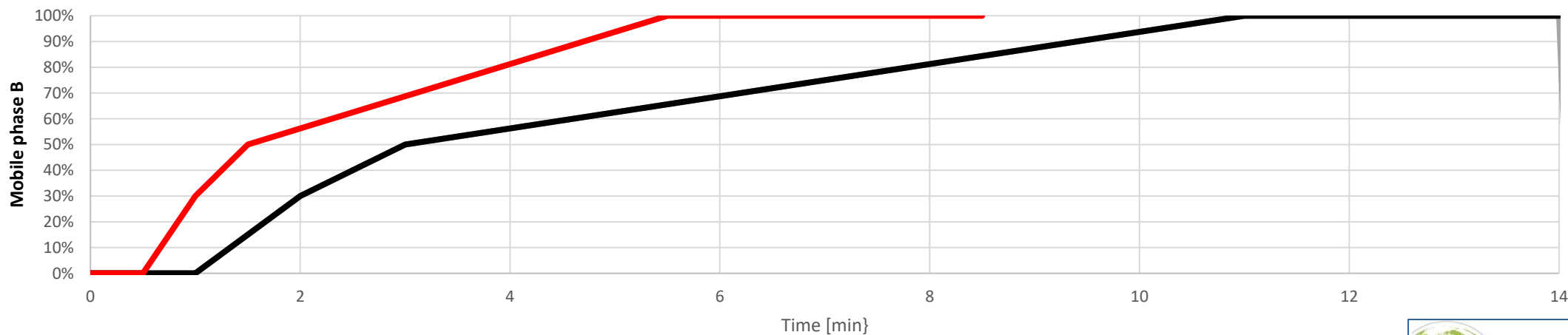
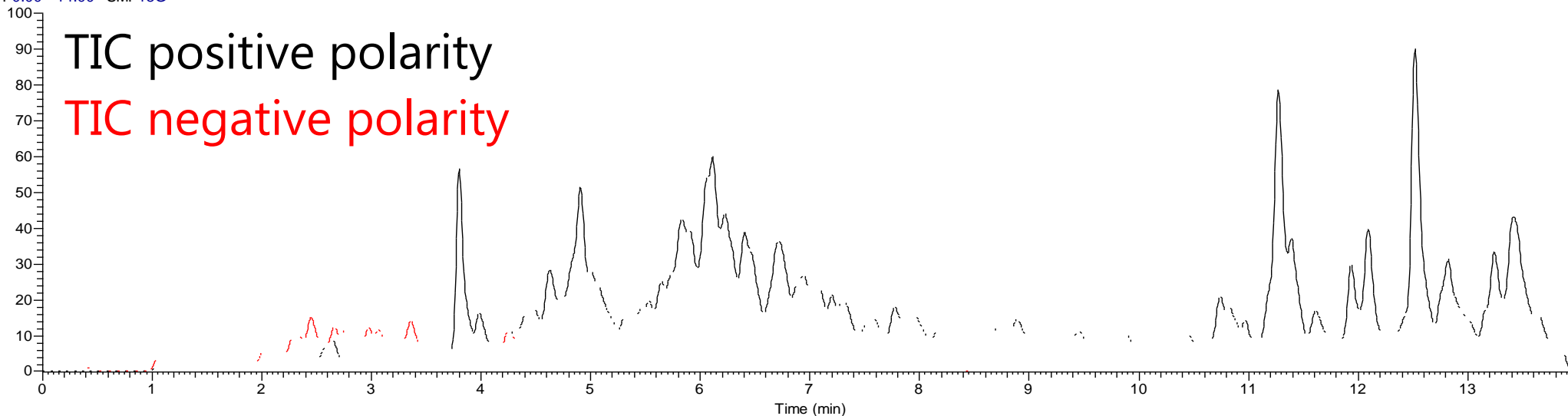




Dual-Channel LC-MS/MS: total ion chromatograms

Onion

RT: 0.00 - 14.00 SM: 15G

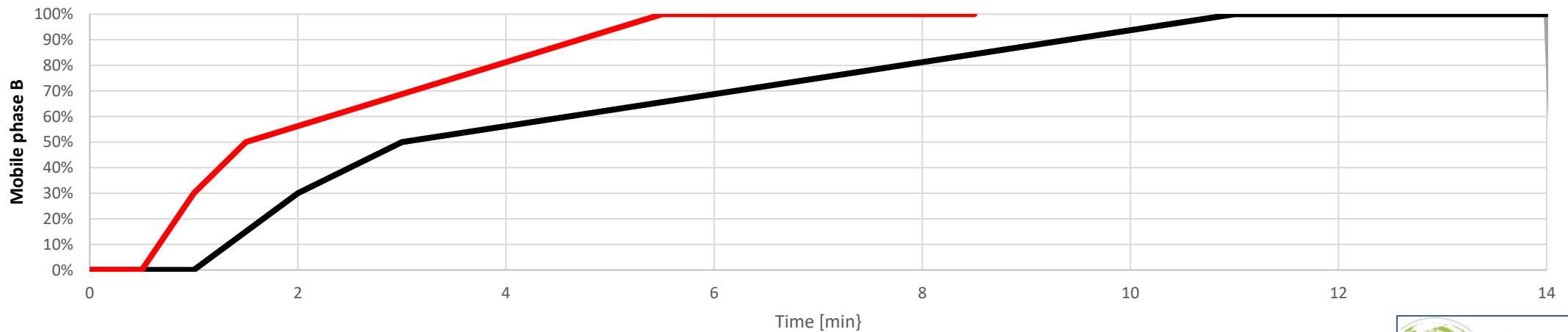
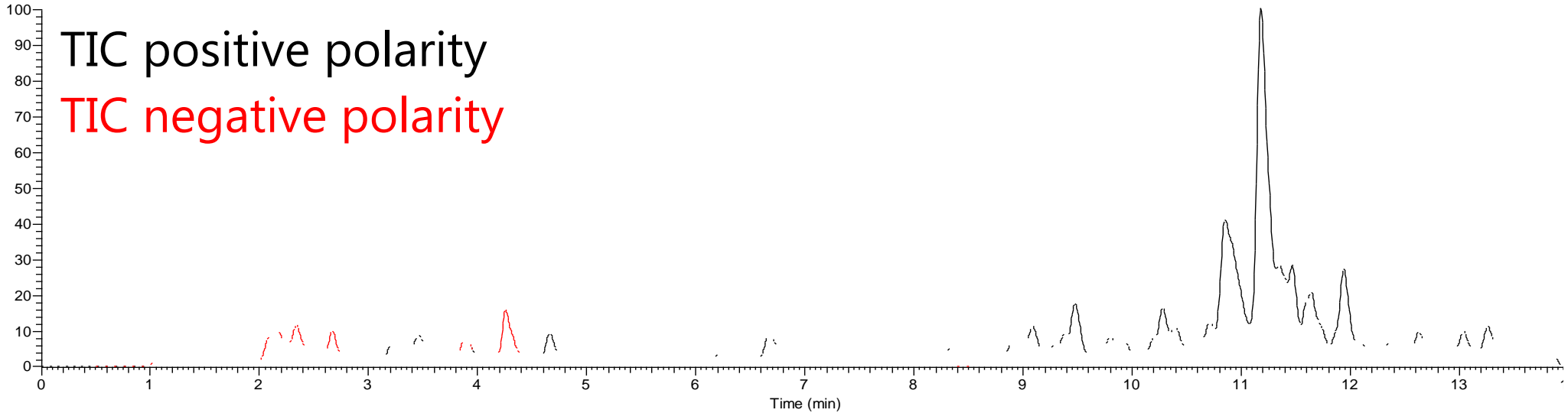




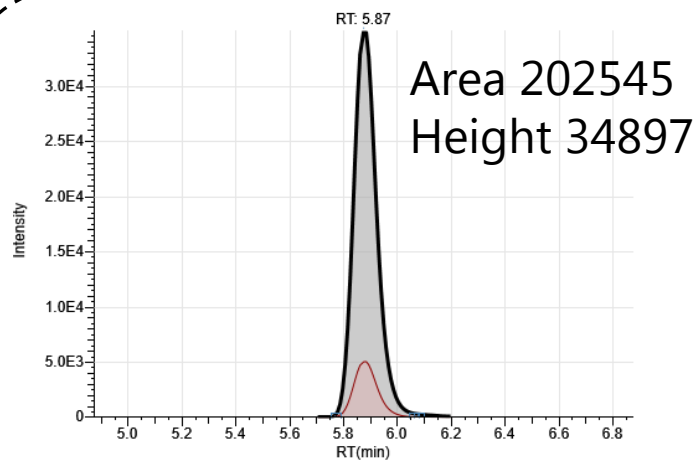
Dual-Channel LC-MS/MS: total ion chromatograms

Avocado

RT: 0.00 - 14.01 SM: 15G

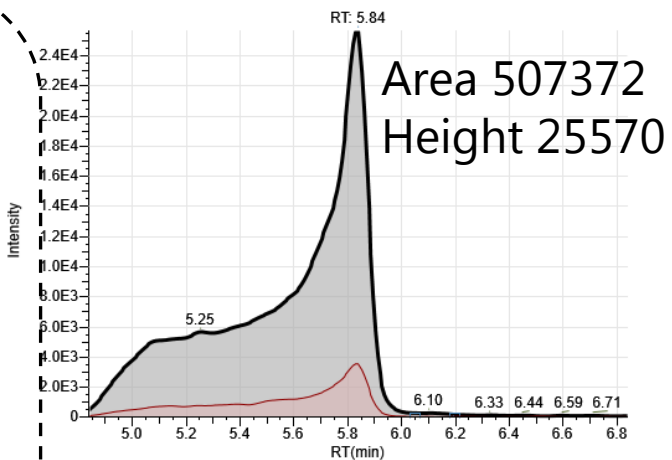


Dual-Channel LC-MS/MS: improved ionisation



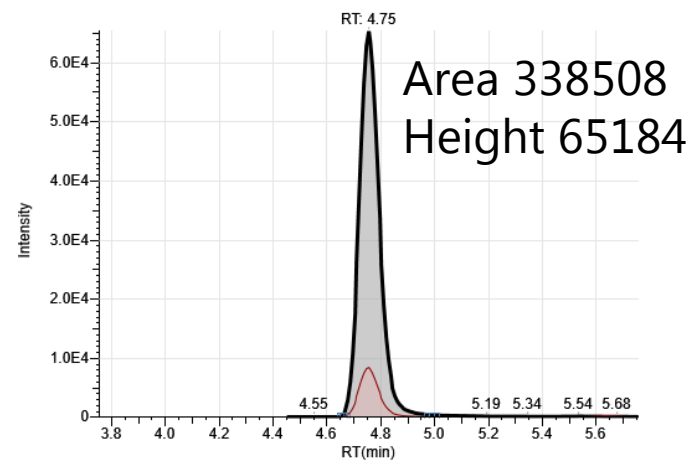
Water/MeOH/formic acid/ammonium formate

Gradient 1

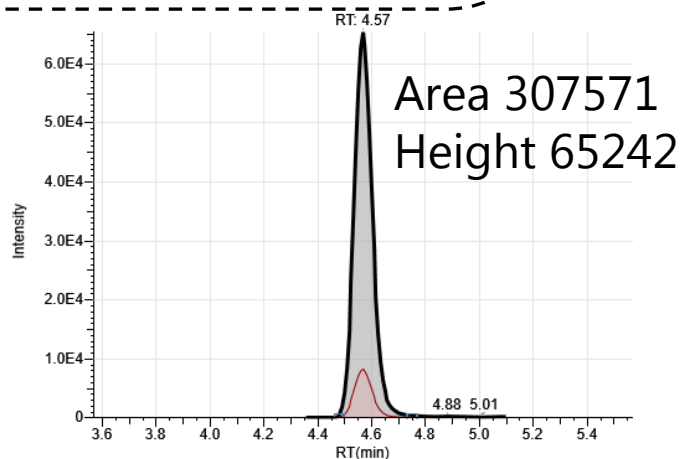


Water/AcN

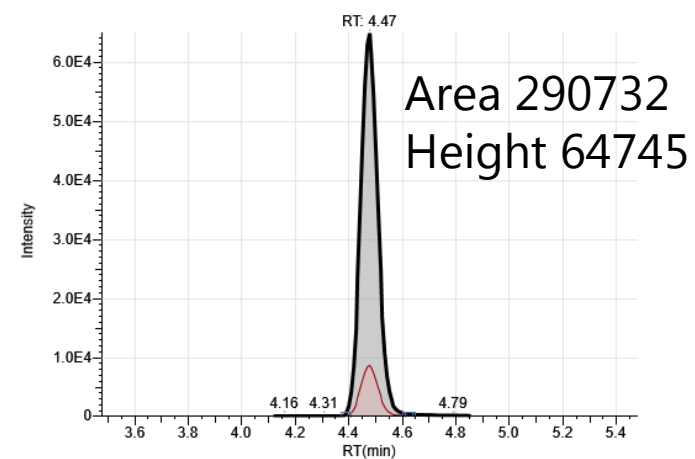
Gradient 2



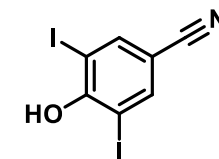
Water/AcN + 0.01 % acetic acid



Water/AcN + 0.02 % acetic acid

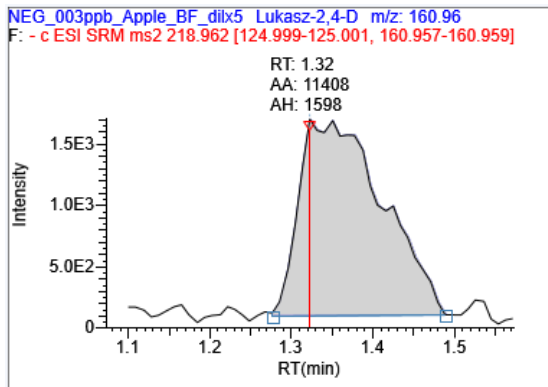


Water/AcN + 0.05 % acetic acid

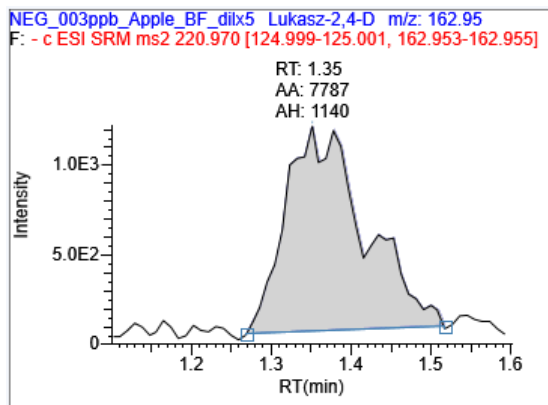


ioxynil
ESI (-)

Dual-Channel LC-MS/MS: improved ionisation



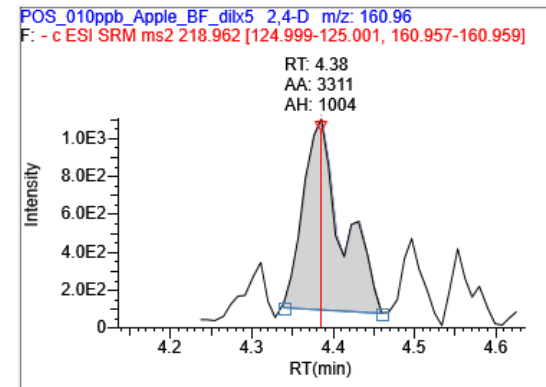
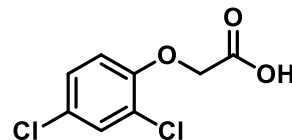
0.003 mg/kg



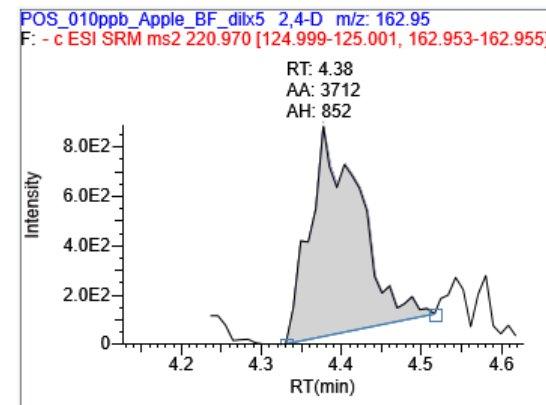
Gradient 2

Water:AcN
Acetic acid (0.05 %)

2,4-D



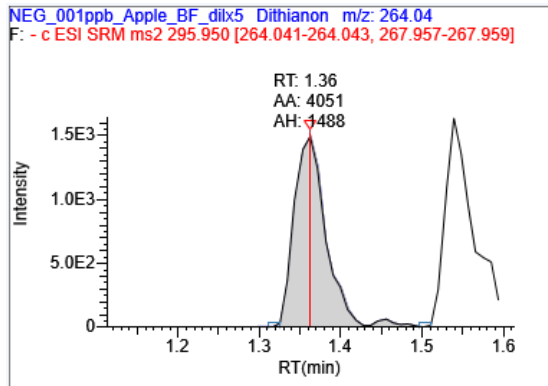
0.010 mg/kg



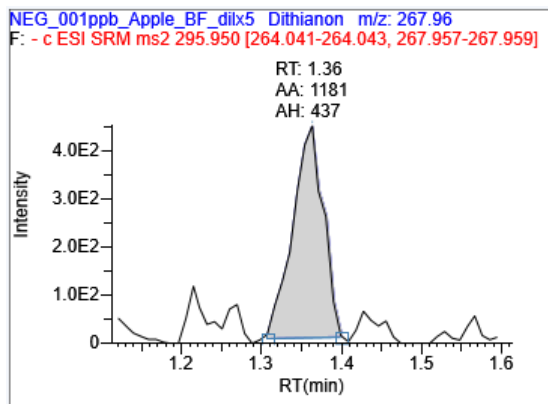
Gradient 1

Water:MeOH
Formic acid (0.1 %)
Ammonium formate (5 mM)

Dual-Channel LC-MS/MS: improved ionisation



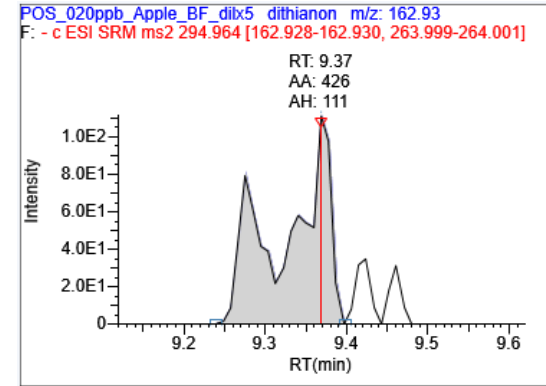
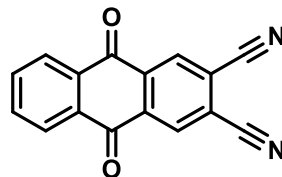
0.001 mg/kg



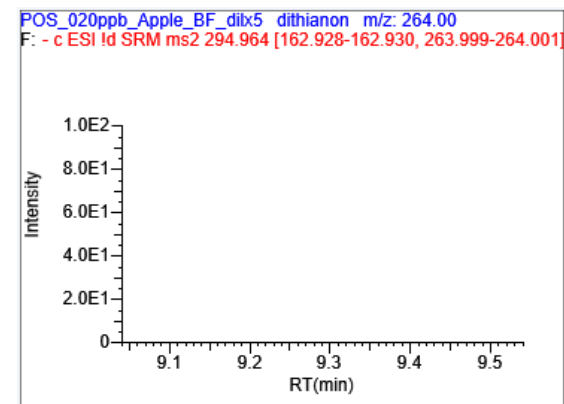
Gradient 2

Water:AcN
Acetic acid (0.05 %)

Dithianon



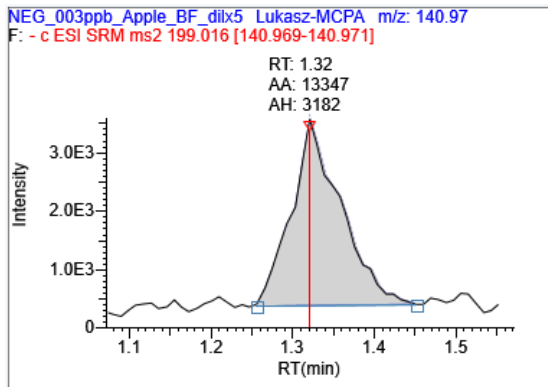
0.020 mg/kg



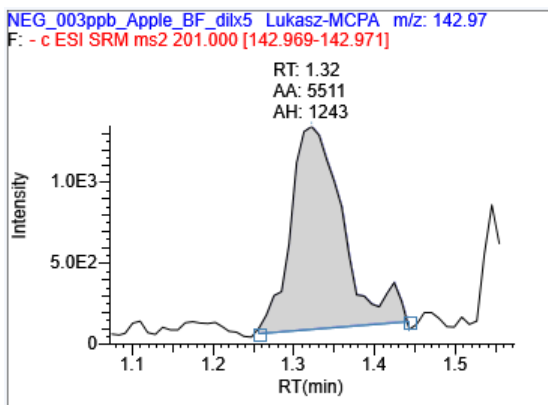
Gradient 1

Water:MeOH
Formic acid (0.1 %)
Ammonium formate (5 mM)

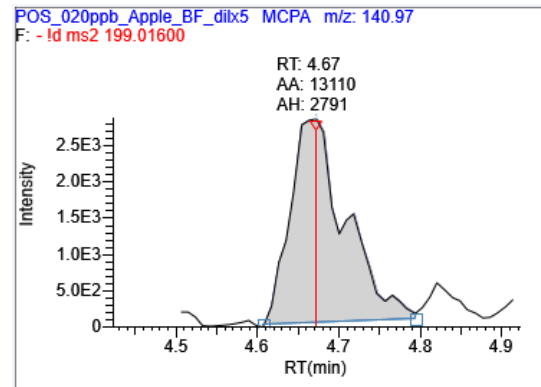
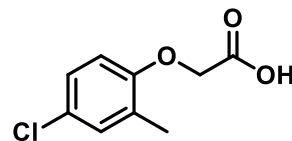
Dual-Channel LC-MS/MS: improved ionisation



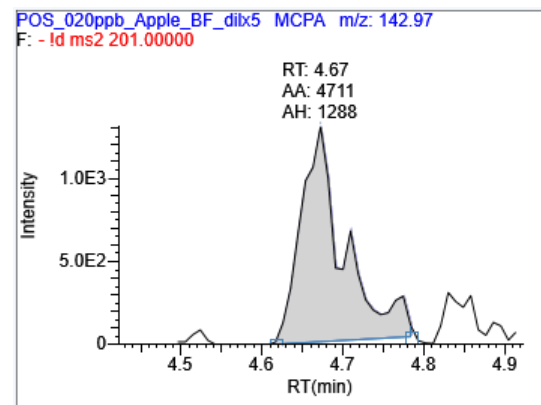
0.003 mg/kg



MCPA



0.020 mg/kg

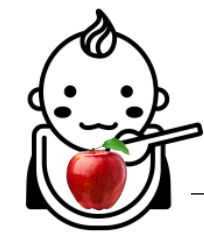


Gradient 2

Water:AcN
Acetic acid (0.05 %)

Gradient 1

Water:MeOH
Formic acid (0.1 %)
Ammonium formate (5 mM)



Dual-Channel LC-MS/MS: apple validation

Gradient 1

Water:MeOH
Formic acid (0.1 %)
Ammonium formate (5 mM)

Gradient 2

Water:AcN
Acetic acid (0.05 %)

Compound	Recoveries 0.003 mg/kg	RSD 0.003 mg/kg	Recoveries 0.006 mg/kg	RSD 0.006 mg/kg	Lowest calibration level (mg/kg)	Highest calibration level (mg/kg)
2,4-D	97 %	11 %	109 %	6 %	0.001	0.02
Bromacil	100 %	5 %	104 %	4 %	0.0005	0.02
Dithiaron	96 %	3 %	96 %	3 %	0.0005	0.02
Diuron	103 %	5 %	101 %	2 %	0.0005	0.02
Fensulfothion	102 %	5 %	100 %	3 %	0.0005	0.02
Fensulfothion-oxon-sulfone	100 %	4 %	103 %	2 %	0.0005	0.02
Fipronil	108 %	4 %	101 %	3 %	0.0005	0.02
Fipronil-desulfinyl	101 %	2 %	100 %	2 %	0.0005	0.02
Fipronil-sulfone	103 %	2 %	108 %	2 %	0.0005	0.02
Flubendiamide	104 %	21 %	98 %	12 %	0.0005	0.02
Fludioxonil	105 %	5 %	102 %	0 %	0.0005	0.02
Haloxypop	98 %	15 %	101 %	6 %	0.003	0.02
Hexaflumuron	94 %	5 %	104 %	11 %	0.0005	0.02
Ioxynil	108 %	2 %	103 %	6 %	0.0005	0.02
Lufenuron	108 %	2 %	102 %	30 %	0.0005	0.02
MCPA	114 %	7 %	99 %	13 %	0.001	0.02
MCPB	-	-	115 %	10 %	0.006	0.02
Meptyldimicop	86 %	14 %	118 %	29 %	0.003	0.02
(E)-Metaflumizone	103 %	2 %	85 %	6 %	0.0005	0.02
(Z)-Metaflumizone	109 %	1 %	102 %	2 %	0.0005	0.02
Penthiopyrad	108 %	2 %	100 %	1 %	0.0005	0.02
Prothioconazole	107 %	12 %	100 %	15 %	0.0005	0.02
Prothioconazole-desthio	106 %	2 %	100 %	2 %	0.0005	0.02
Teflubenzuron	100 %	9 %	105 %	2 %	0.0005	0.02
TFNA	-	-	98 %	7 %	0.006	0.02
TFNG	103 %	28 %	101 %	9 %	0.003	0.02



Dual-Channel LC-MS/MS: apple validation

264 total pesticide residues (ESI+ and ESI-)

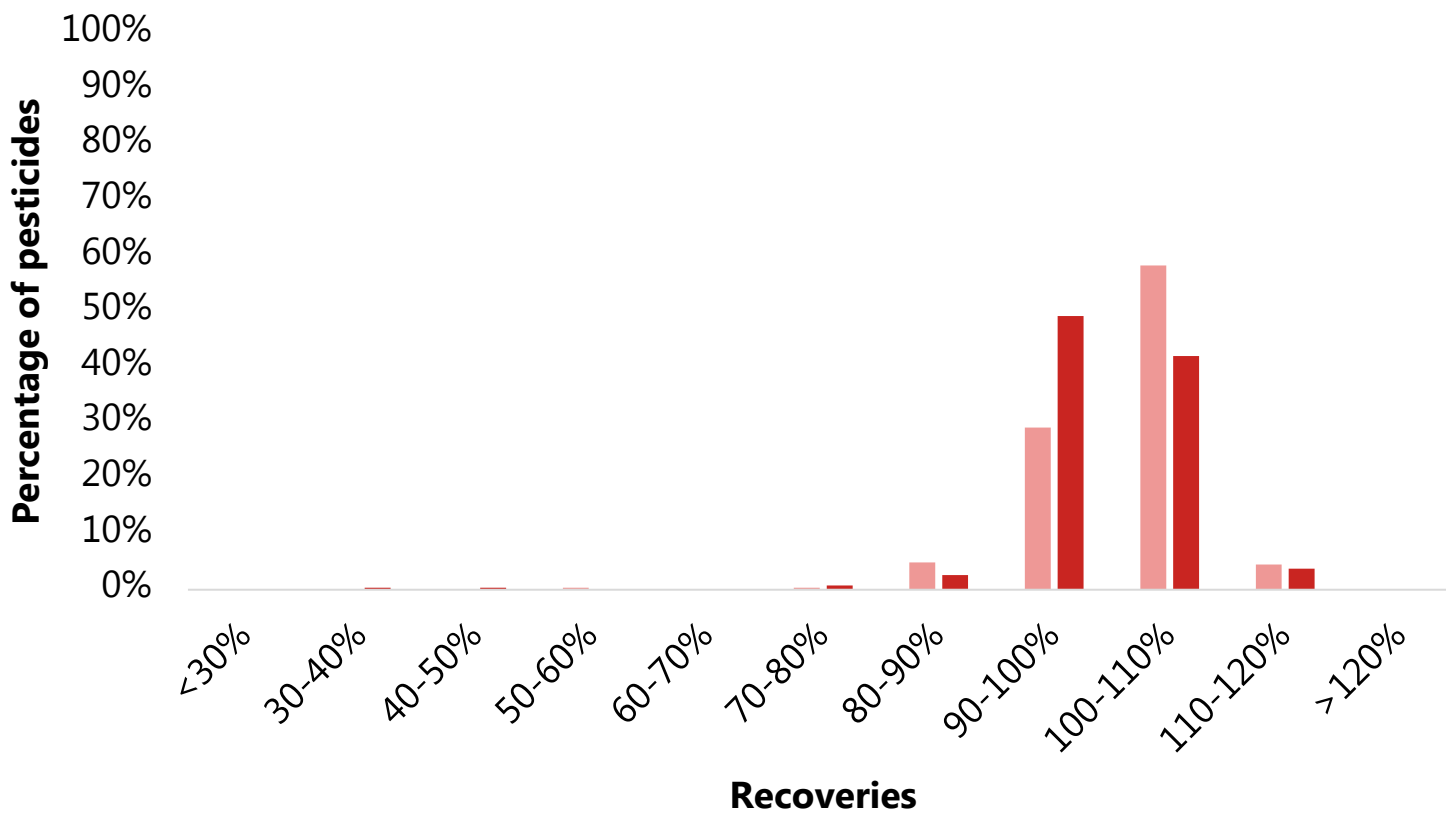
Technique	<70%	70-120%	>120%
Dual-Channel 0.003 mg/kg	1	257	-
Dual-Channel 0.006 mg/kg	2	260	-

256 pesticide residues validated at 0.003 mg/kg

260 pesticide residues validated at 0.006 mg/kg



Bias



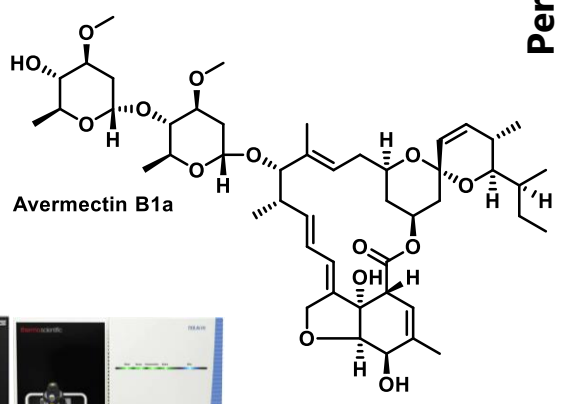
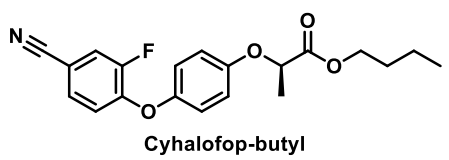
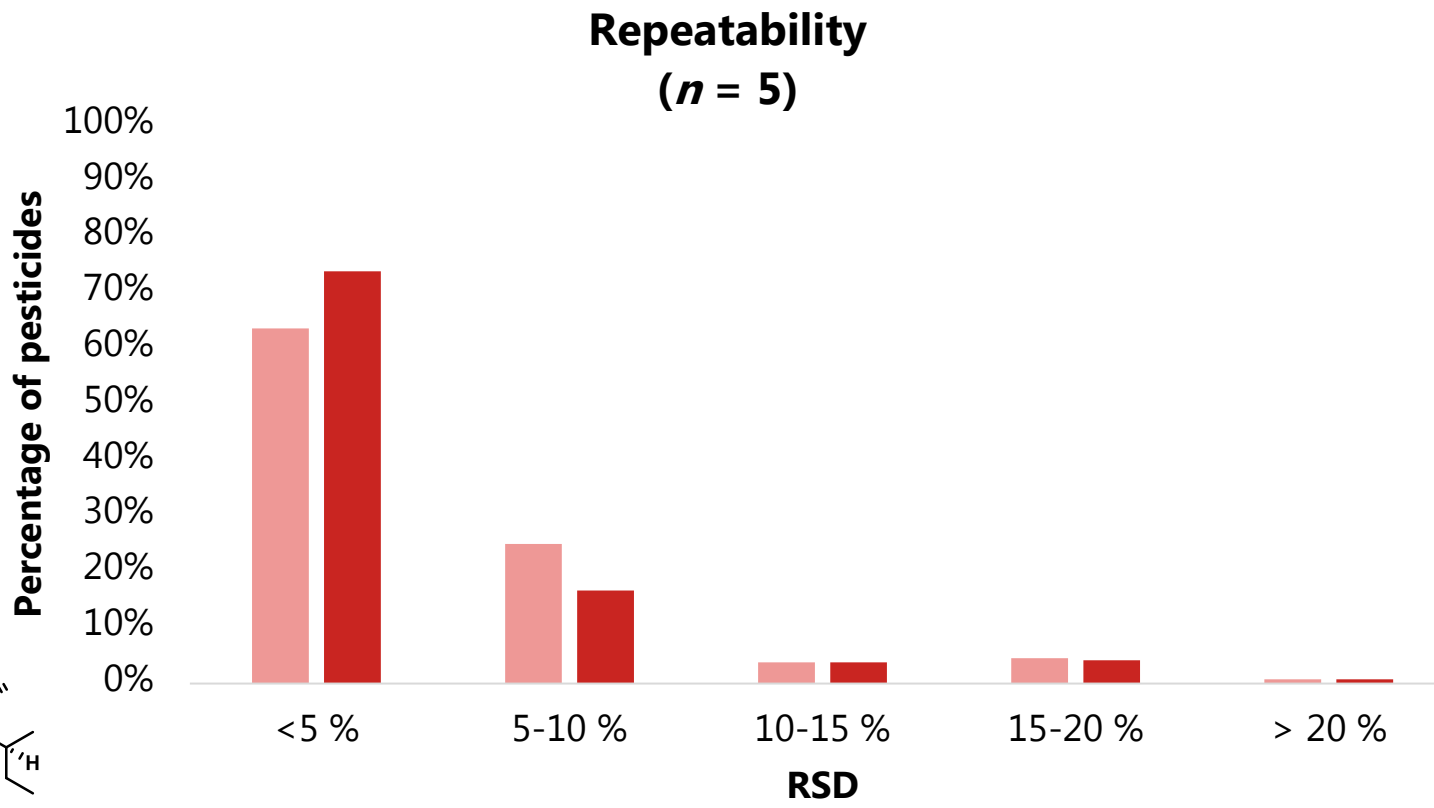
■ 0.003 mg/kg ■ 0.006 mg/kg



Dual-Channel LC-MS/MS: apple validation

264 total pesticide residues (ESI+ and ESI-)

Technique	<5%	5-20%	>20%
Dual-Channel 0.003 mg/kg	64%	33%	1%
Dual-Channel 0.006 mg/kg	74%	25%	1%



■ 0.003 mg/kg ■ 0.006 mg/kg

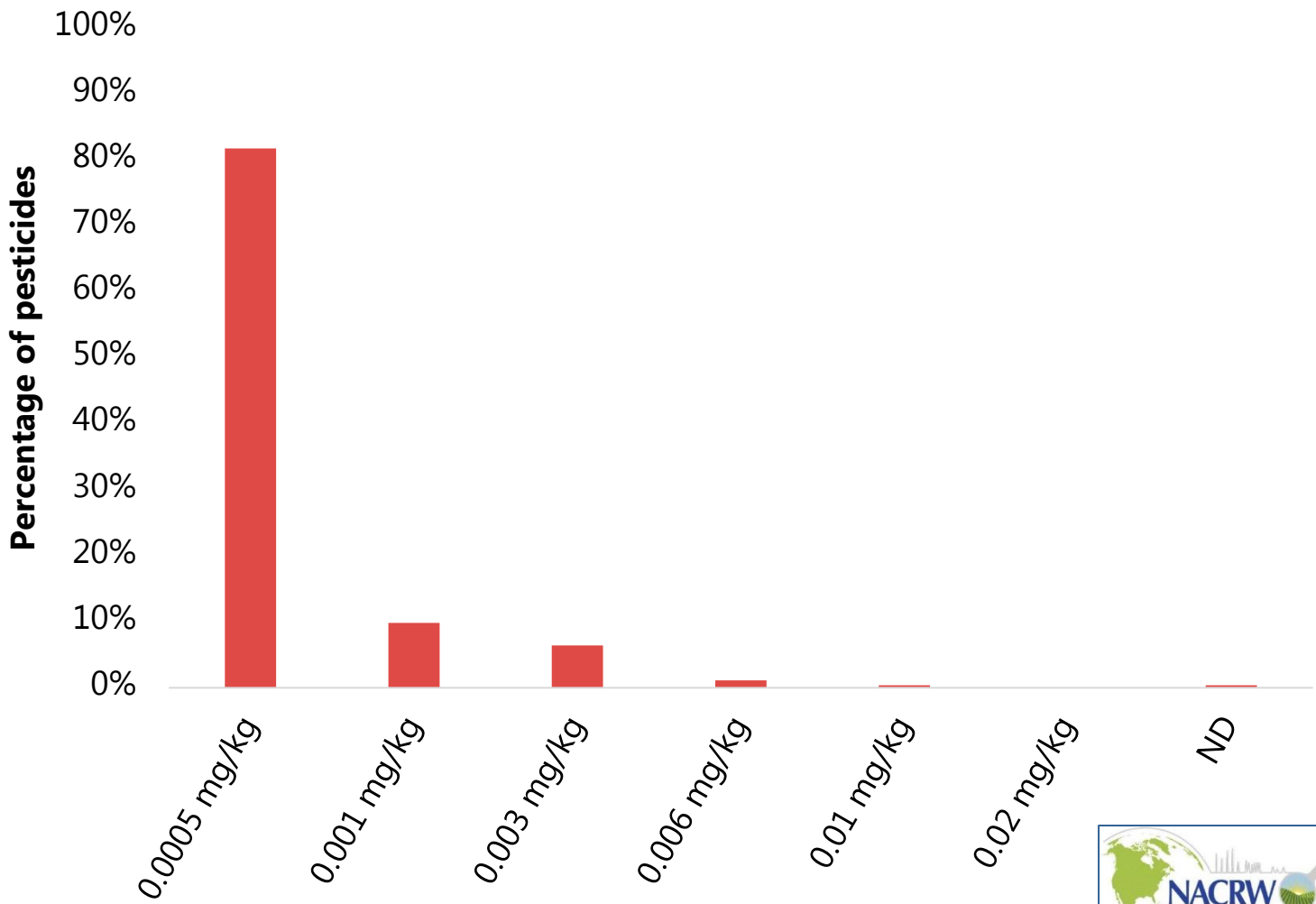


Dual-Channel LC-MS/MS: apple validation

264 total pesticide residues (ESI+ and ESI-)

Calibration level (mg/kg)	No. of analytes
0.0005	216
0.001	26
0.003	17
0.006	3
0.010	1
0.020	0
ND	1

Lowest calibration level

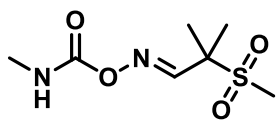




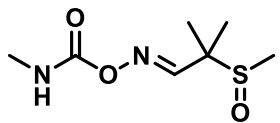
Dual-Channel LC-MS/MS: apple ND

Non detections

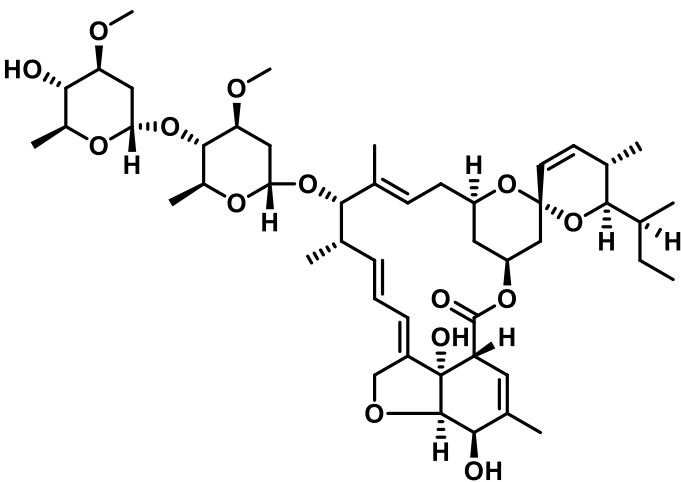
0.006 mg/kg



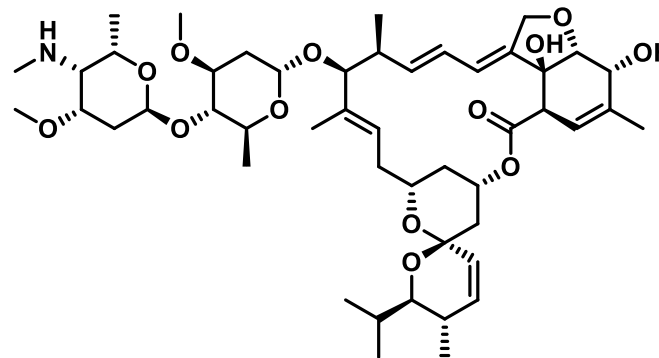
Aldicarb-sulfone



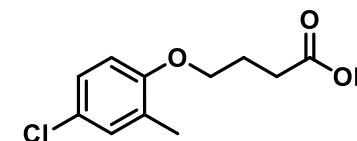
Aldicarb-sulfoxide



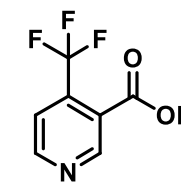
Avermectin B1a



Emamectin B1b



MCPB



TFNA





Dual-Channel LC-MS/MS: banana & orange validation

Gradient 1

Water:MeOH
Formic acid (0.1 %)
Ammonium formate (5 mM)

Gradient 2

Water:AcN
Acetic acid (0.05 %)

Compound	Recoveries 0.003 mg/kg	RSD 0.003 mg/kg	Recoveries 0.006 mg/kg	RSD 0.006 mg/kg	Lowest calibration level (mg/kg)	Highest calibration level (mg/kg)
2,4-D	94 %	10 %	128 %	8 %	0.0003	0.02
Bromacil	100 %	6 %	100 %	4 %	0.0005	0.02
Dithiaron	81 %	6 %	86 %	6 %	0.003	0.02
Diuron	106 %	4 %	100 %	4 %	0.0005	0.02
Fensulfothion	99 %	4 %	104 %	2 %	0.0005	0.02
Fensulfothion-oxon-sulfone	105 %	4 %	100 %	5 %	0.0005	0.02
Fipronil	97 %	2 %	108 %	6 %	0.0005	0.02
Fipronil-desulfinyl	98 %	6 %	105 %	4 %	0.0005	0.02
Fipronil-sulfone	99 %	6 %	102 %	3 %	0.0005	0.02
Flubendiamide	98 %	14 %	104 %	2 %	0.0005	0.02
Fludioxonil	102 %	10 %	102 %	8 %	0.0005	0.02
Haloxypop	102 %	4 %	103 %	10 %	0.001	0.02
Hexaflumuron	95 %	6 %	84 %	36 %	0.0005	0.02
Ioxynil	103 %	2 %	102 %	2 %	0.0005	0.02
Lufenuron	95 %	17 %	103 %	20 %	0.0005	0.02
MCPA	102 %	73 %	98 %	10 %	0.003	0.02
MCPB	-	-	115 %	18 %	0.006	0.02
Meptyldimicop	93 %	16 %	119 %	14 %	0.003	0.02
(E)-Metaflumizone	89 %	40 %	98 %	18 %	0.0005	0.02
(Z)-Metaflumizone	102 %	5 %	108 %	8 %	0.0005	0.02
Penthiopyrad	99 %	2 %	100 %	2 %	0.0005	0.02
Prothioconazole	98 %	5 %	108 %	12 %	0.0005	0.02
Prothioconazole-desthio	107 %	5 %	106 %	2 %	0.0005	0.02
Teflubenzuron	105 %	15 %	109 %	17 %	0.0005	0.02
TFNA	-	-	99 %	3 %	0.006	0.02
TFNG	96 %	9 %	95 %	5 %	0.003	0.02



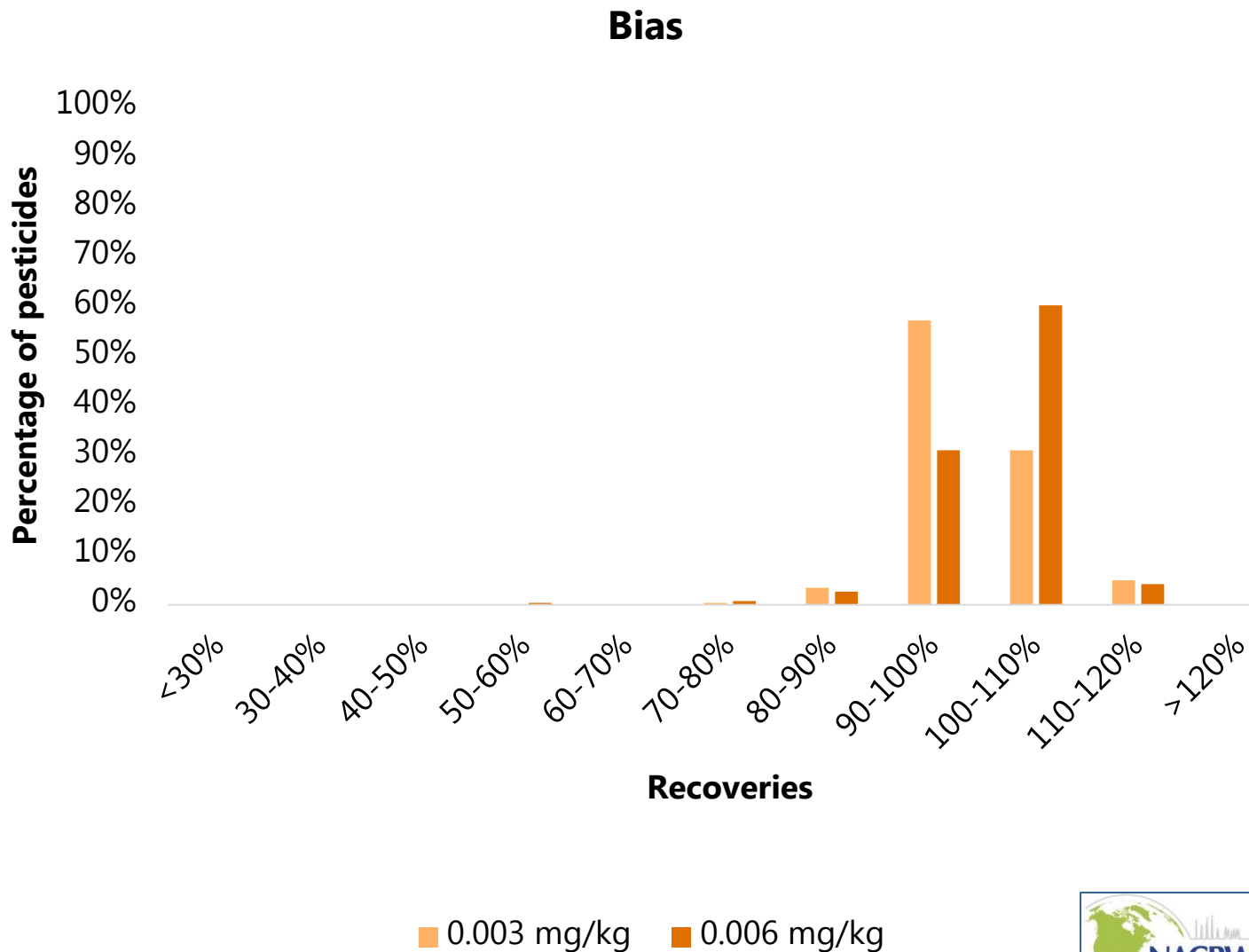
Dual-Channel LC-MS/MS: banana & orange validation

264 total pesticide residues (ESI+ and ESI-)

Technique	<70%	70-120%	>120%
Dual-Channel 0.003 mg/kg	0	256	-
Dual-Channel 0.006 mg/kg	1	261	-

256 pesticide residues validated at 0.003 mg/kg

260 pesticide residues validated at 0.006 mg/kg

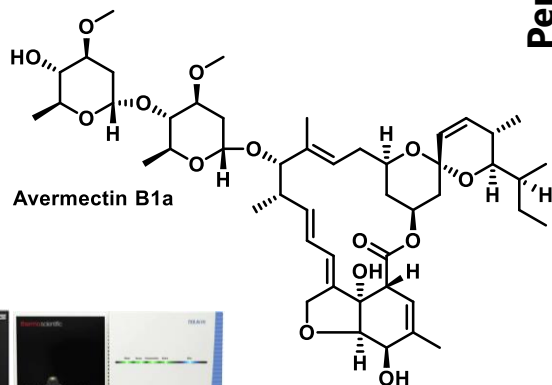
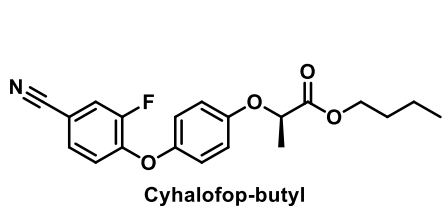
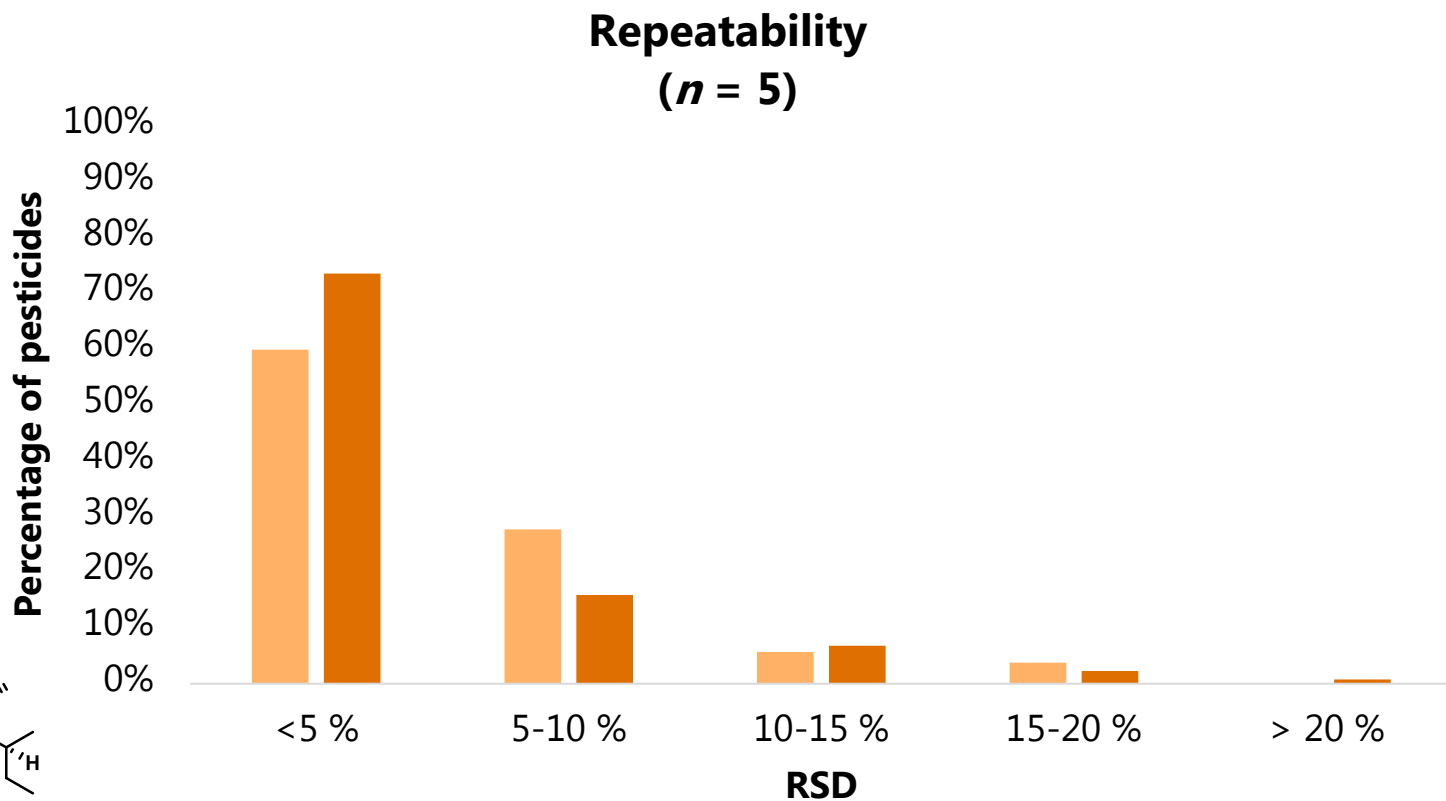




Dual-Channel LC-MS/MS: banana & orange validation

264 total pesticide residues (ESI+ and ESI-)

Technique	<5%	5-20%	>20%
Dual-Channel 0.003 mg/kg	60%	37%	-
Dual-Channel 0.006 mg/kg	73%	25%	<1%





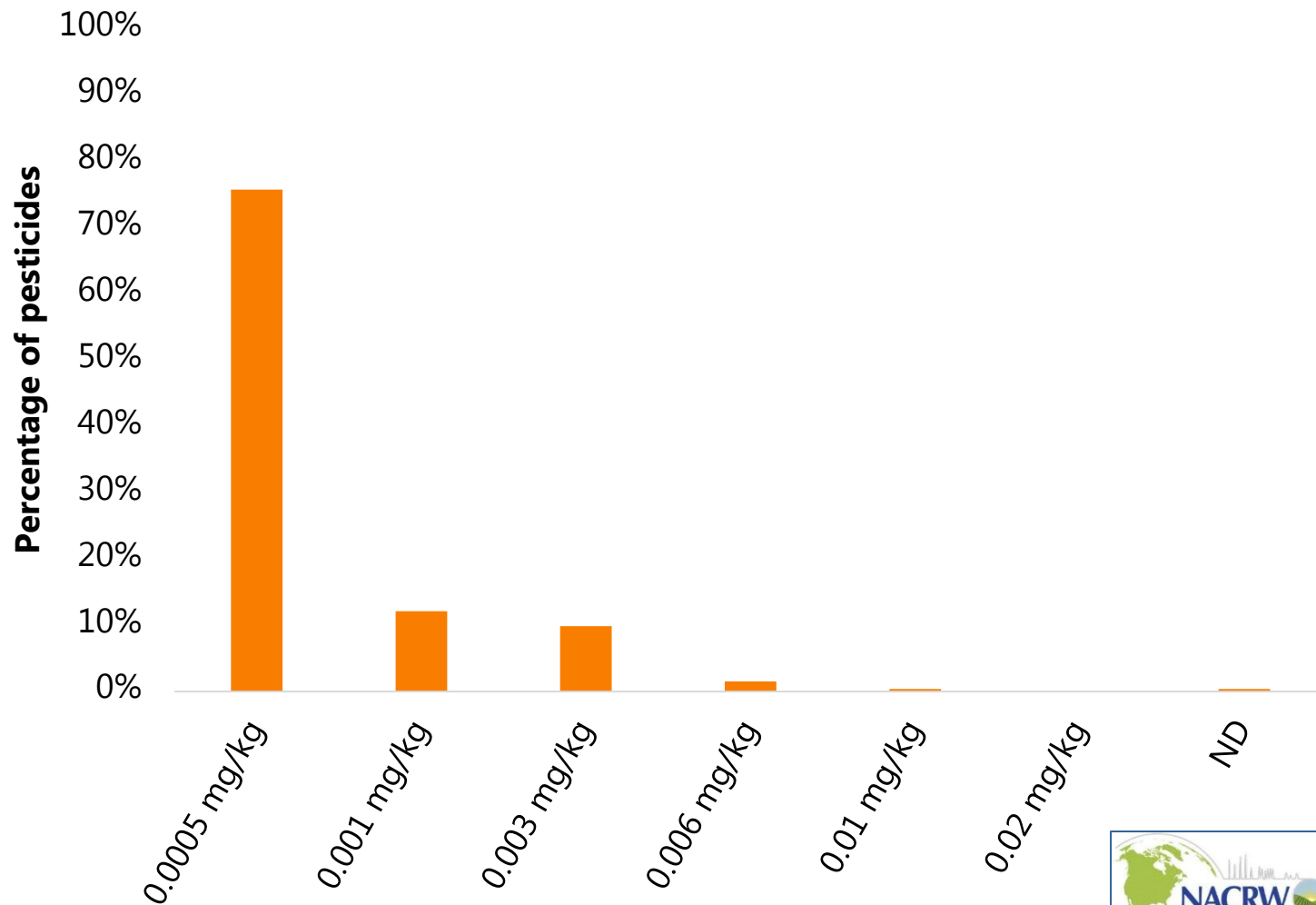
Dual-Channel LC-MS/MS: banana & orange validation

264 total pesticide residues (ESI+ and ESI-)

Calibration level (mg/kg)	No. of analytes
0.0005	200
0.001	32
0.003	26
0.006	4
0.010	1
0.020	0
ND	1



Lowest calibration level

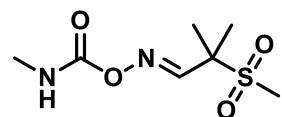




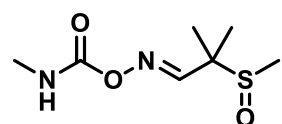
Dual-Channel LC-MS/MS: banana & orange ND

Non detections

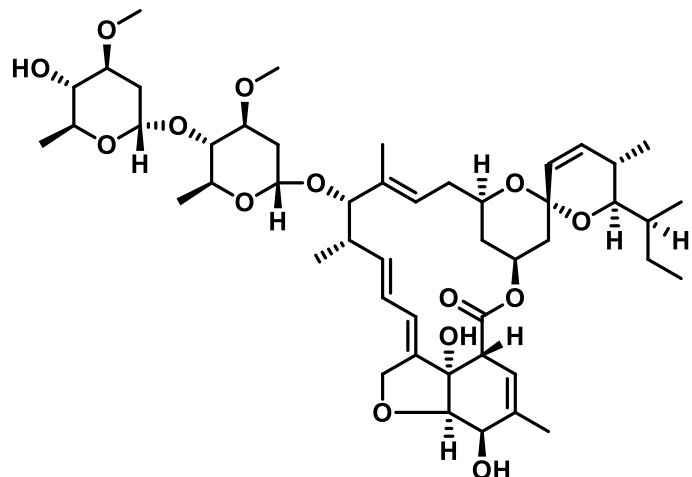
0.006 mg/kg



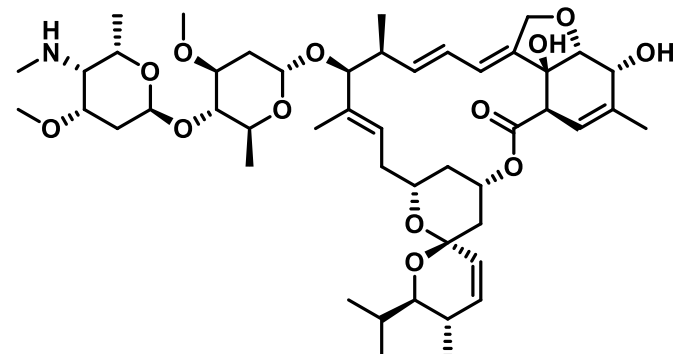
Aldicarb-sulfone



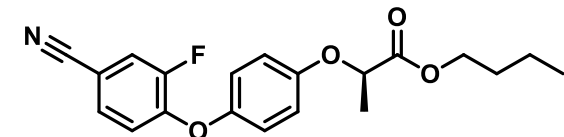
Aldicarb-sulfoxide



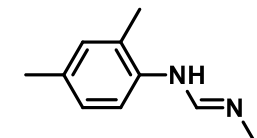
Avermectin B1a



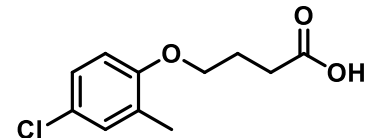
Emamectin B1b



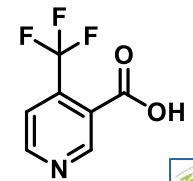
Cyhalofop-butyl



DMPF



MCPB



TFNA





Dual-Channel LC-MS/MS: carry over test

Sequence:

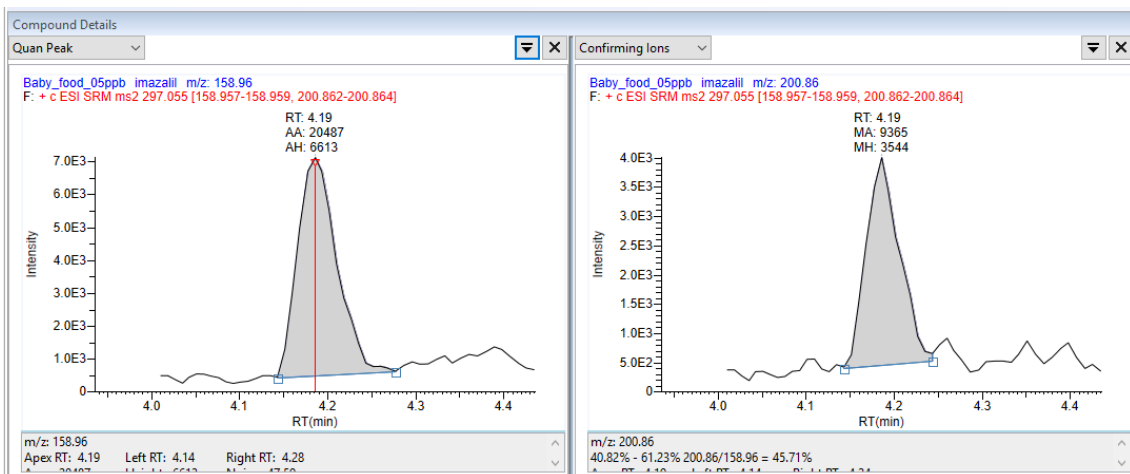
1. Calibration curve 0.0005 – 0.020 mg/kg (ppb)
2. 3 injections at 0.020 mg/kg
3. Baby food blank
4. 6 injections at 0.020 mg/kg
5. Baby food blank
6. 12 injections at 0.020 mg/kg
7. Baby food blank

Compound	Carry over after 3 injections [ppb]	Carry over after 3 injections [%]	Carry over after 6 injections [ppb]	Carry over after 6 injections [%]	Carry over after 12 injections [ppb]	Carry over after 12 injections [%]
Acetamiprid	0.2	1.0 %	0.2	1.0 %	0.2	1.1 %
DEET	0.6	2.8 %	0.5	2.7 %	0.5	2.6 %
Demeton- <i>S</i> -methyl	0.9	4.6 %	0.9	4.6 %	1.0	5.1 %
Fluometuron	0.7	3.4 %	0.6	3.1 %	0.7	3.3 %
Dimethomorph	0.2	1.1 %	0.2	1.2 %	0.2	0.9 %
Fenamiphos-sulfoxide	0.5	2.6 %	0.5	2.6 %	0.5	2.7 %
Imazalil	0.3	1.3 %	0.2	0.8 %	0.2	0.9 %
Imidacloprid	0.4	2.2 %	0.5	2.4 %	0.4	2.1 %
Oxadixyl	0.2	1.1 %	0.3	1.3 %	0.2	1.1 %
Pendimethalin	3.6	18.2 %	3.2	16.2 %	2.9	14.7 %
2,4-D	0.8	4.1 %	1.1	5.3 %	1.1	5.4 %





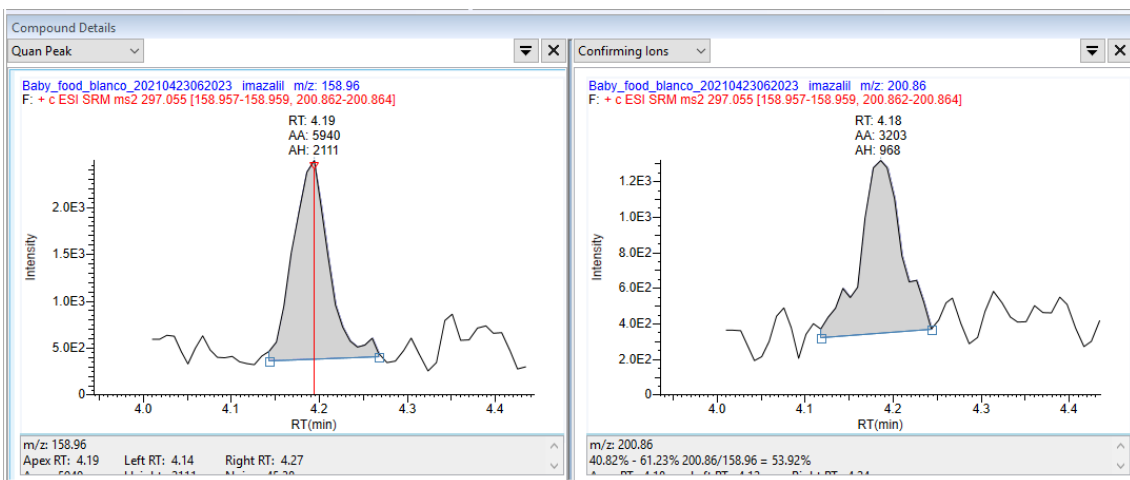
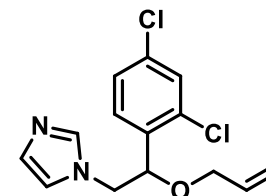
Dual-Channel LC-MS/MS: carry over test



Imazalil

0.5 ppb standard in baby food

Quant ion peak area 2.0E4



Imazalil

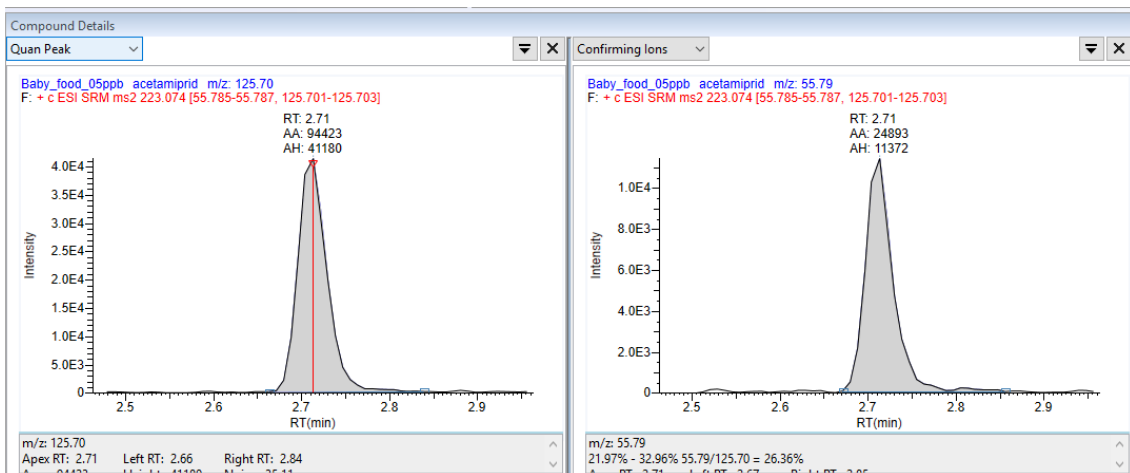
Blank baby food after 12 injections of

20 ppb standard

Quant ion peak area 6.0E3



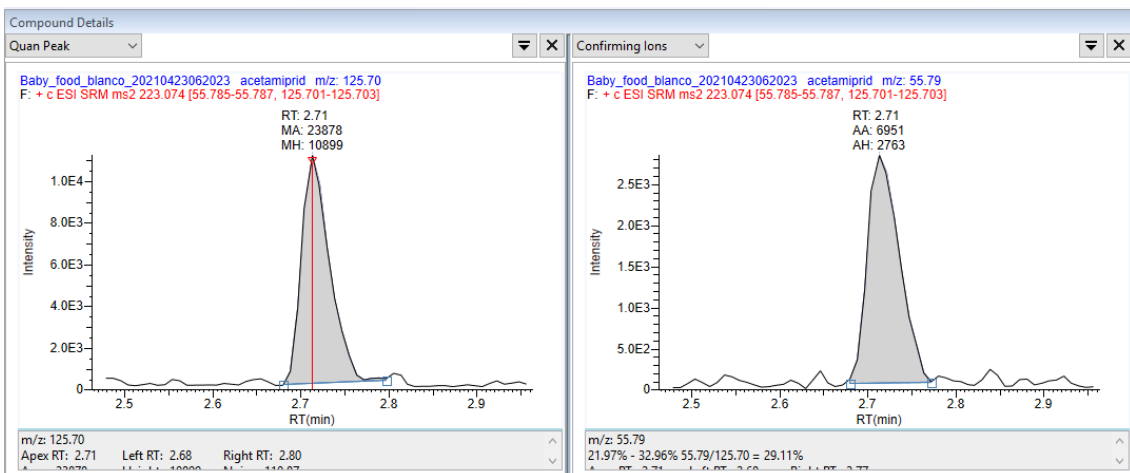
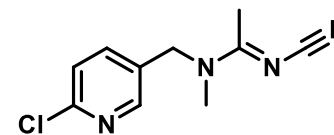
Dual-Channel LC-MS/MS: carry over test



Acetamiprid

0.5 ppb standard in baby food

Quant ion peak area 9.4E4



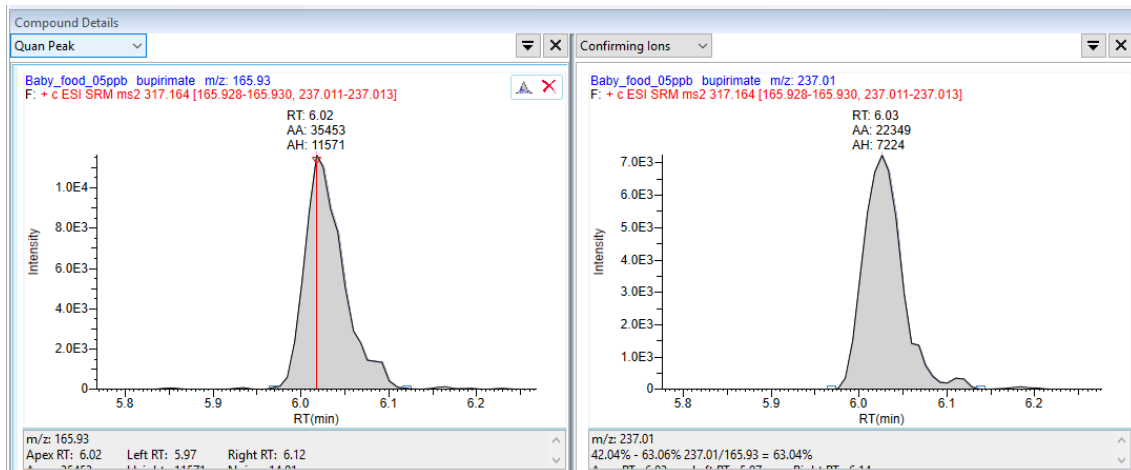
Acetamiprid

Blank baby food after 12 injections of 20 ppb standard

Quant ion peak area 2.4E4



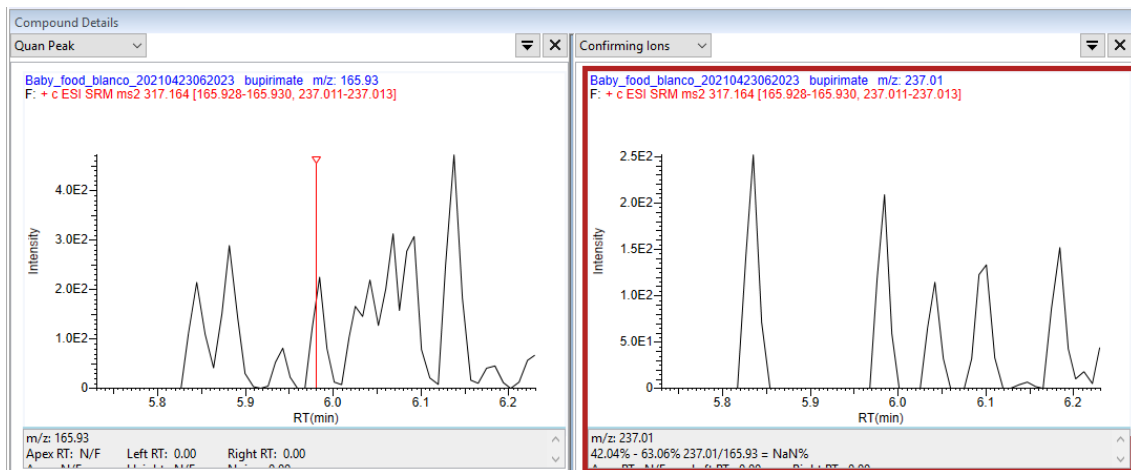
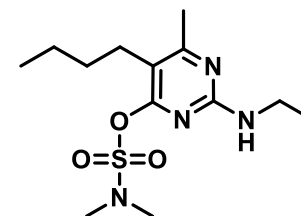
Dual-Channel LC-MS/MS: carry over test



Bupirimate

0.5 ppb standard in baby food

Quant ion peak area 1.2E4



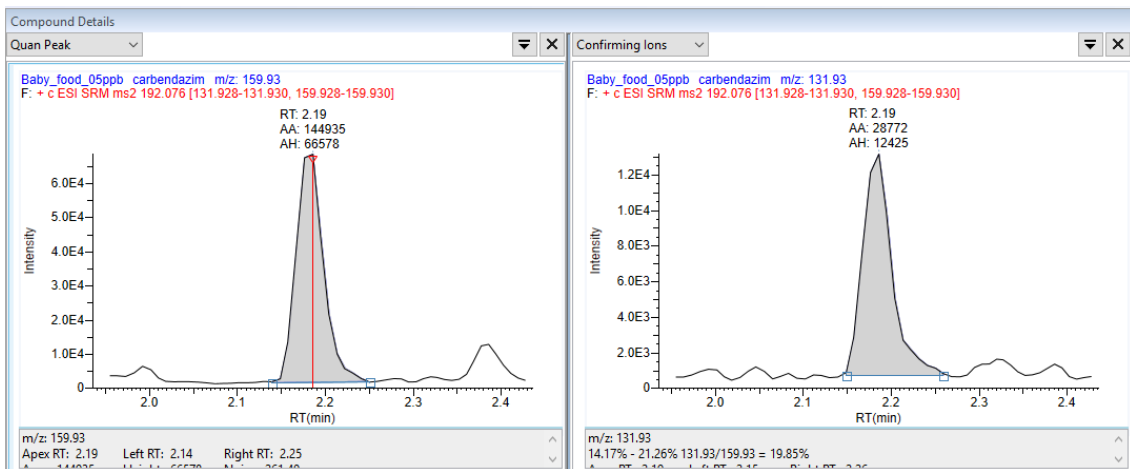
Bupirimate

Blank baby food after 12 injections of
20 ppb standard

Quant ion peak area 0.0E0



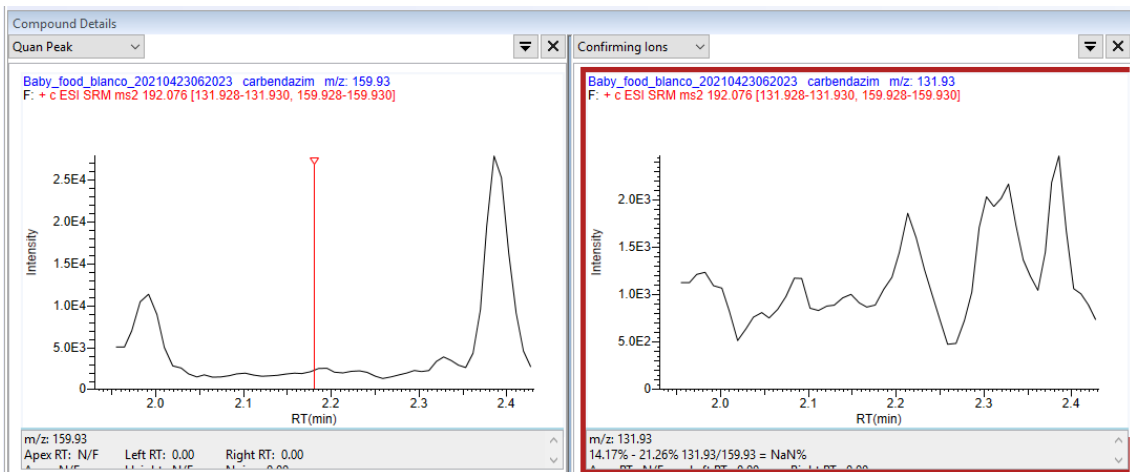
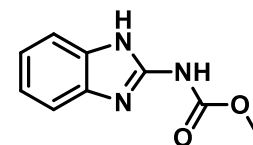
Dual-Channel LC-MS/MS: carry over test



Carbendazim

0.5 ppb standard in baby food

Quant ion peak area 1.4E5



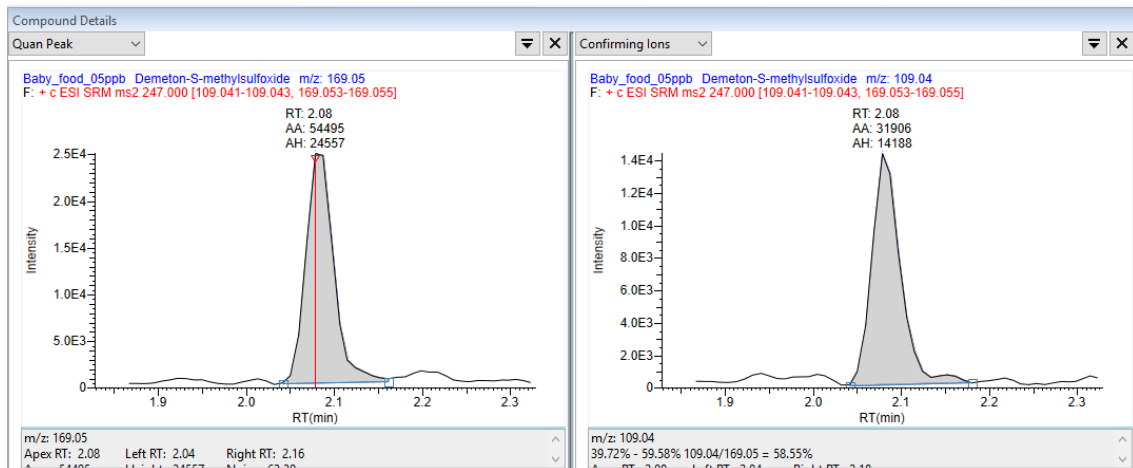
Carbendazim

Blank baby food after 12 injections of 20 ppb standard

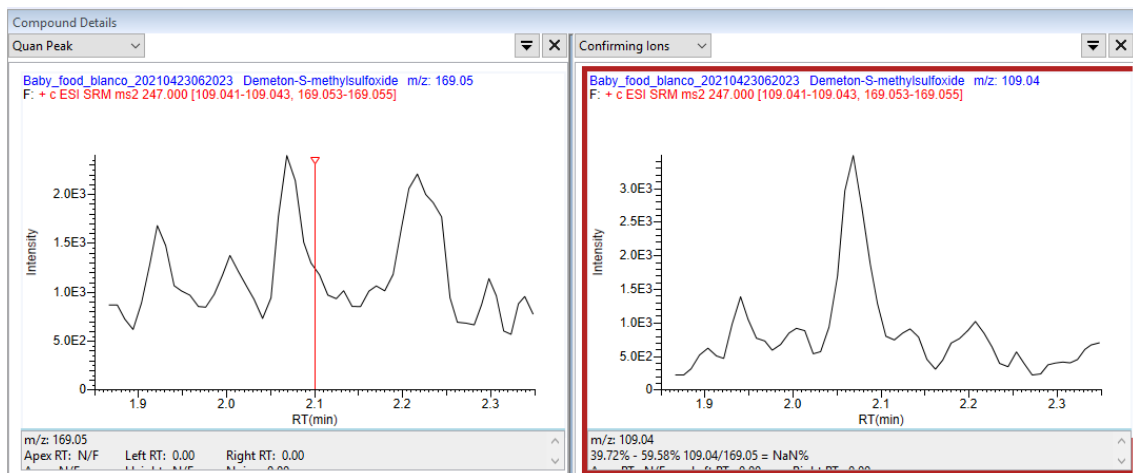
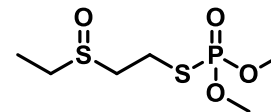
Quant ion peak area 0.0E0



Dual-Channel LC-MS/MS: carry over test



Demeton-S-methylsulfoxide
0.5 ppb standard in baby food
Quant ion peak area 5.5E4



Demeton-S-methylsulfoxide
Blank baby food after 12 injections of
20 ppb standard
Quant ion peak area 0.0E0



Dual-Channel LC-MS/MS: accepted for publication

1 **Cutting-edge approach using dual-channel chromatography to overcome the sensitivity issues**
2 **associated with polarity switching in pesticide residues analysis**

3 **Abstract**

4

5 Optimal mobile phase modifiers are not equivalent for positive and negative ionisation modes in
6 electrospray. For this reason, the use of polarity switching in a multiresidue analysis with a mobile phase
7 optimised for positive mode compounds will typically limit the response for compounds measured in the
8 negative mode. This issue can be overcome by independently injecting a sample twice. For the first

**Work on baby food with two mobile phases
submitted to scientific journal**



Conclusions

- This technique can be used to **improve selectivity** without sacrificing analysis time
- Furthermore, **two different mobile phases** can be employed simultaneously
- Most compounds could be **validated** on baby food at **0.003 mg/kg**, with minimum carry-over
- In summary, Dual-Channel instrumentation provides laboratories advantages in **analysis time**, **selectivity**, and **sensitivity**



References

- Rajski, Ł., Jesús, F., Díaz-Galiano, F.J., Fernández-Alba, A.R. Dual-channel chromatography a smart way to improve the analysis efficiency in liquid chromatography coupled to mass spectrometry. *J. Chrom. A* **2020**, *1633*, 461614.
- Cutting-edge approach using dual-channel chromatography to overcome the sensitivity issues associated with polarity switching in pesticide residues analysis. Díaz-Galiano, F.J., Rajski, Ł., Parrilla, P.; Ferrer, C.; Fernández-Alba, A.R. *Accepted for publication*.

Thank you for your attention



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