Dual-channel chromatography a smart way to enhance the laboratory throughput

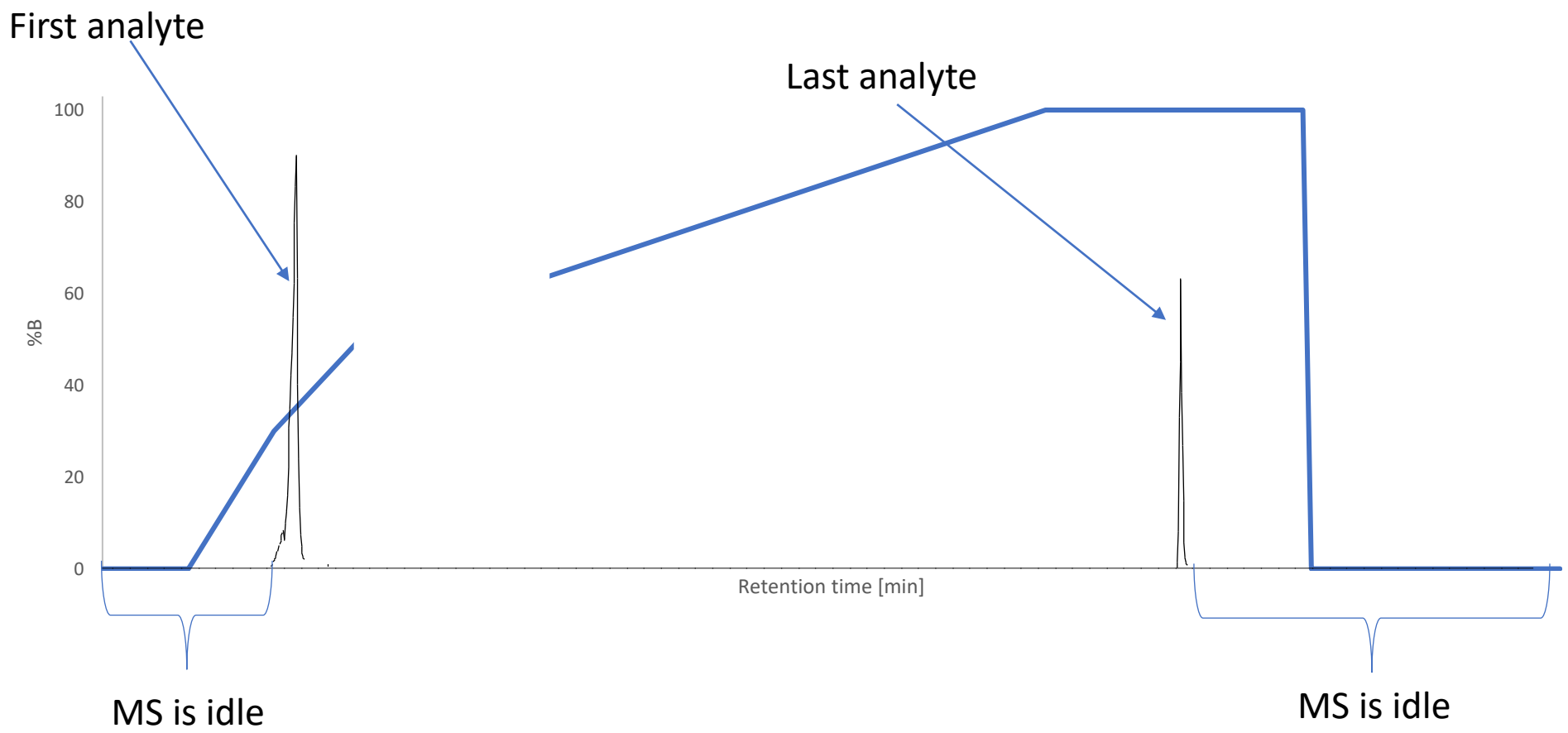
Dr. Łukasz Rajski

Introduction

How to decrease the analysis time?

- Shorter column, steeper gradient, higher flow:
  - Compromised separation
    - More coeluting pesticides
      - Shorter dwell times -> lower sensitivity
      - Longer duty cycle -> Less data points per chromatographic peak -> worse peak area reproducibility
      - Common transitions
      - Possible cross-talk
    - More coeluting matrix (especially in “dirty matrices”)
      - Higher matrix effects -> lower sensitivity
      - Possible interferences

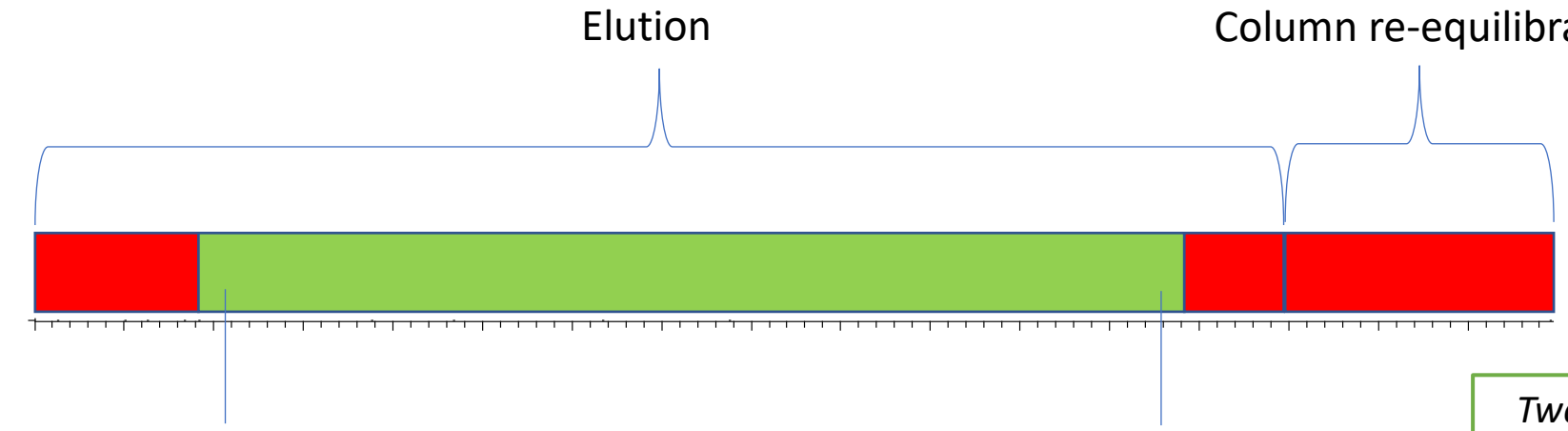
Another option to decrease the analysis time?



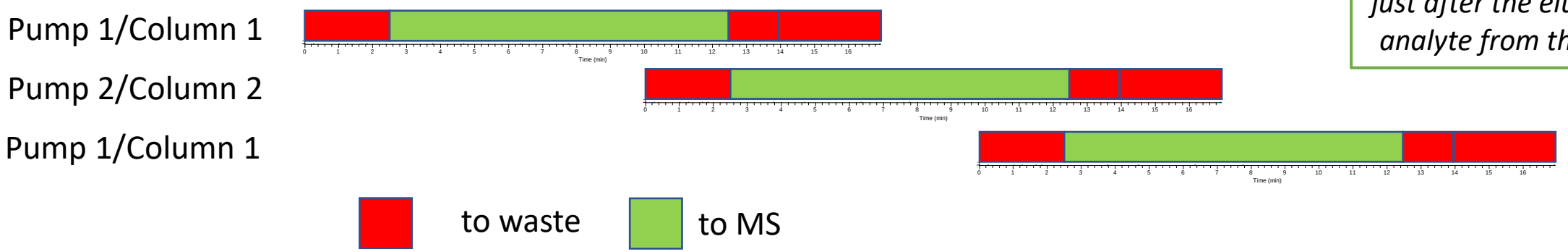
Analysis time can be decreased by the application of multi-channel chromatography and reduction of the idle time of the mass spectrometer

Hardware

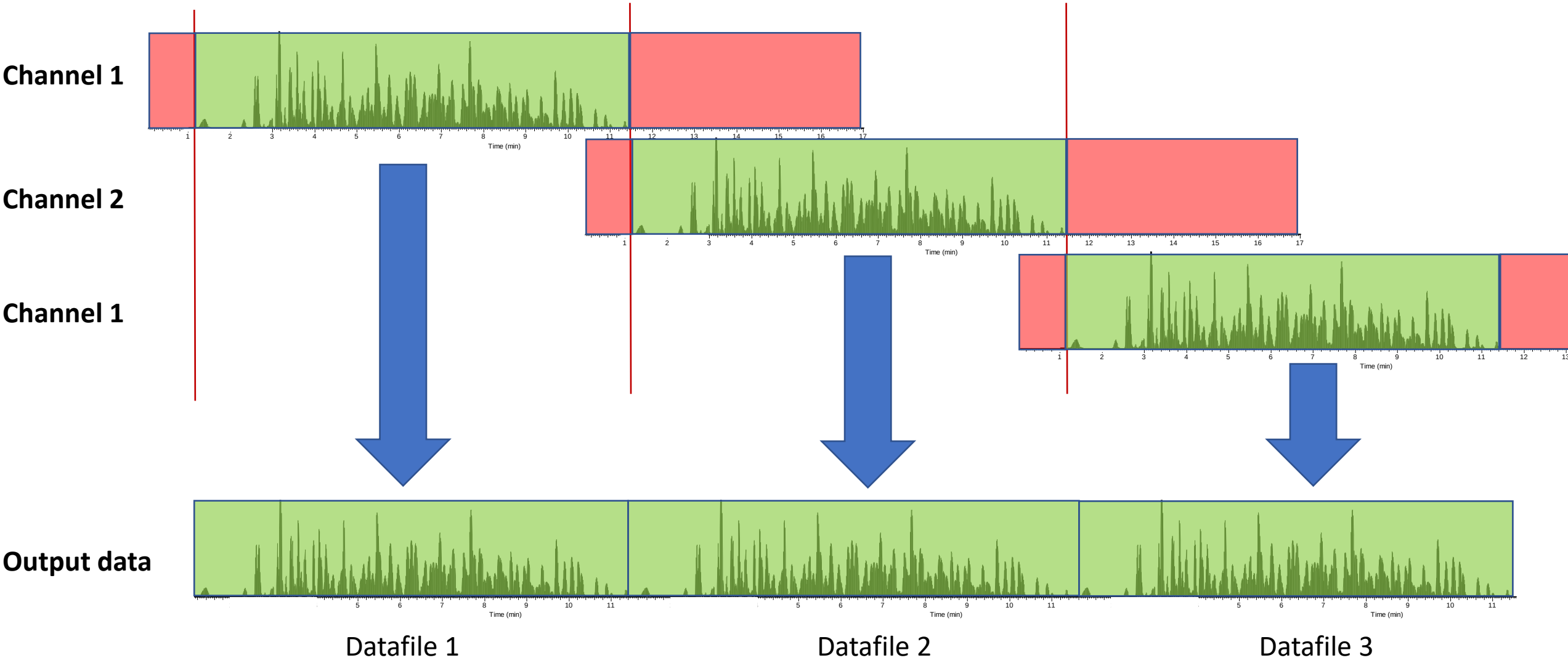
How does a dual-channel system work?



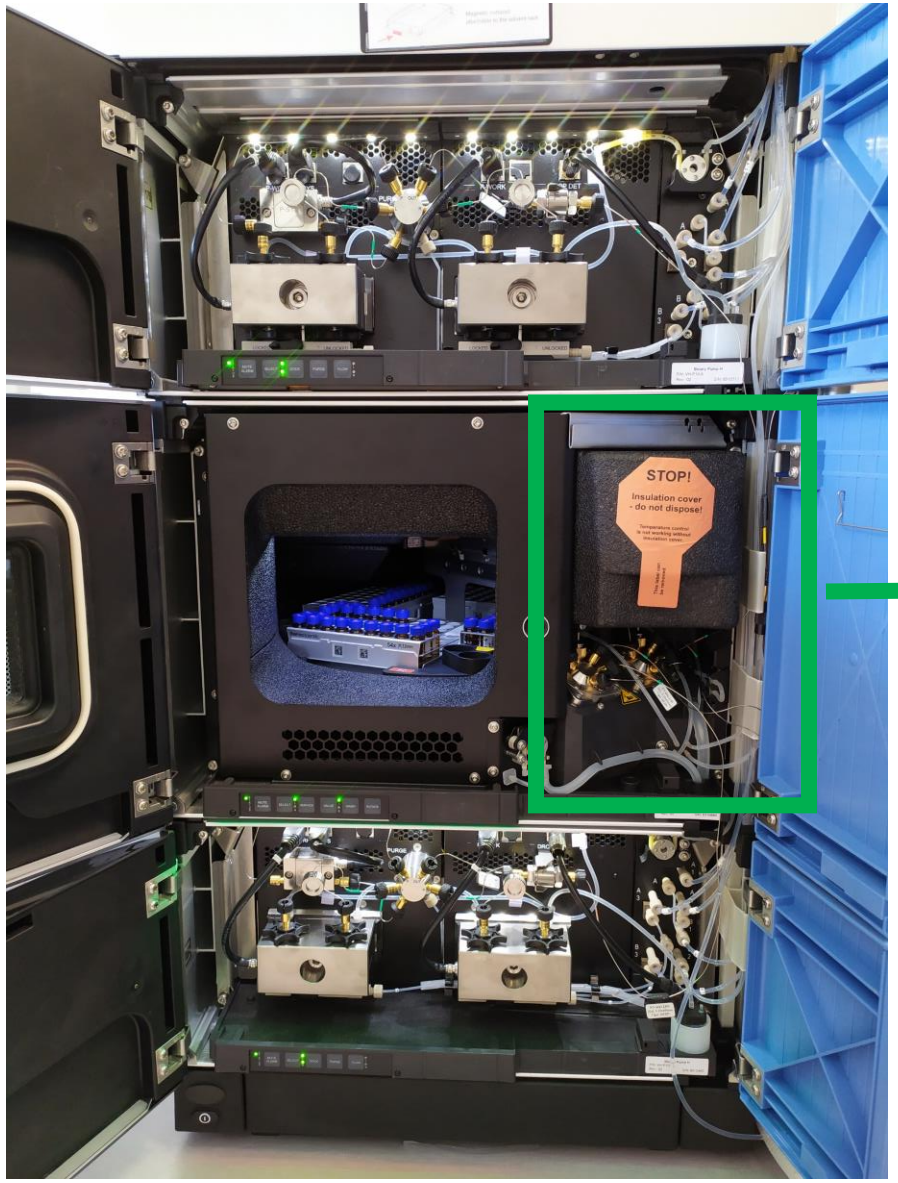
Two columns are operated in parallel. Then, consecutive injections are partially overlapped and synchronised in the way that the first analyte from the second column elutes just after the elution of the last analyte from the first column.



Chromatographic output from a dual-channel system

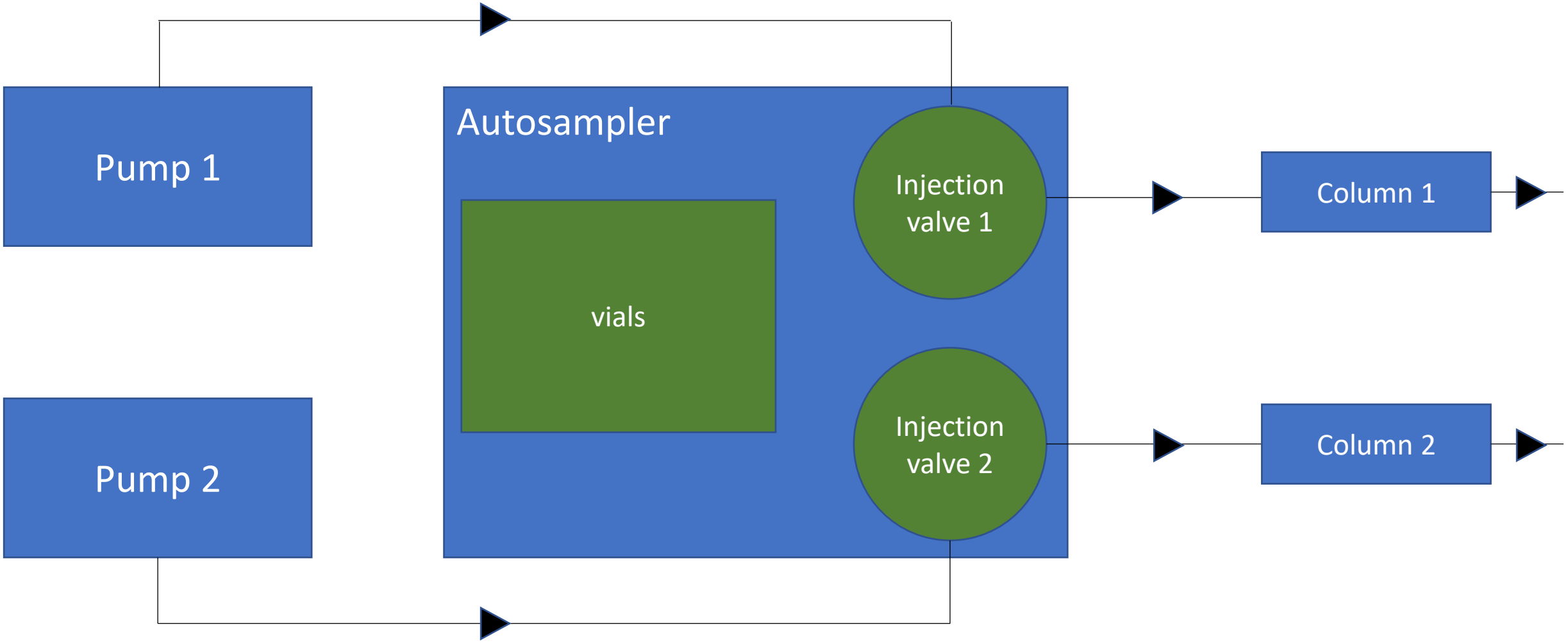



Pump 2
Autosampler with two independent injection units
Pump 1
Column oven 1
Column oven 2

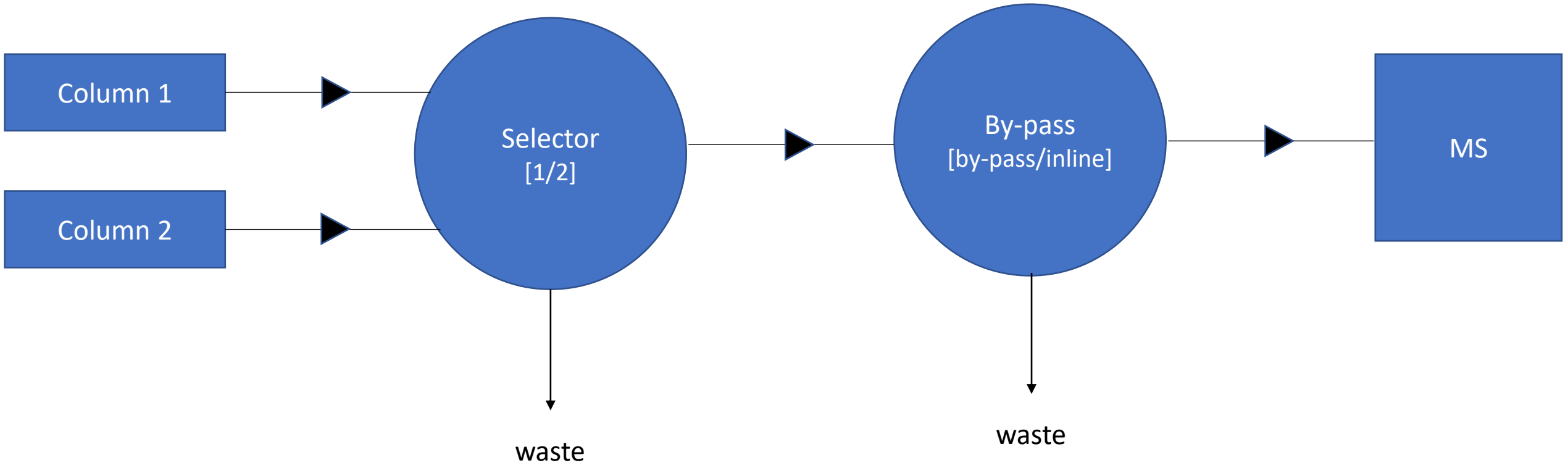


Autosampler is equipped with two sample loops and two injection valves.

Schematic of the Dual Channel Configuration

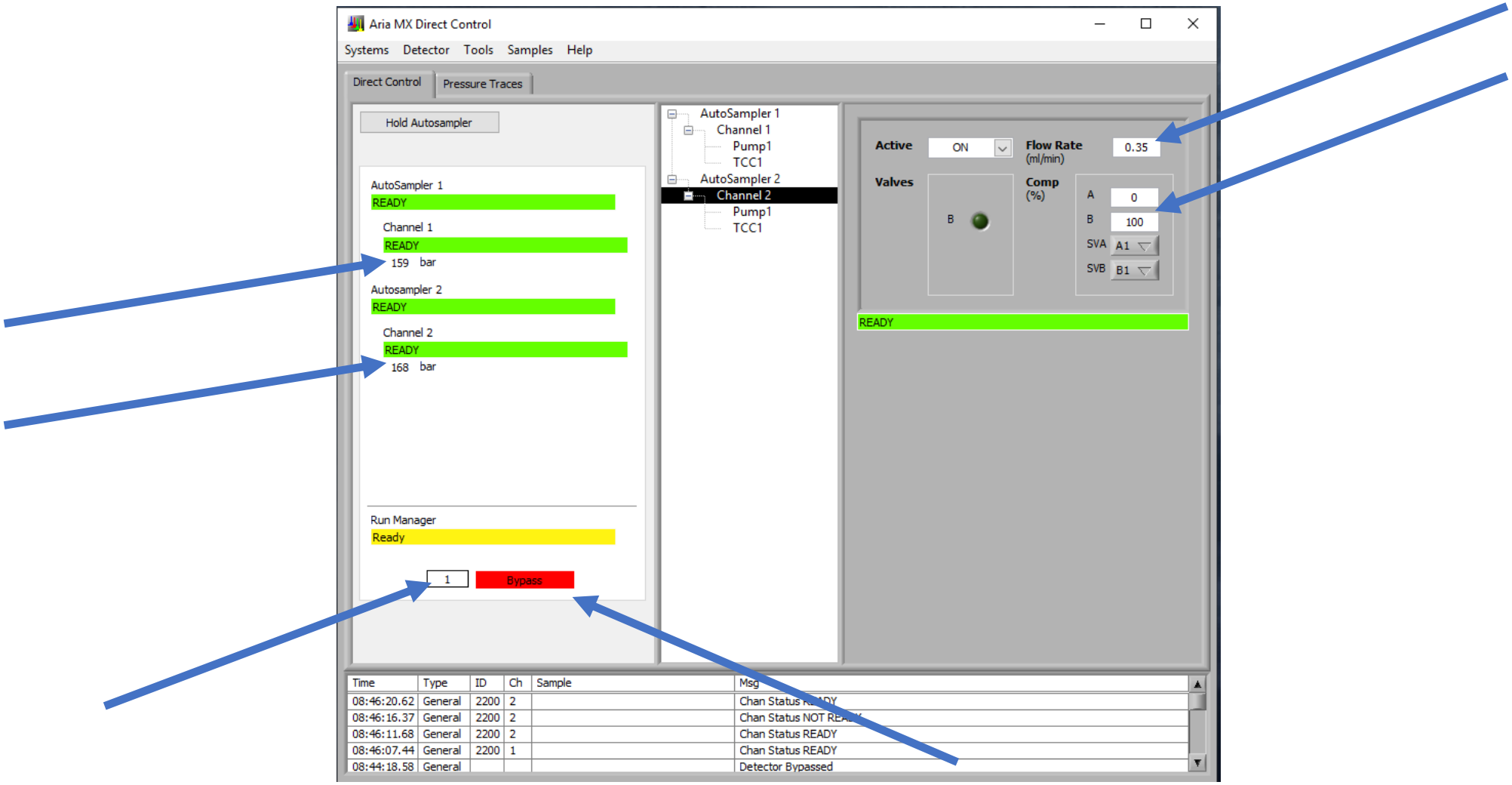


Dual Channel Configuration– channel selector



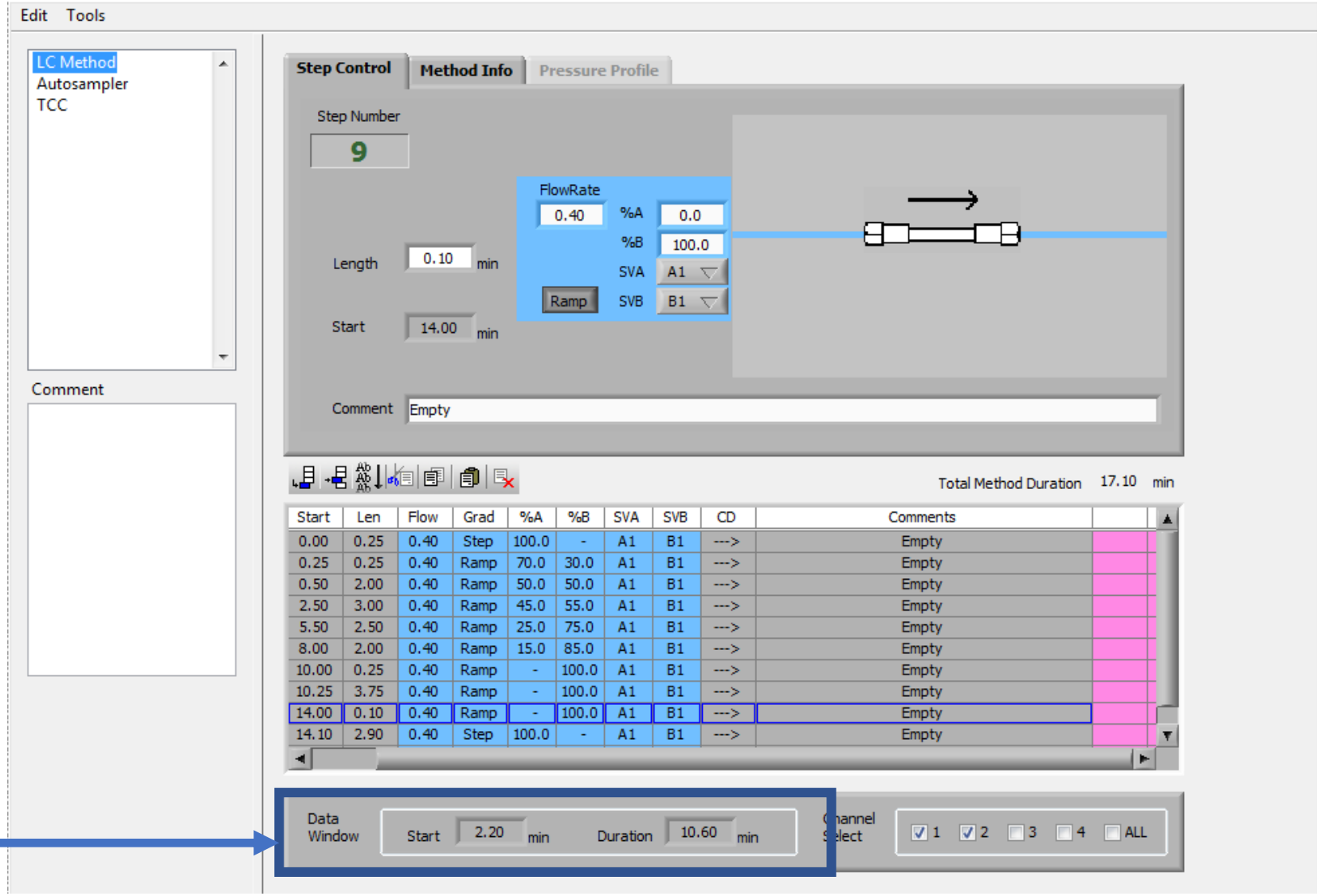
Software

Aria MX


Aria MX Direct Control
Systems
Detector
Tools
Samples
Help
Direct Control
Pressure Traces
Hold Autosampler
AutoSampler 1
READY
Channel 1
READY
159 bar
Autosampler 2
READY
Channel 2
READY
168 bar
Run Manager
Ready
1
Bypass
AutoSampler 1
Channel 1
Pump1
TCC1
AutoSampler 2
Channel 2
Pump1
TCC1
Active
ON
Flow Rate
(ml/min)
0.35
Valves
B
Comp
(%)
A
0
B
100
SVA
A1
SVB
B1
READY
Time
Type
ID
Ch
Sample
Msg
08:46:20.62
General
2200
2
Chan Status READY
08:46:16.37
General
2200
2
Chan Status NOT READY
08:46:11.68
General
2200
2
Chan Status READY
08:46:07.44
General
2200
1
Chan Status READY
08:44:18.58
General
Detector Bypassed

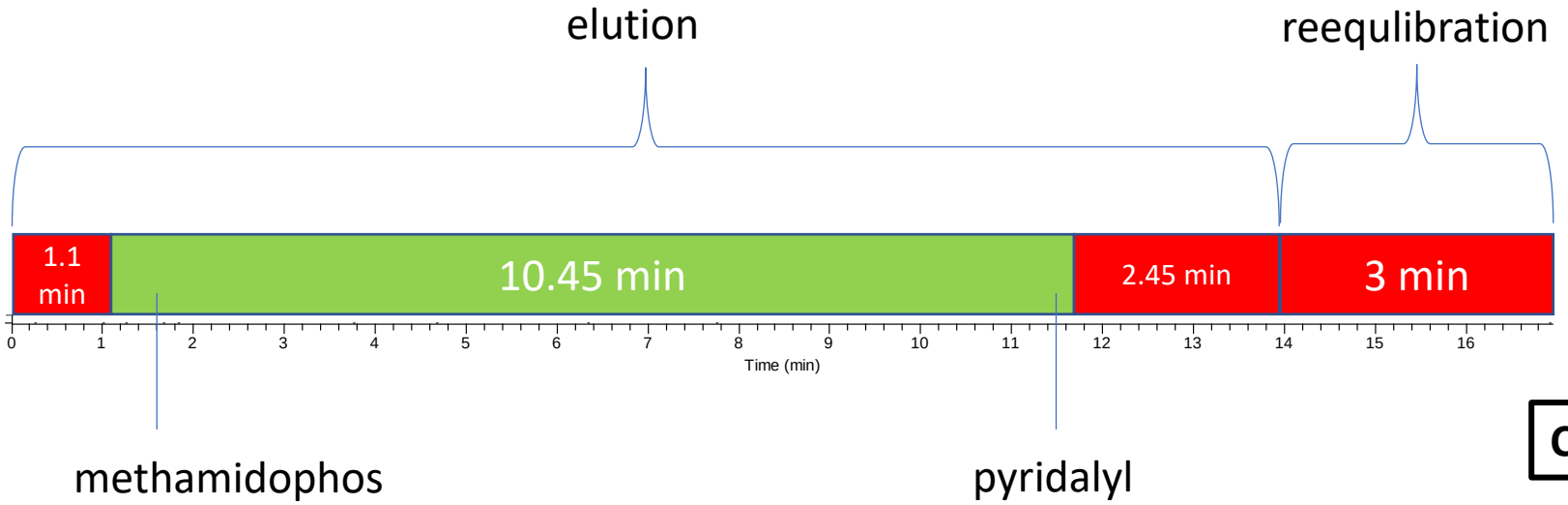
Aria MX Method setup

Method setup is very easy. The user has to specify only the retention time when the acquisition should start and how long it should take. Other parameters are the same as in a single-channel system.



Evaluation of 100 mm columns

Time segments in dual-channel chromatography

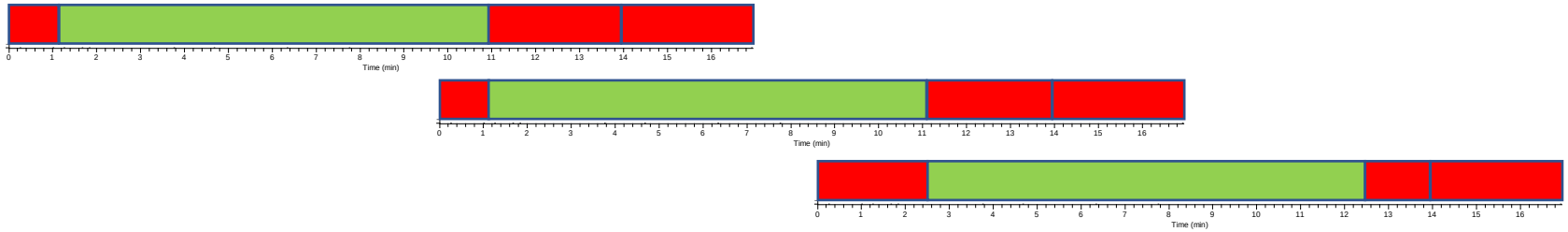


Column length 100 mm

Channel 1

Channel 2

Channel 1

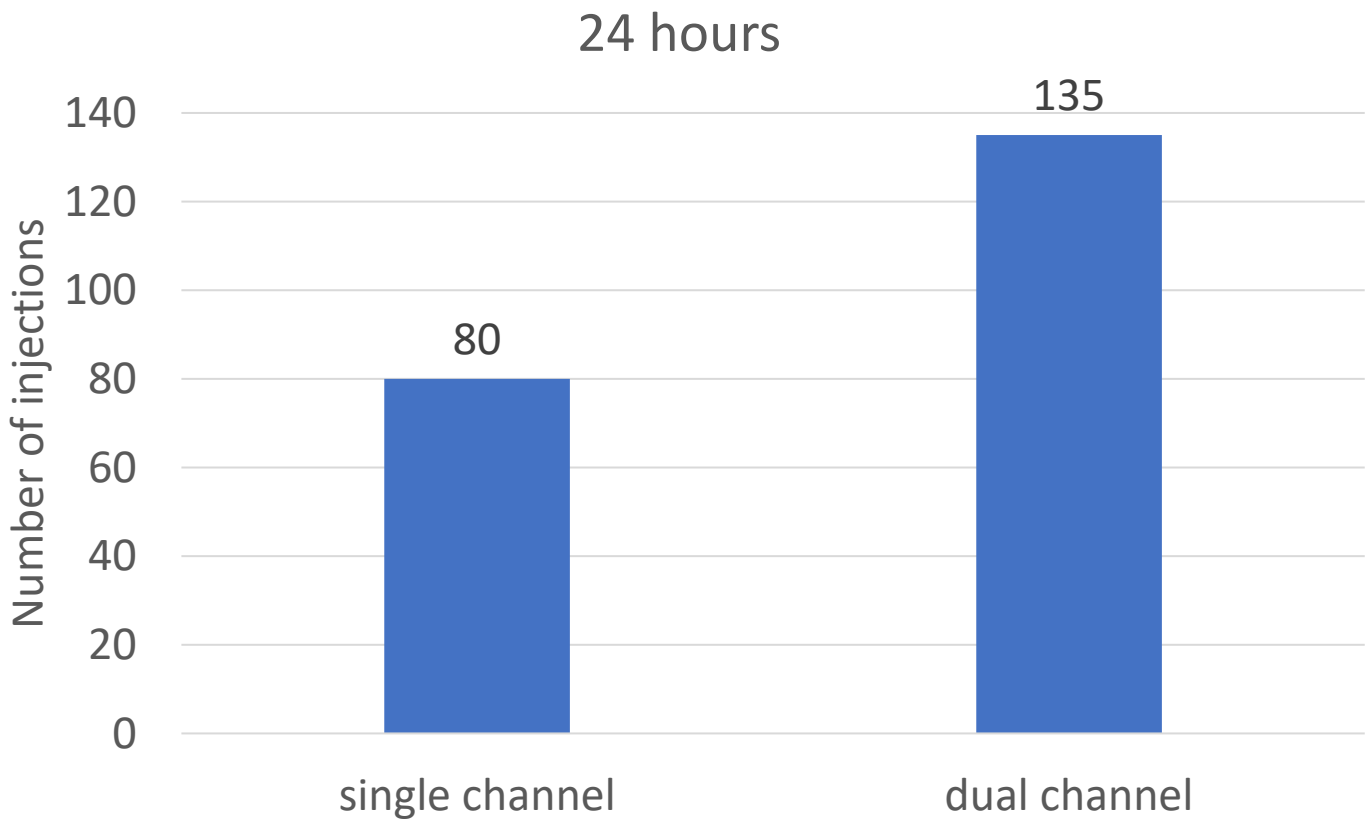


to waste

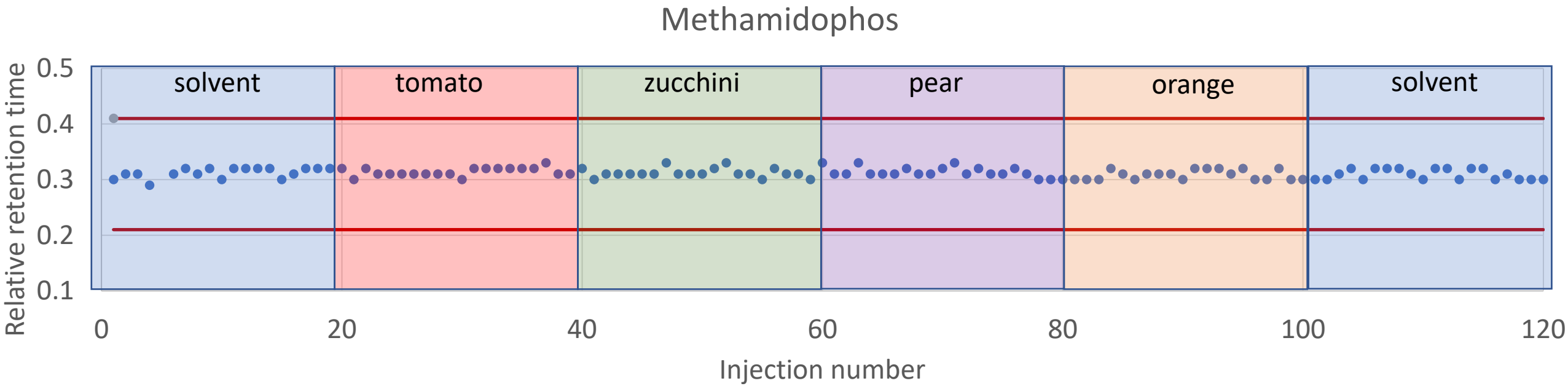
to MS (**acquisition time 10.45 min**)

Total time in a single-channel system: 17 min
(+ 1 minute for needle wash, sample aspiration, etc.)

Improved sample throughput using a 100 mm column



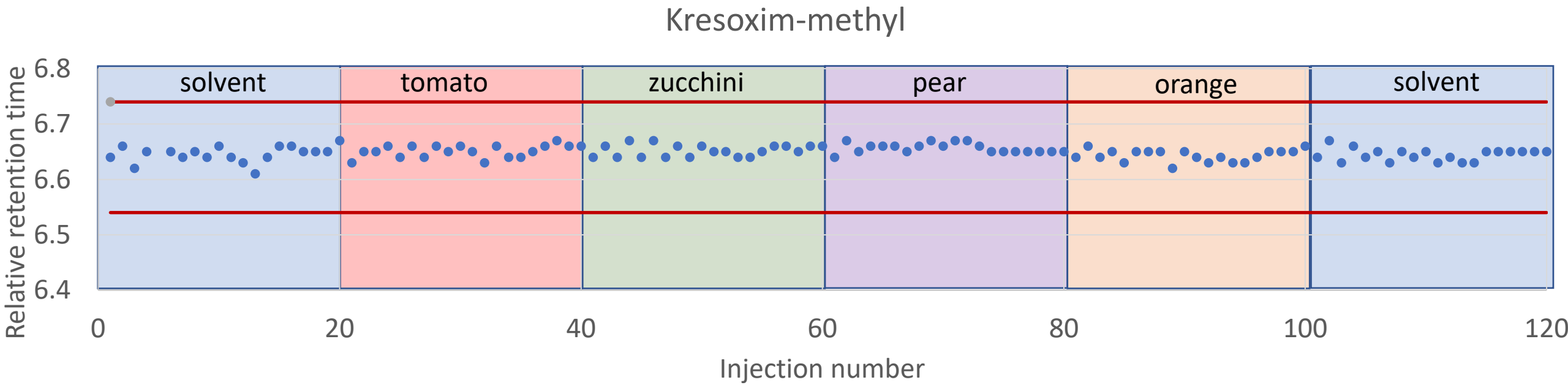
Retention time stability (methamidophos)



The red lines mark ± 0.1 min

120 injections alternating on column 1 & column 2

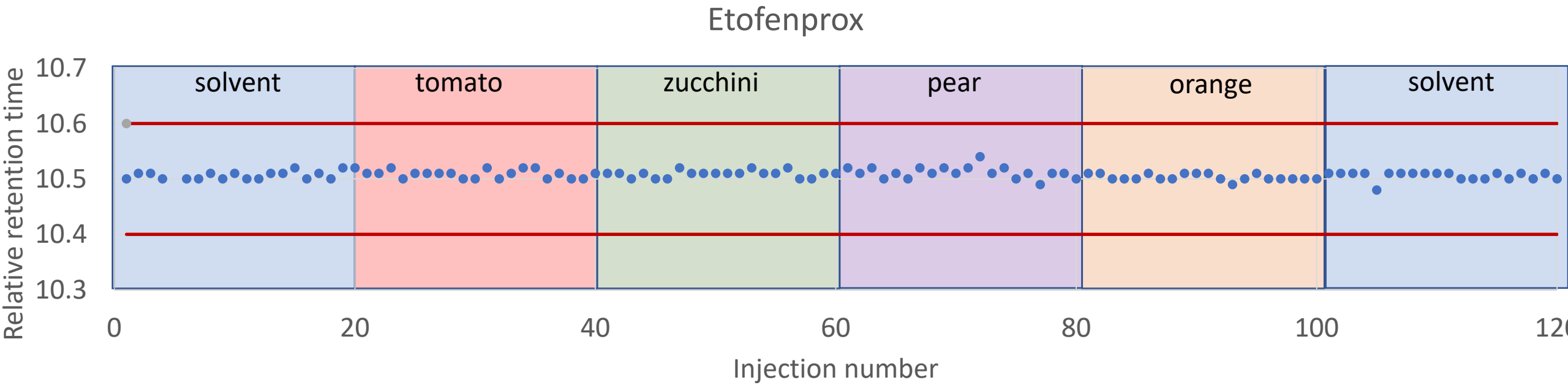
Retention time stability (kresoxim-methyl)



The red lines mark ± 0.1 min

120 injections alternating on column 1 & column 2

Retention time stability (Etofenprox)

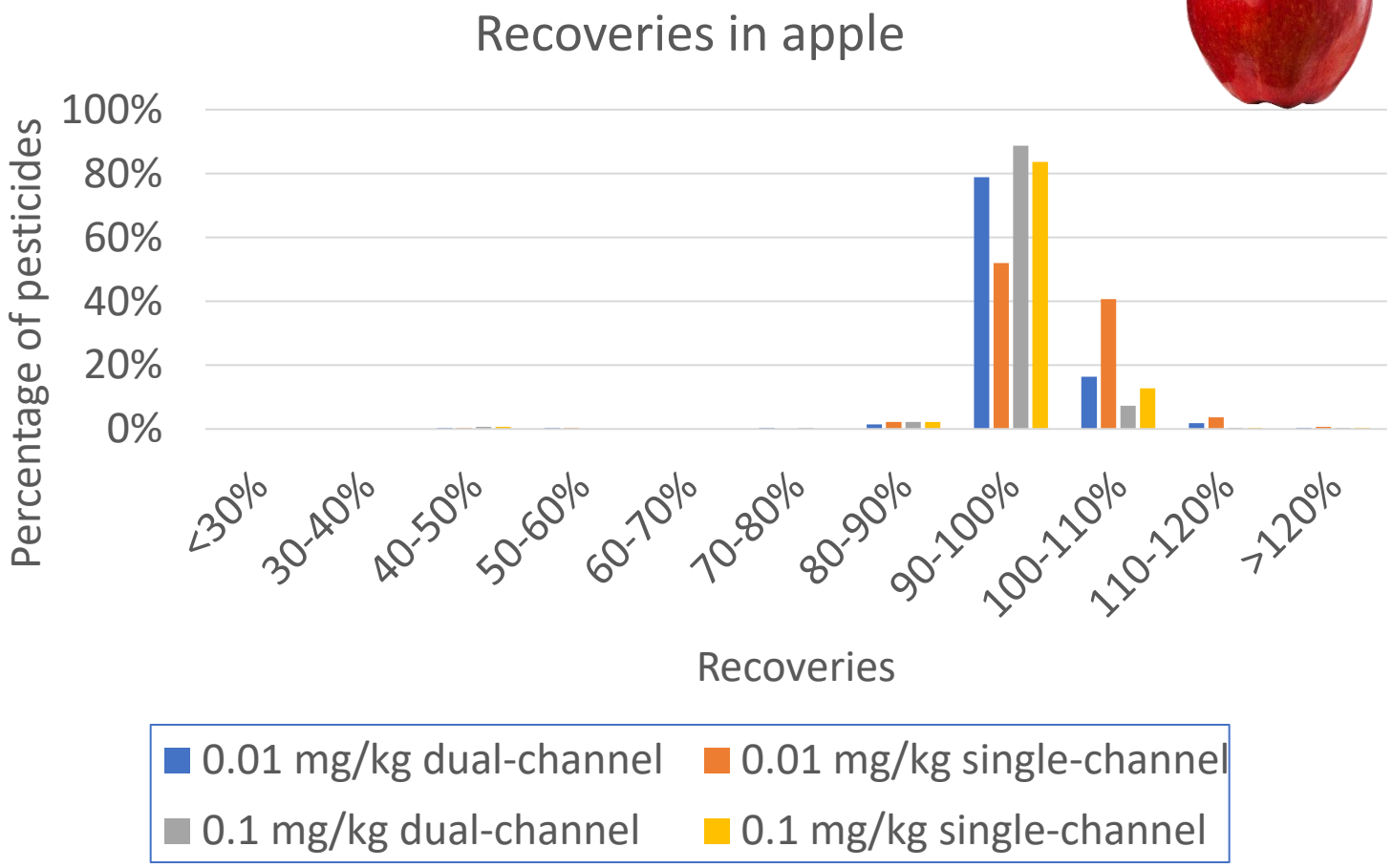


The red lines mark ± 0.1 min

120 injections alternating on column 1 & column 2

Recovery data (apple): single-channel vs dual-channel

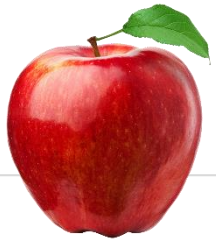
	<70%	70-120%	>120%
Single channel 0.01 mg/kg	2	269	2
Dual channel 0.01 mg/kg	2	270	1
Single channel 0.1 mg/kg	2	270	1
Dual channel 0.1 mg/kg	2	270	1



Number of compounds: 273

Repeatability data (apple): single-channel vs dual-channel

	<5%	5-20%	>20%
Single channel 0.01 mg/kg	87%	13%	-
Dual channel 0.01 mg/kg	88%	12%	-
Single channel 0.1 mg/kg	98%	2%	-
Dual channel 0.1 mg/kg	98%	2%	-



Number of compounds: 273

Recovery data (bell pepper): single-channel vs dual-channel

	<70%	70-120%	>120%
Single channel 0.01 mg/kg	2	271	-
Dual channel 0.01 mg/kg	2	271	-
Single channel 0.1 mg/kg	2	271	-
Dual channel 0.1 mg/kg	2	271	-

Number of compounds: 273

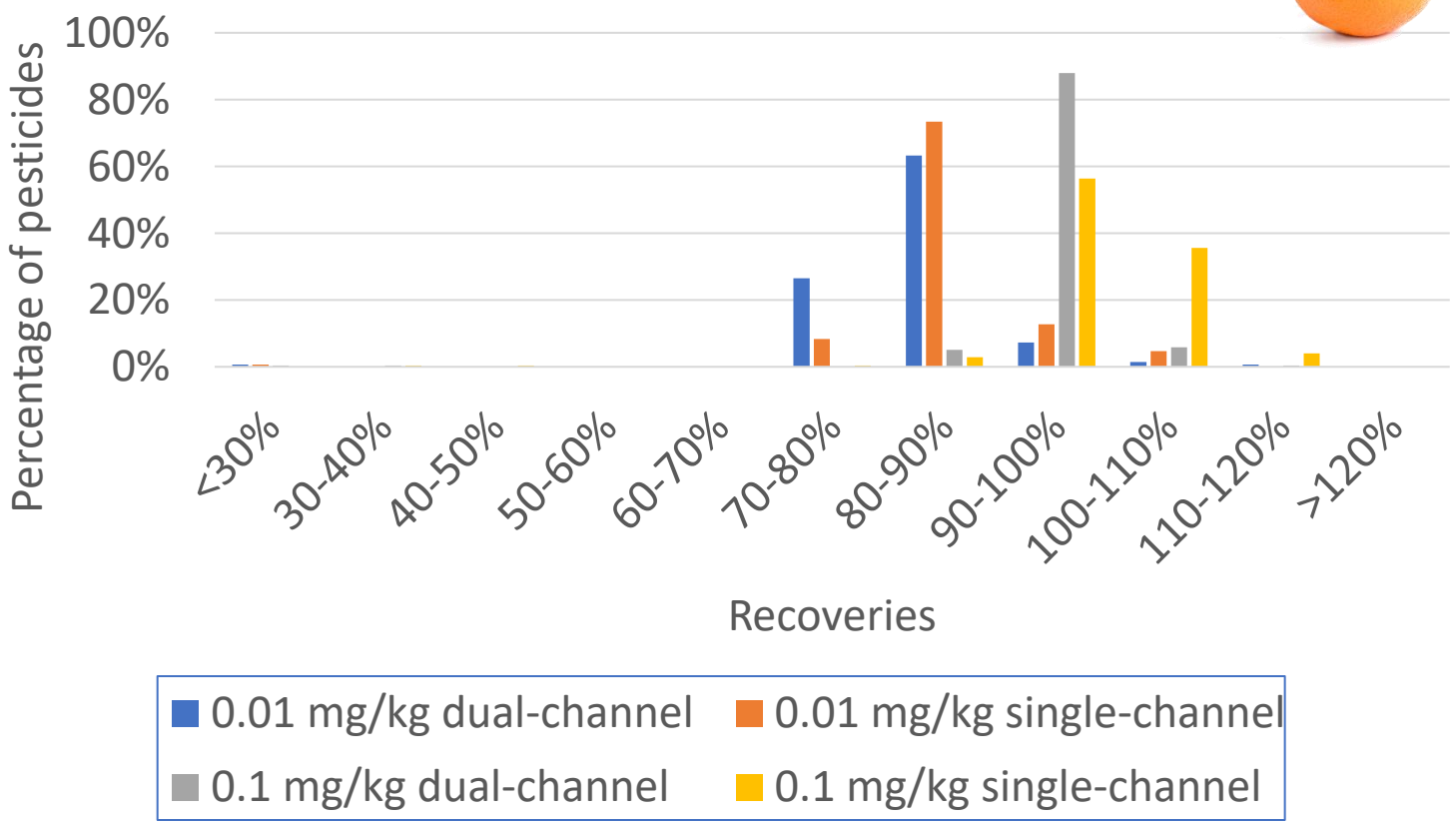
Repeatability data (bell pepper): single-channel vs dual-channel

	<5%	5-20%	>20%
Single channel 0.01 mg/kg	89%	11%	-
Dual channel 0.01 mg/kg	91%	9%	-
Single channel 0.1 mg/kg	98%	2%	-
Dual channel 0.1 mg/kg	98%	2%	-

Number of compounds: 273

Recovery data (orange): single-channel vs dual-channel

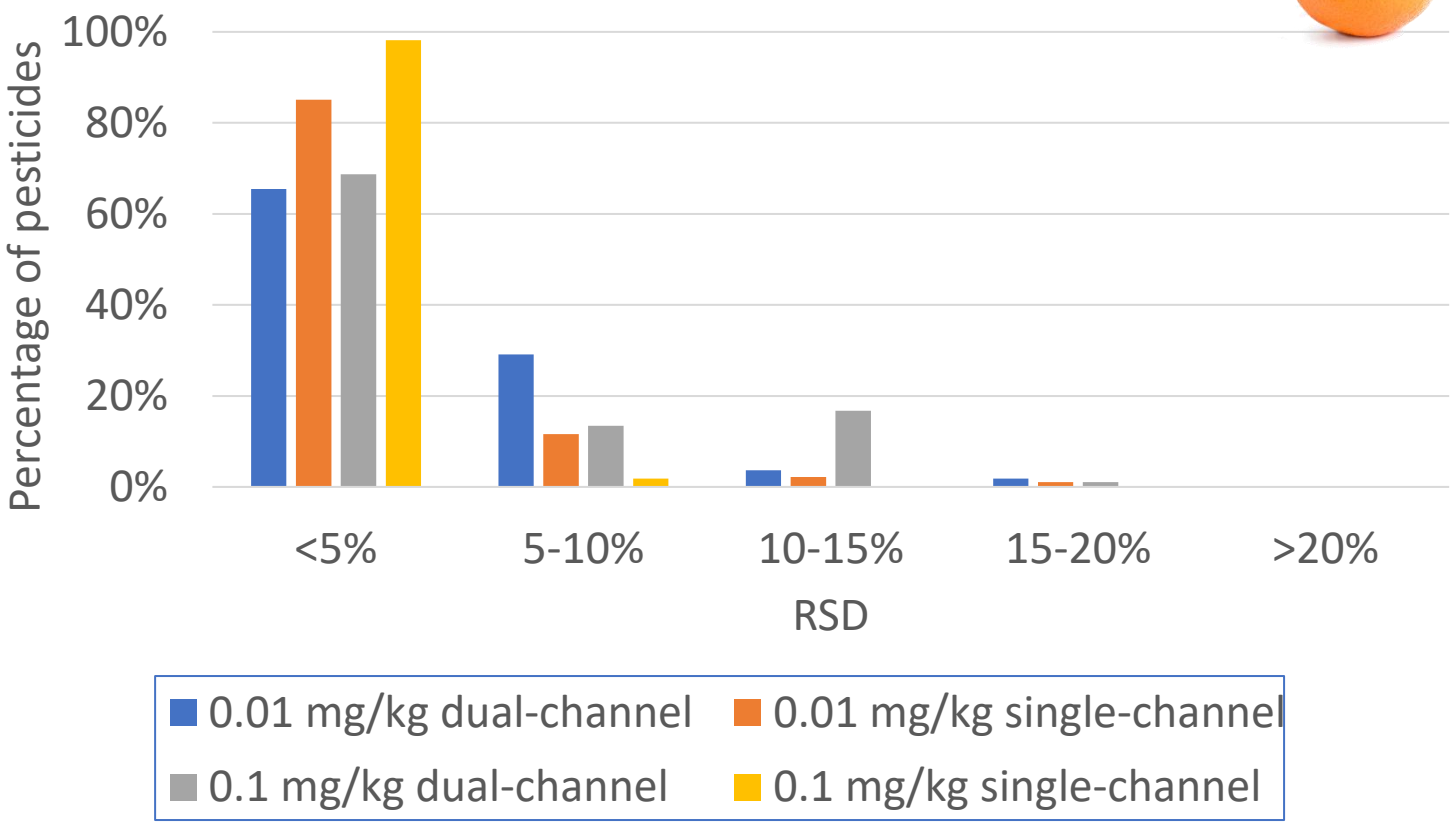
	<70%	70-120%	>120%
Single channel 0.01 mg/kg	2	271	-
Dual channel 0.01 mg/kg	2	271	-
Single channel 0.1 mg/kg	2	271	-
Dual channel 0.1 mg/kg	2	271	-



Number of compounds: 273

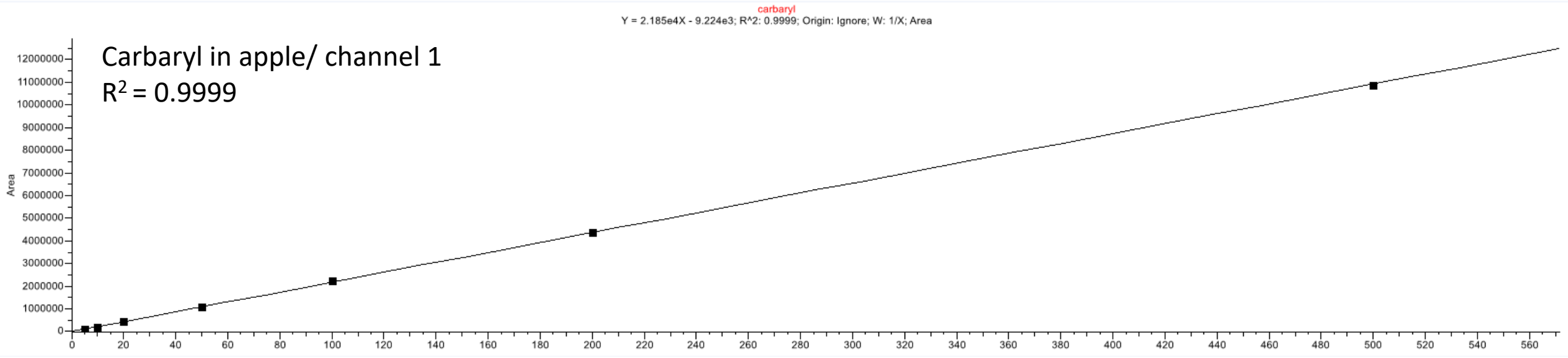
Repeatability data (orange): single-channel vs dual-channel

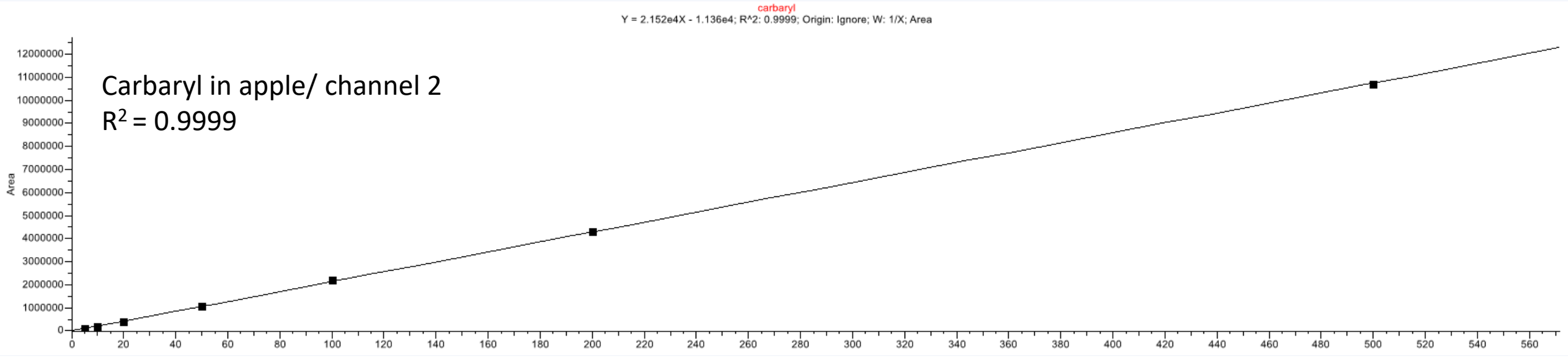
	<5%	5-20%	>20%
Single channel 0.01 mg/kg	85%	15%	-
Dual channel 0.01 mg/kg	65%	35%	-
Single channel 0.1 mg/kg	98%	2%	-
Dual channel 0.1 mg/kg	69%	31%	-



Number of compound: 273

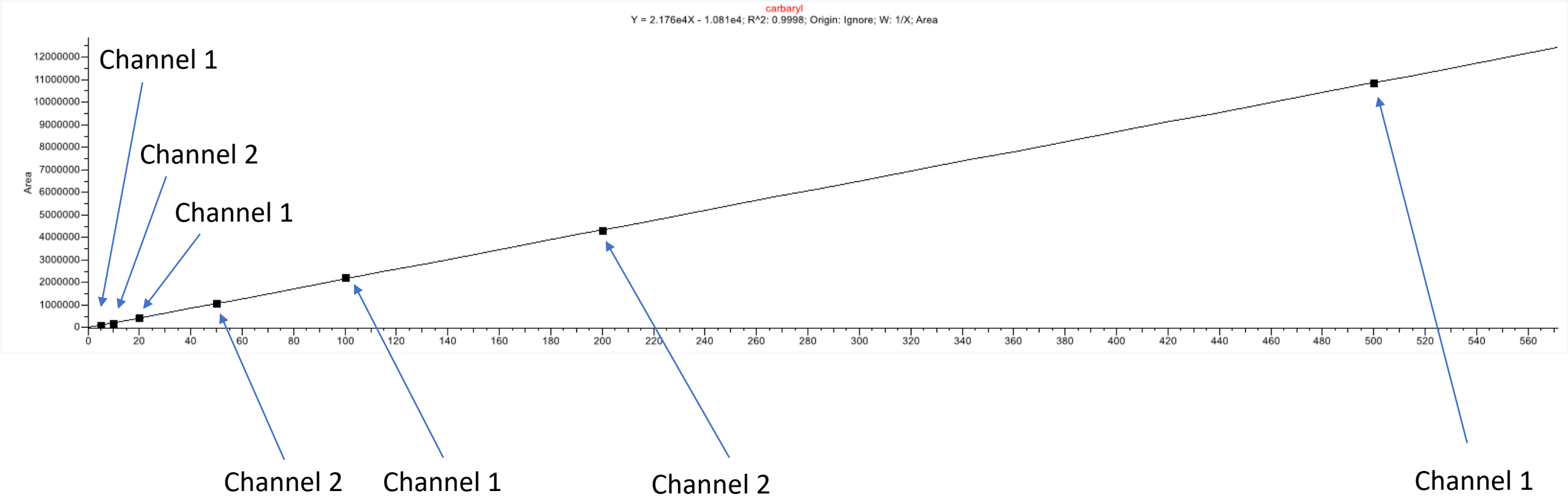
Single-channel calibration for carbaryl in apple

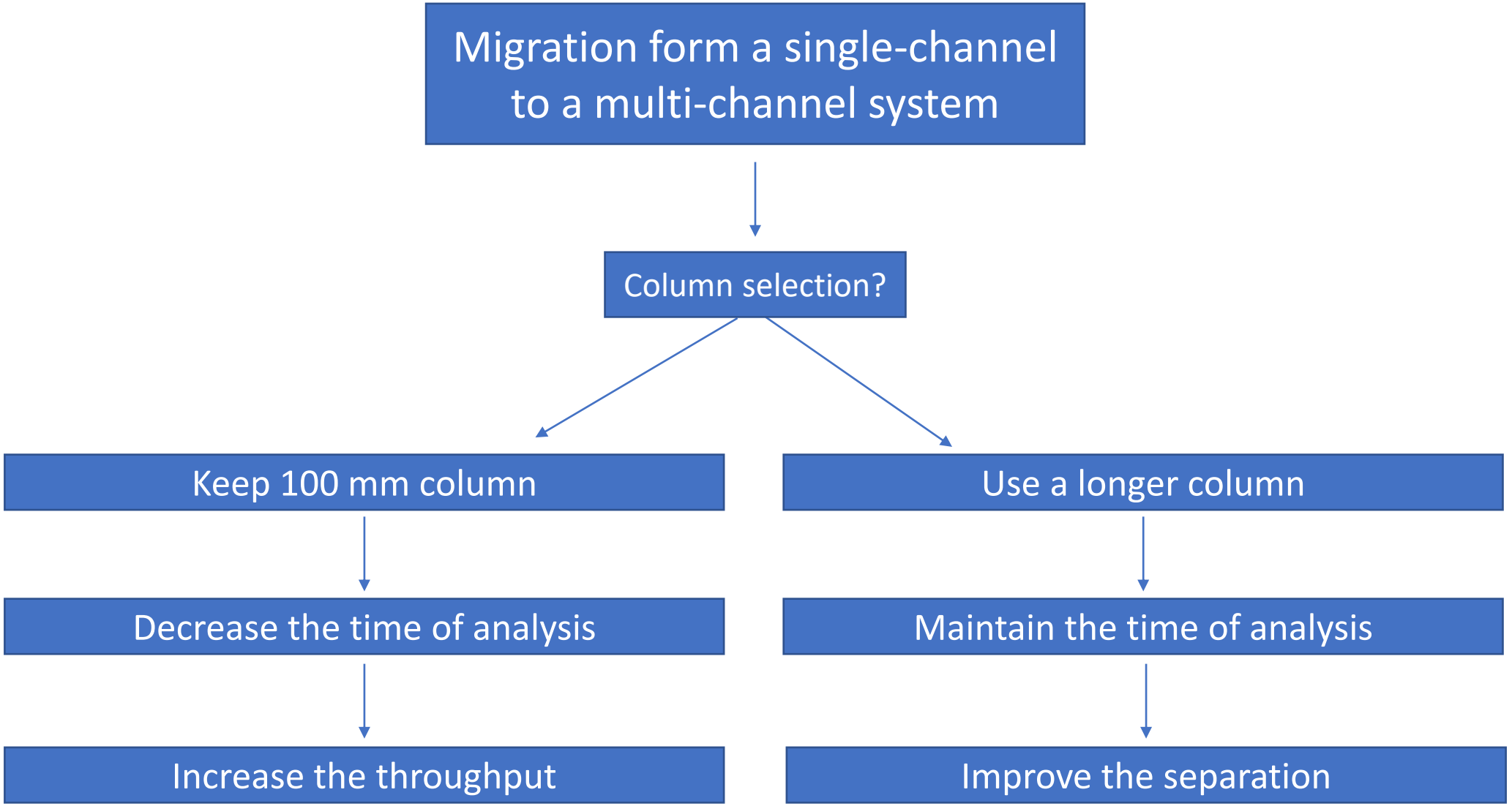




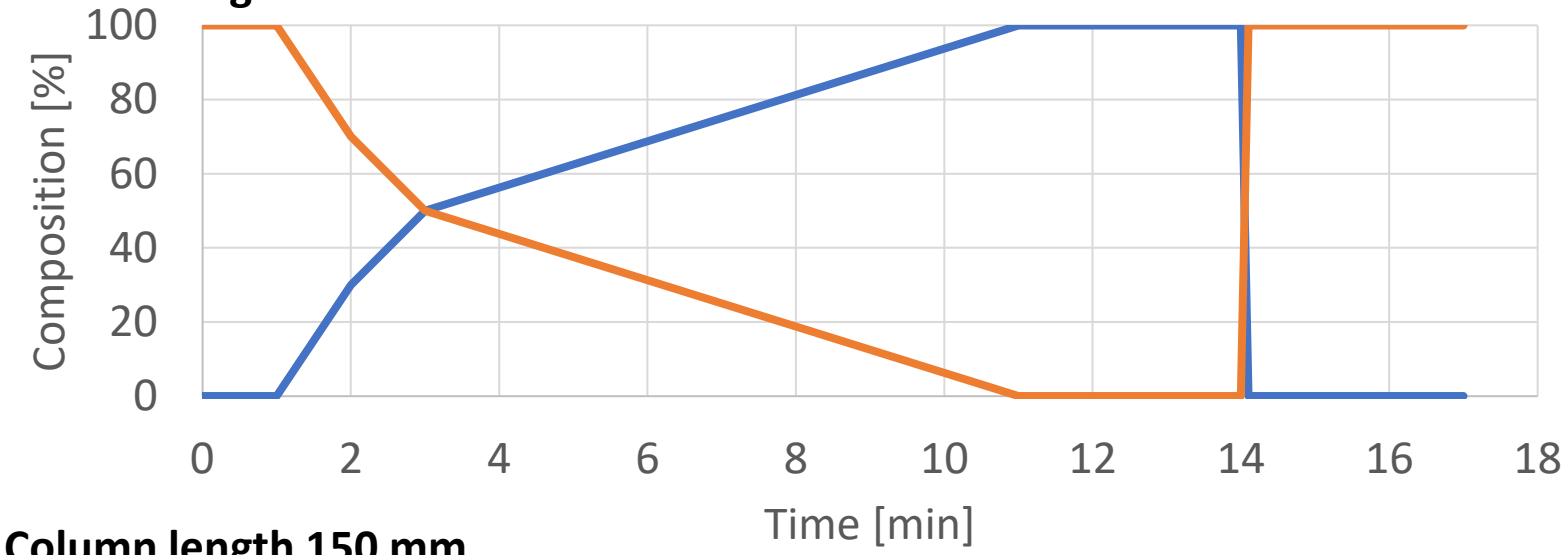
Cross-channel calibration for carbaryl in apple

Carbaryl in apple/ **cross-channel**
$R^2 = 0.9998$

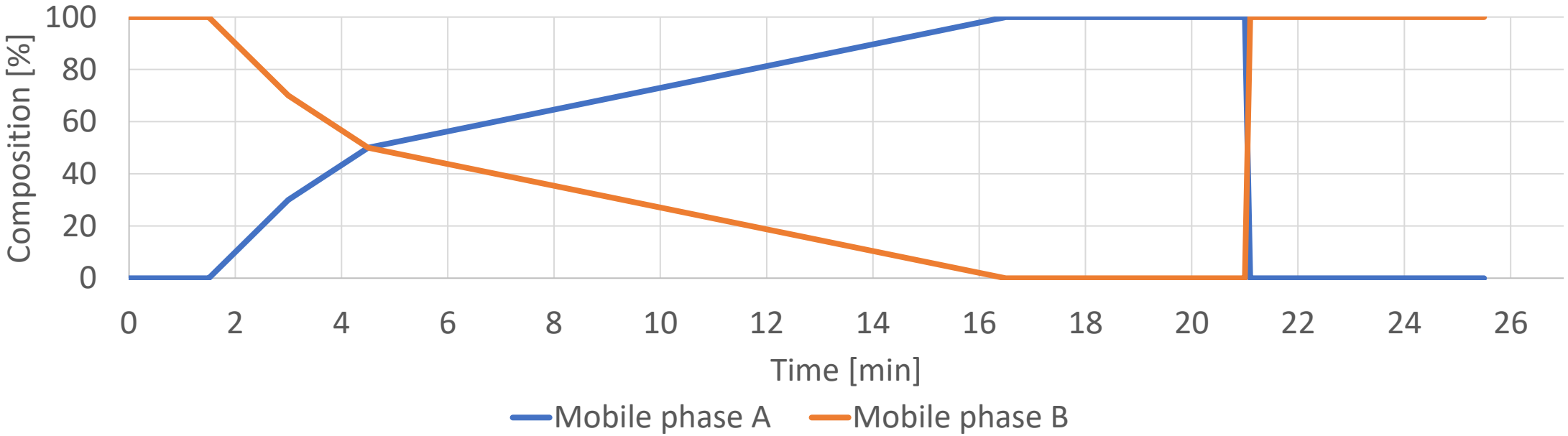



Migration form a single-channel to a multi-channel system
Column selection?
Keep 100 mm column
Use a longer column
Decrease the time of analysis
Maintain the time of analysis
Increase the throughput
Improve the separation

Column lenghth 100 mm

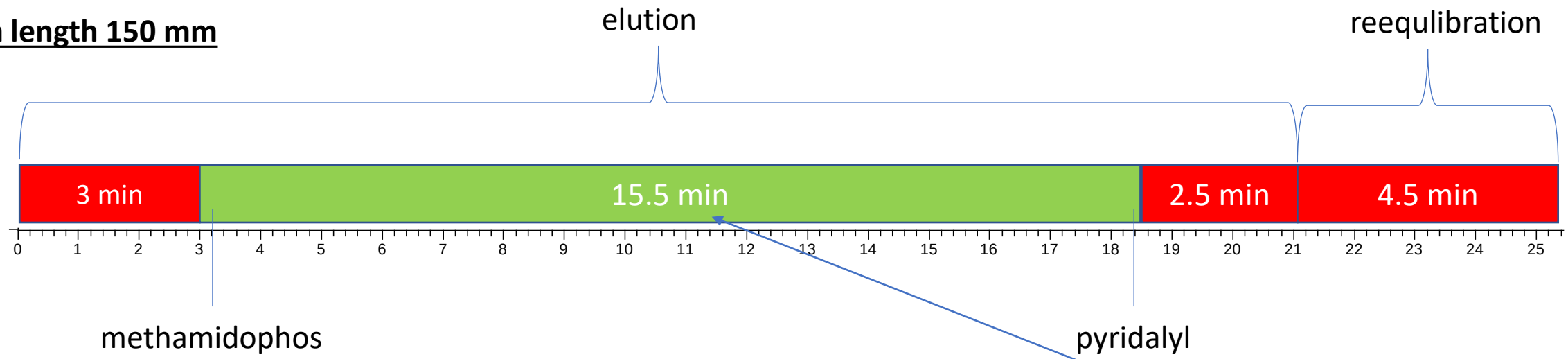


Column length 150 mm



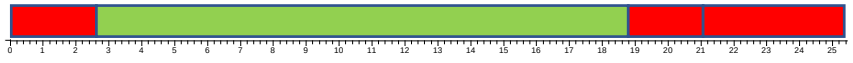
Time segments in dual-channel chromatography

Column length 150 mm

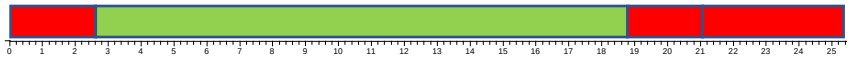


Less than the 100 mm column in a single-channel system!

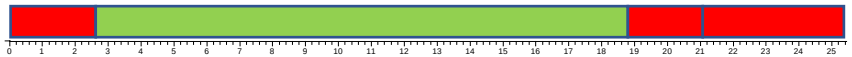
Channel 1



Channel 2



Channel 1

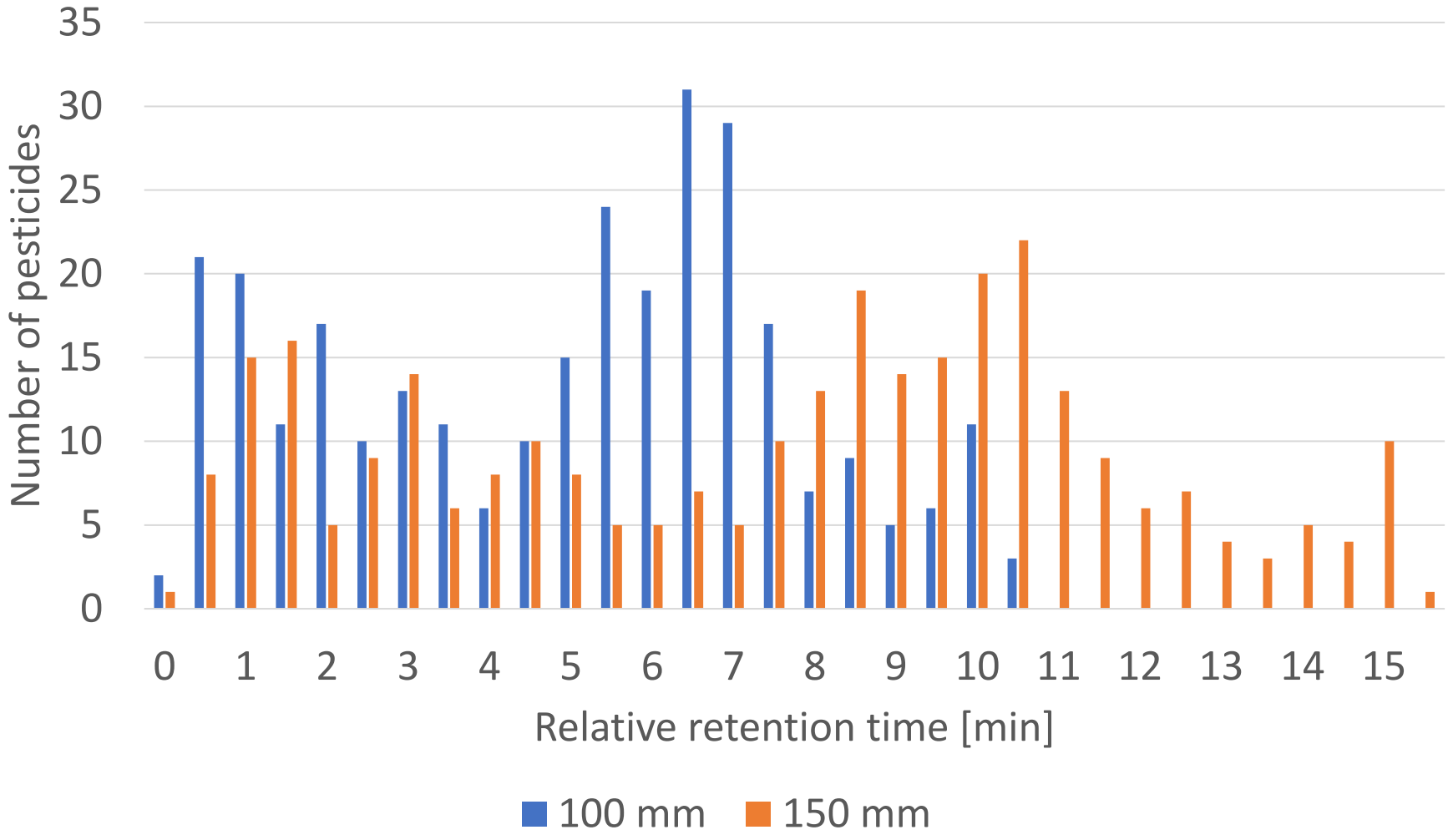


to waste

to MS (**acquisition time 15.5 min**)

Total time in a single-channel system 25.5 min
(+ 1 minute for needle wash, sample aspiration, etc.)

Distribution of pesticides



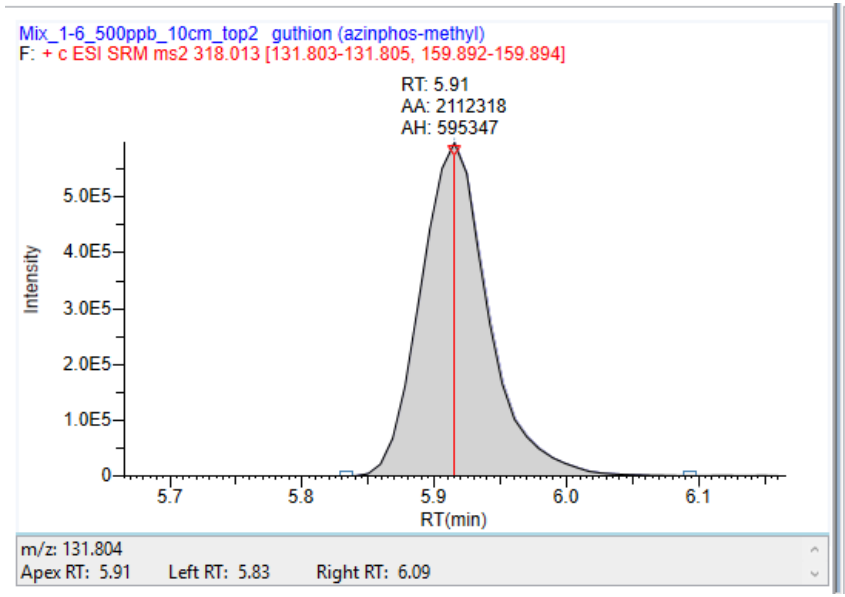
Co-elution of analytes with a 100 mm column and QQQ MS

Triple quadrupole

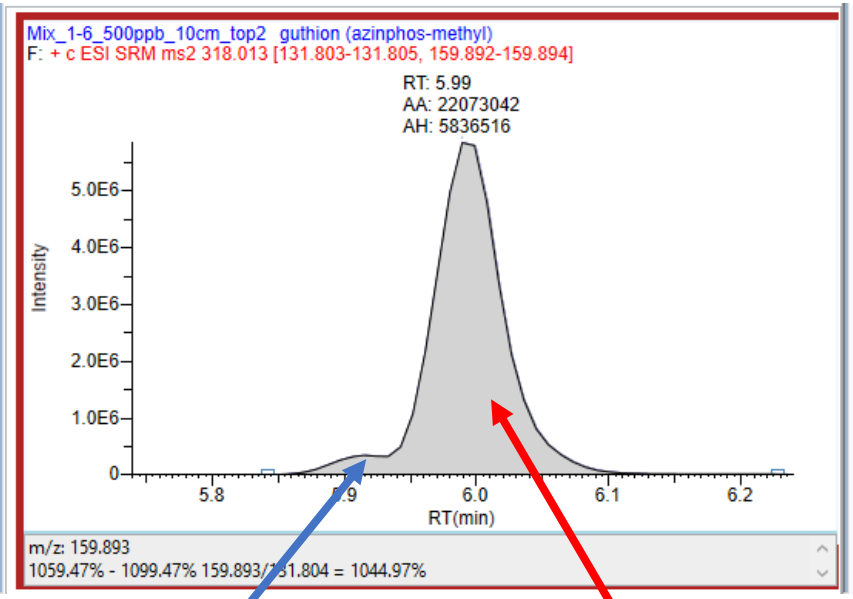
100 mm column

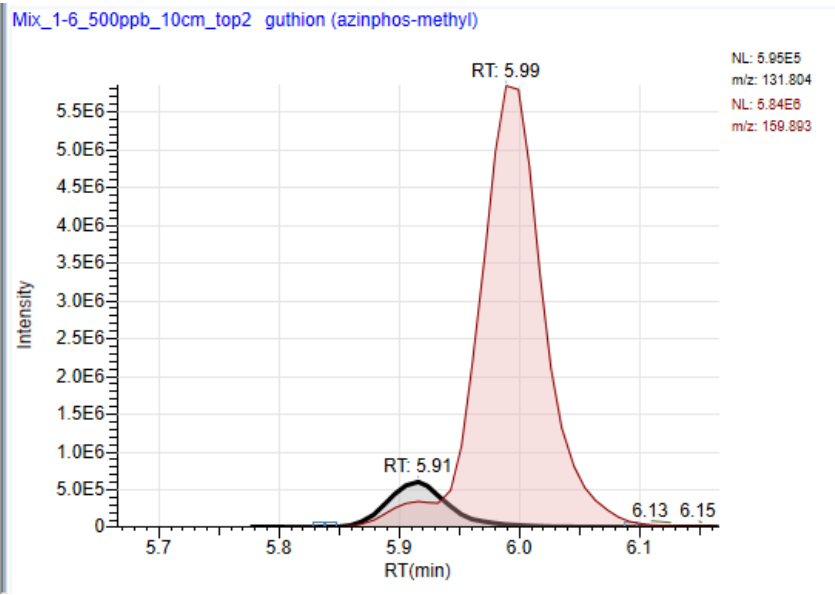
Azinphos methyl

***m/z* 318 -> 132**



***m/z* 318 -> 159**





Azinphos methyl **Interfering transition of phosmet**

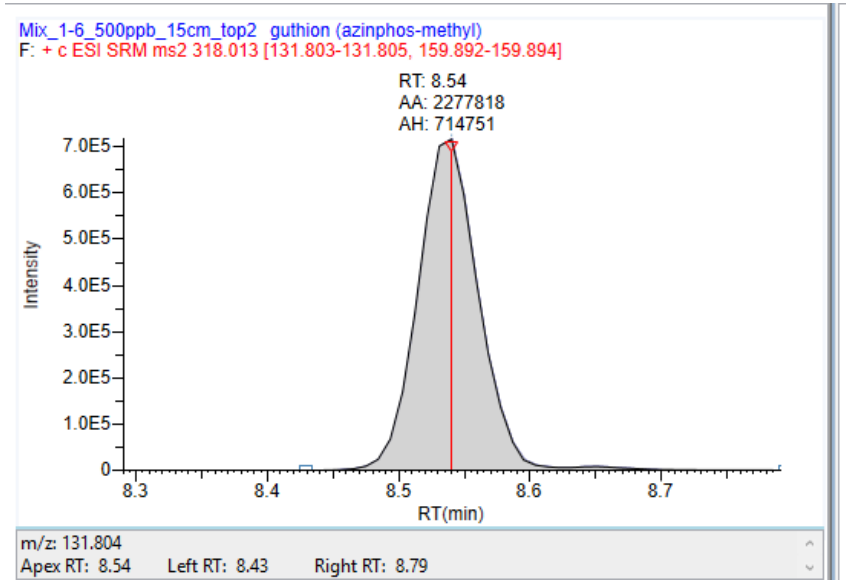
Using a longer column to resolve co-elution in QQQ MS

Triple quadrupole

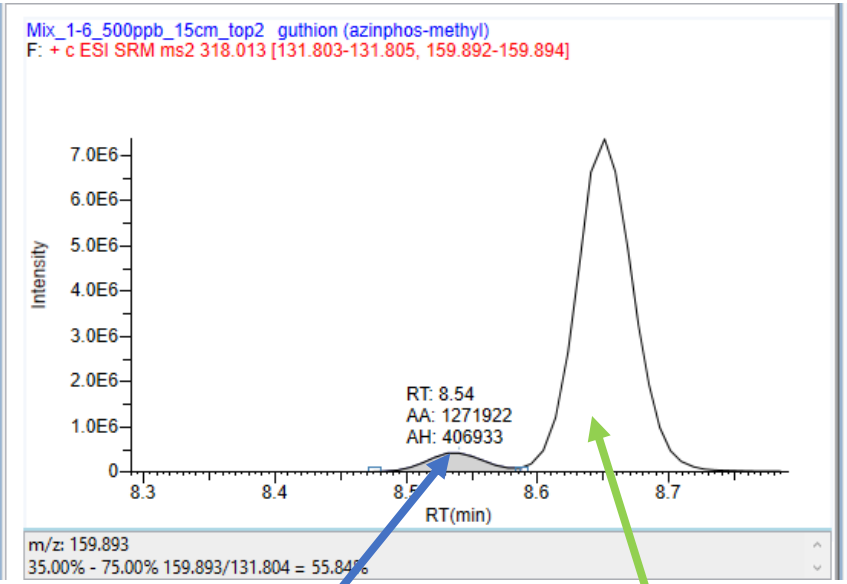
<u>150 mm column</u>

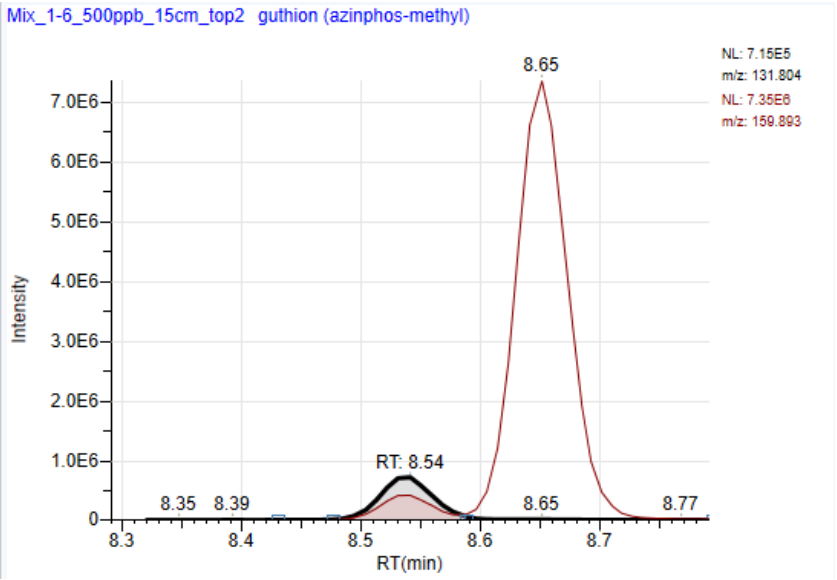
Azinphos methyl

***m/z* 318 -> 132**



***m/z* 318 -> 159**





Azinphos methyl

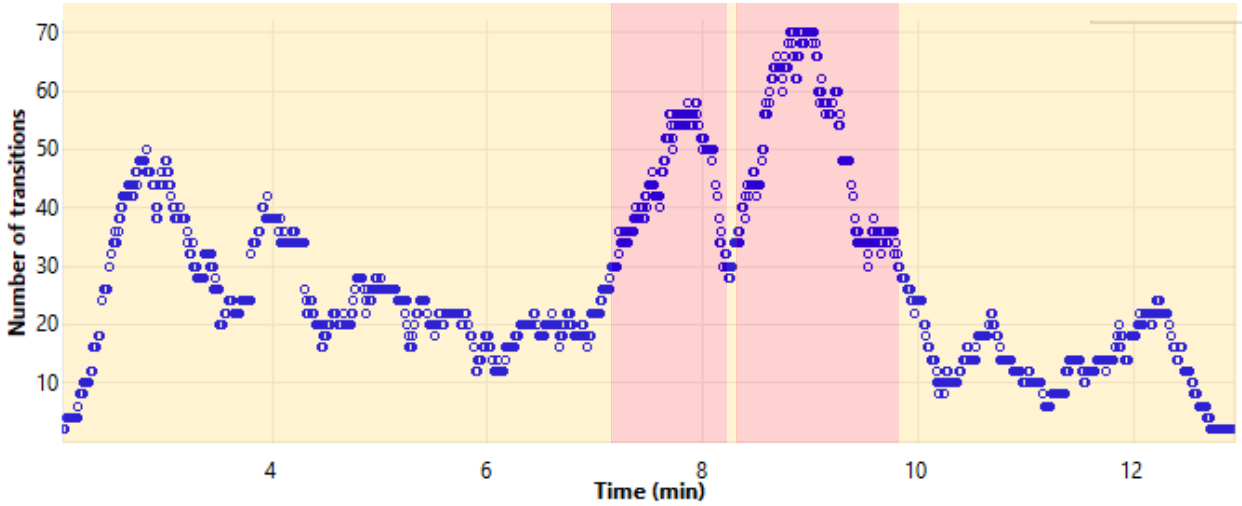
Phosmet is separated form azinphos methyl

Use of a longer column can increase the sensitivity of QQQ MS

300 pesticides / 600 transitions

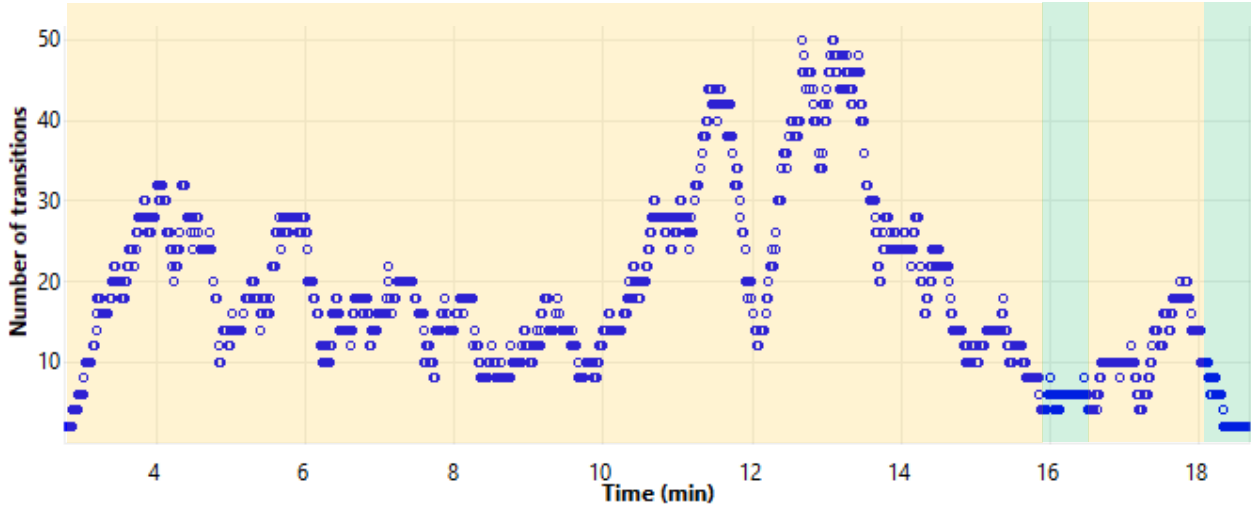
100 mm column

Number of transitions per cycle



150 mm column

Number of transitions per cycle



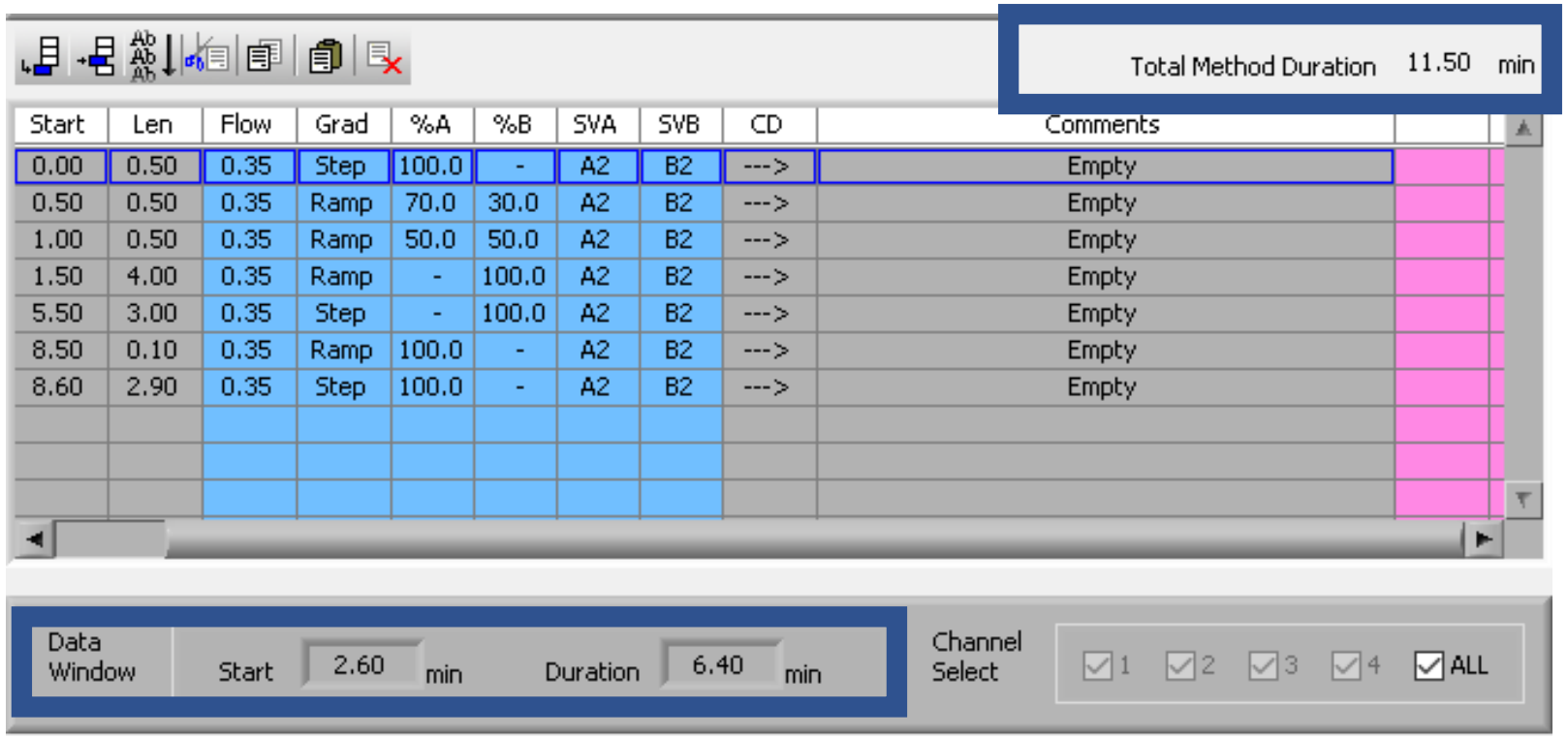
Dwell time < 10 ms

Dwell time 10 – 50 ms

Dwell time > 50 ms

A longer column separates better the analytes. The dwell times can be increased without increasing the duty cycle.

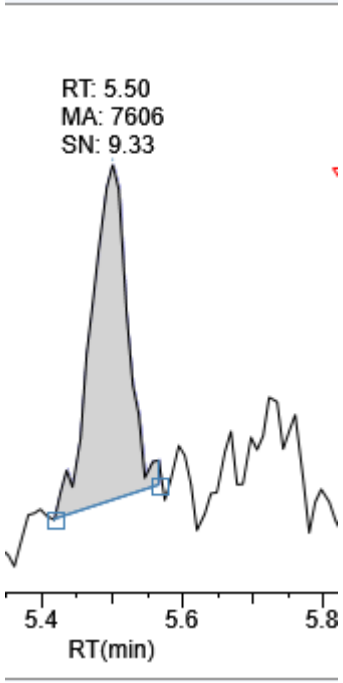
Special method for negative-polarity compounds



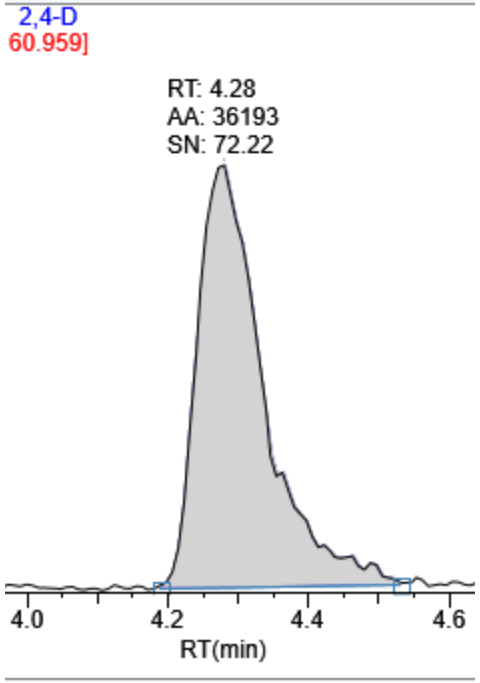
Mobile phase A: water/0.05% acetic acid
Mobile phase B: acetonitrile/0.05% acetic acid

Special method for negative-polarity compounds

2,4-D



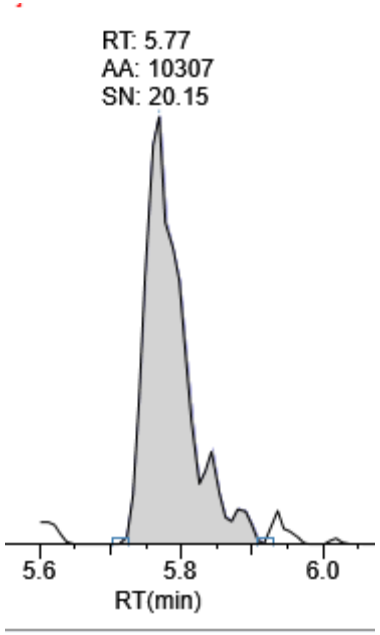
Current method/all pesticides
MeOH/H2O/formic acid/ammonium formate
Peak area 7 606



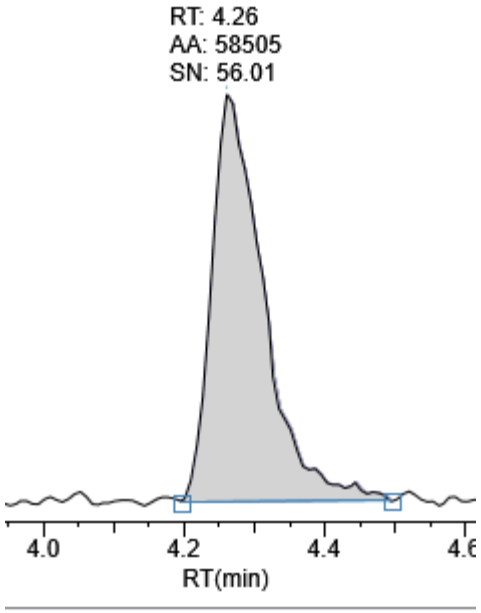
Only negative polarity pesticides
ANC/H2O/0.05% acetic acid
Peak area 36 193

Special method for negative-polarity compounds

MCPA



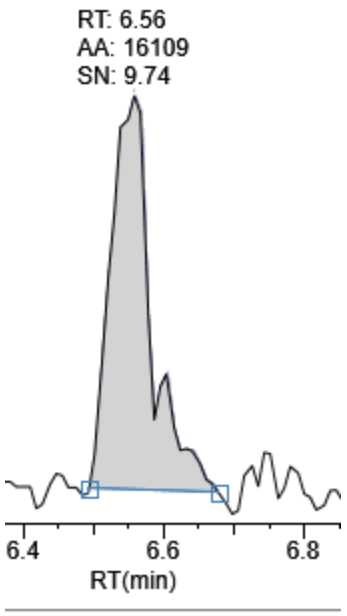
Current method/all pesticides
MeOH/H2O/formic acid/ammonium formate
Peak area 10 307



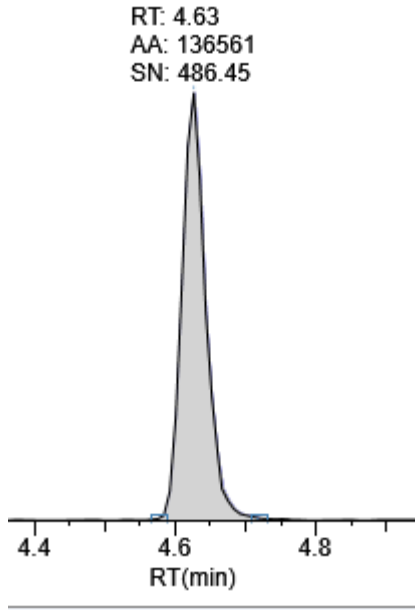
Only negative polarity pesticides
ANC/H2O/0.05% acetic acid
Peak area 58 505

Special method for negative-polarity compounds

Ethiprole



Current method/all pesticides
MeOH/H2O/formic acid/ammonium formate
Peak area 16 109



Only negative polarity pesticides
ANC/H2O/0.05% acetic acid
Peak area 136 561

Summary

- Multi-channel chromatpgraphy improves the utilisation of the mass spectrometer
  - 100 mm columns increase the sample throughput
  - 150 mm columns enhance sensitivity and selectivity

- Dual-channel mode provides results equivalent to single-channel mode
- Retention times in the dual-channel system are very stable
- Conversion of a single-channel chromatographic method into a dual-channel method is fast and simple
- Software is user-friendly and reliable

Łukasz Rajski; Florencia Jesús; Francisco José Díaz Galiano; Amadeo R. Fernández-Alba
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Journal of Chromatography A 1633 (2020) 461614
https://doi.org/10.1016/j.chroma.2020.461614

http://www.eurl-pesticides.eu

Thank You for Your Attention

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