

Automatisation and miniaturization In Pesticide Residue Analysis

USE OF HYDROGEN AS A CARRIER GAS IN GC- MS/MS.

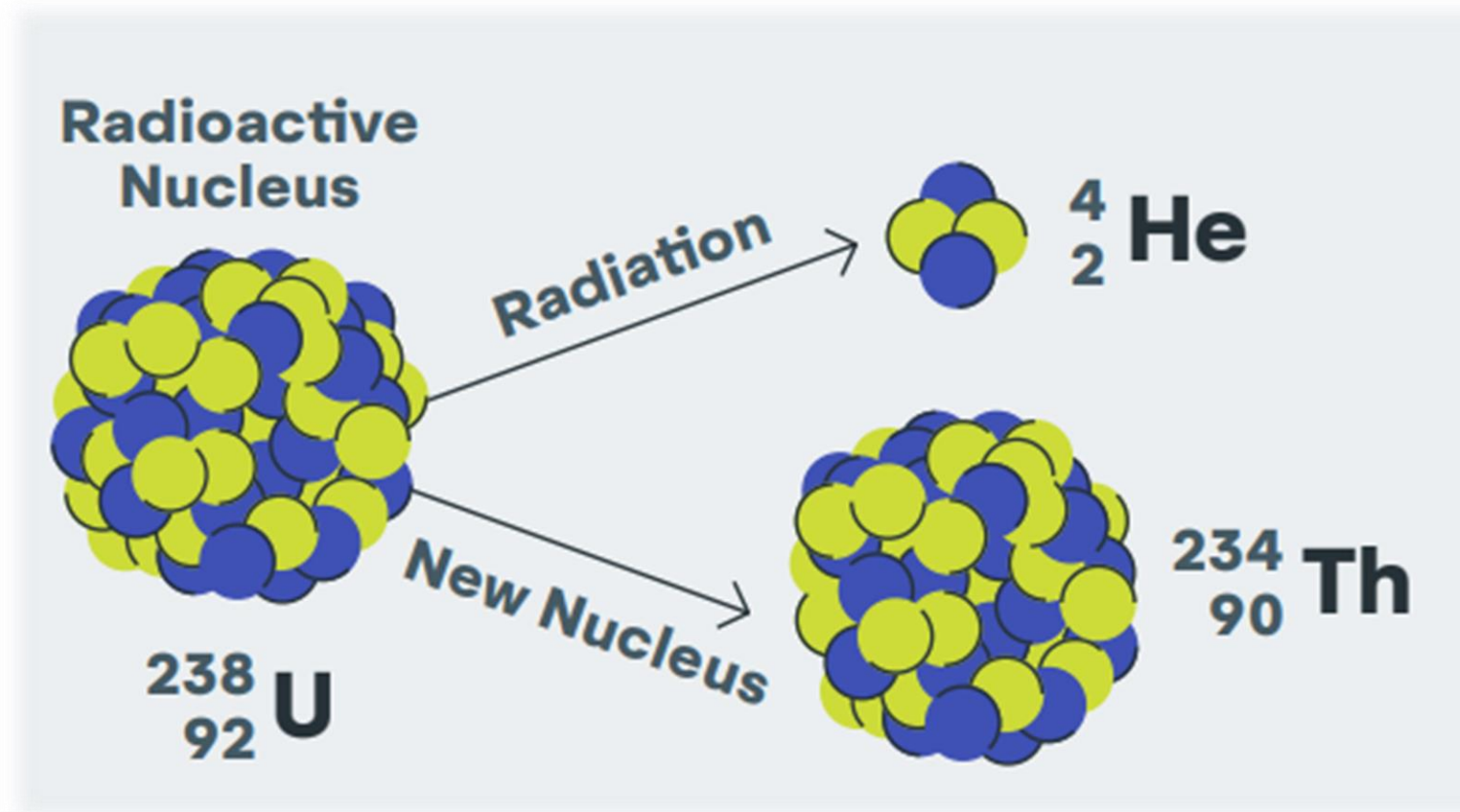
VÍCTOR MANUEL CUTILLAS JUÁREZ
UAL



PESTICIDES IN FRUITS
AND VEGETABLES

01/10/2024 - ALMERÍA

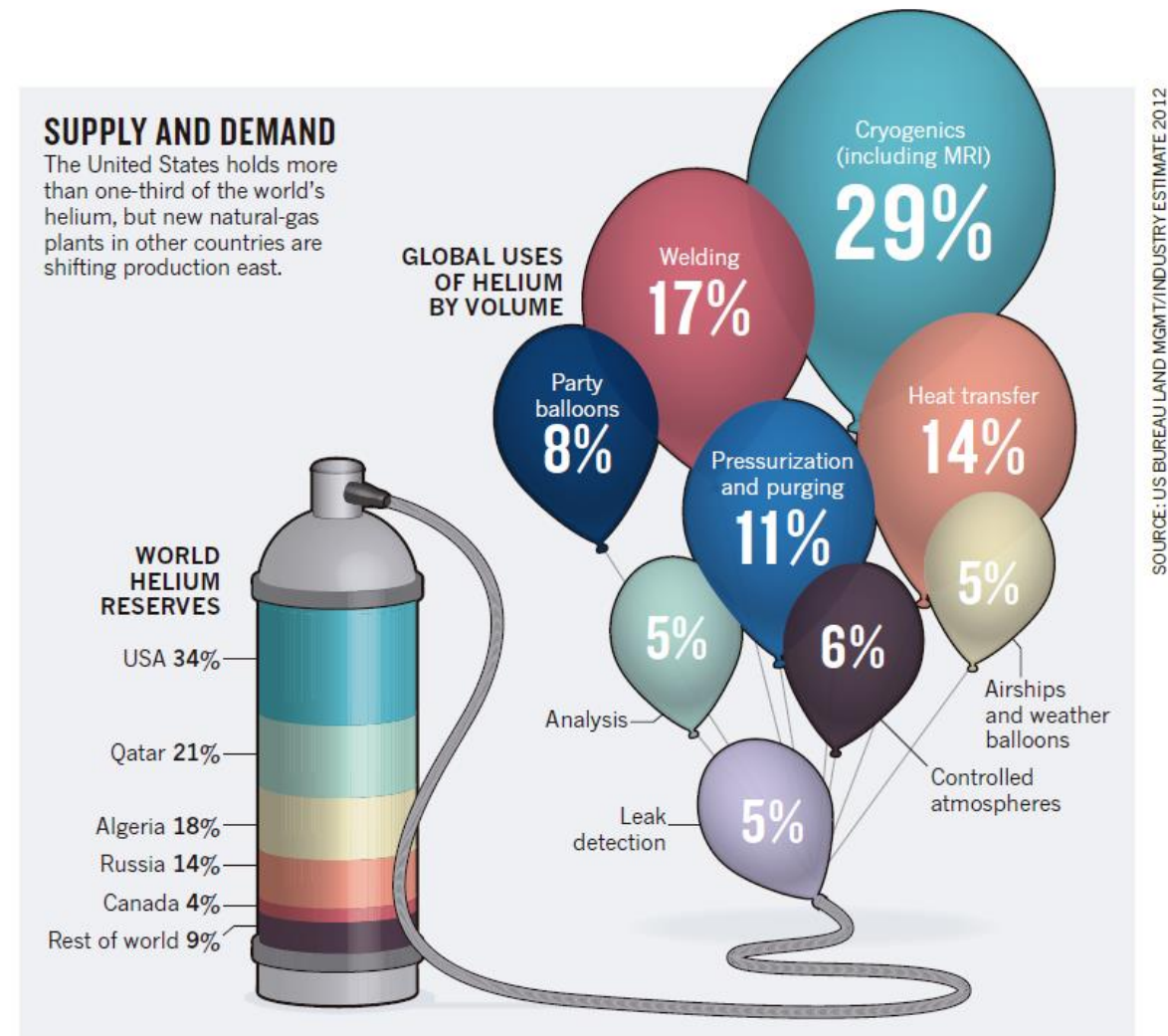
The majority of helium originates from the radioactive decay of uranium and thorium. This gas is located under the Earth's crust, alongside other natural gases. When the helium concentration surpasses 0.3%, it is commercially extracted from natural gas.



Helium – A gas facing extinction. ACS Green Chemistry institute

Helium shortage

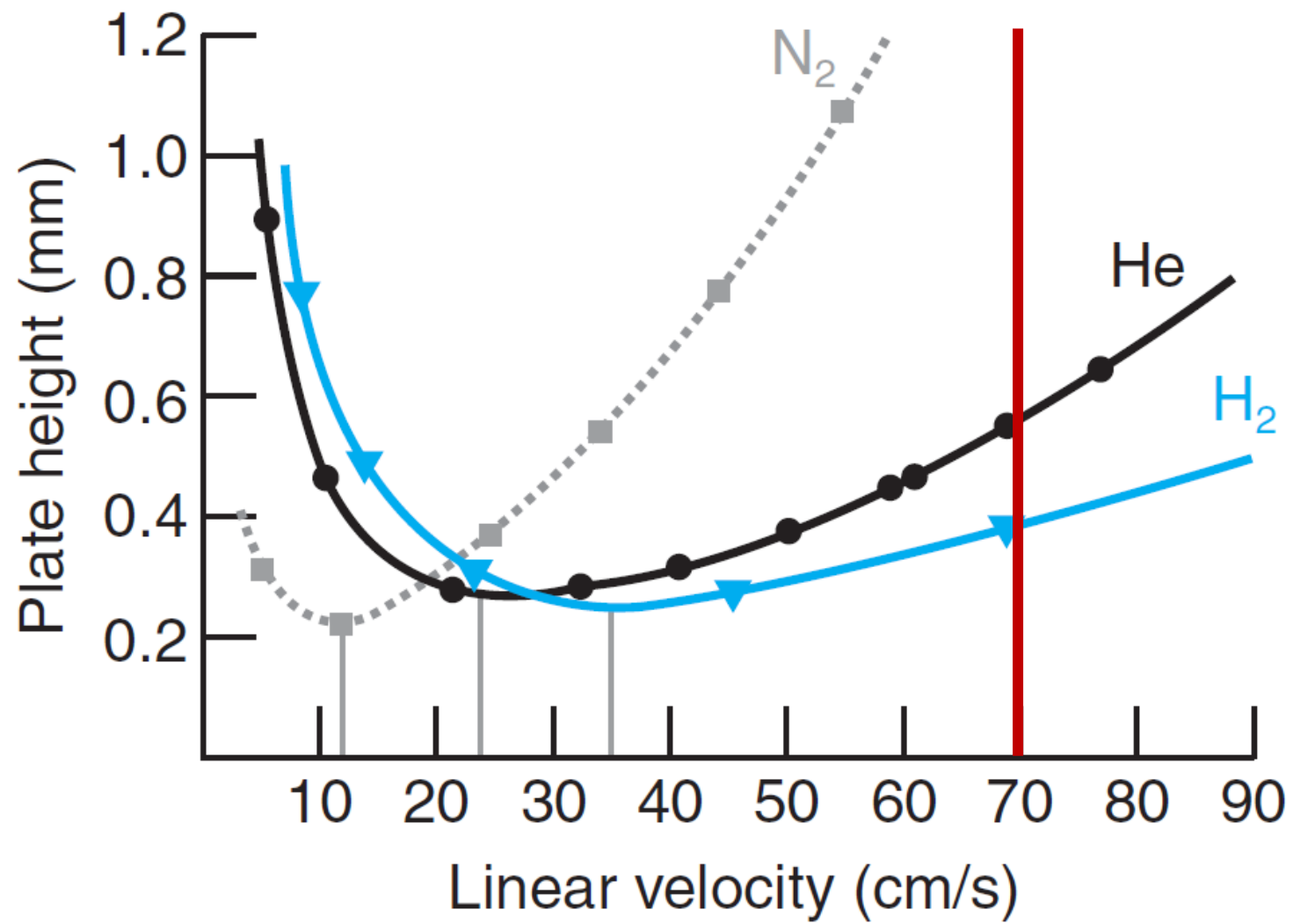
Nuttall, W. J.; Clarke, R. H.;
Glowacki, B. A. Stop
Squandering Helium. *Nature*
2012, 485 (7400), 573–575.



Hydrogen generator Precision Trace 250cc



- Suitable for flame gas and carrier gas at trace detection limits
- 99.9999% purity
- Internal leak detection with automatic shutdown features
- Proven PEM technology to generate hydrogen safely and reliably
- Regenerative PSA dryers to ensure highest level of purity
- Automatic loading pump as standard
- Maintenance limited to replacing de-ionizer cartridge
- Creates hydrogen on demand, minimal storage of hydrogen in the system
- Short and easy start-up and shutdown procedures



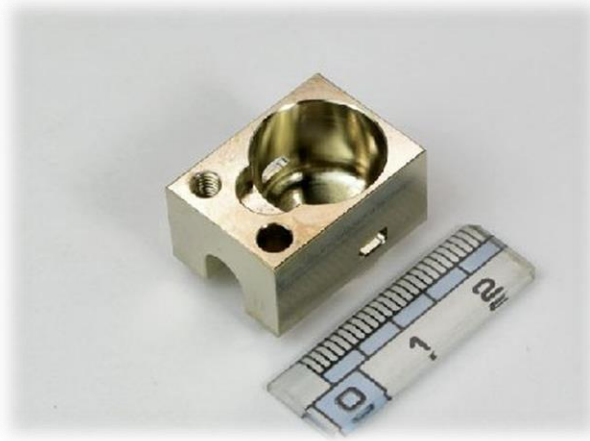
Quantitative Chemical Analysis, Daniel C. Harris, 8th Edition

	Helium	Nitrogen	Hydrogen
Diffusivity	+	-	++
Viscosity	-	-	+
Cost	--	+	+
Availability	--	+	+
Inertness	+	+	-
Others	For some detection techniques (e.g. BID) it is the only solution	Peak resolution worsens with increasing velocities	Cannot be used with some detectors, explosion risk (!)
Conclusion	Ideal carrier gas	Alternative to helium for easy to separate components	For many applications, good results and faster

Shimadzu solutions for helium shortage – Nerea Lorenzo Parodi

INERTNESS

Hydrogenation/dechlorination of some compounds



Vacuum performance



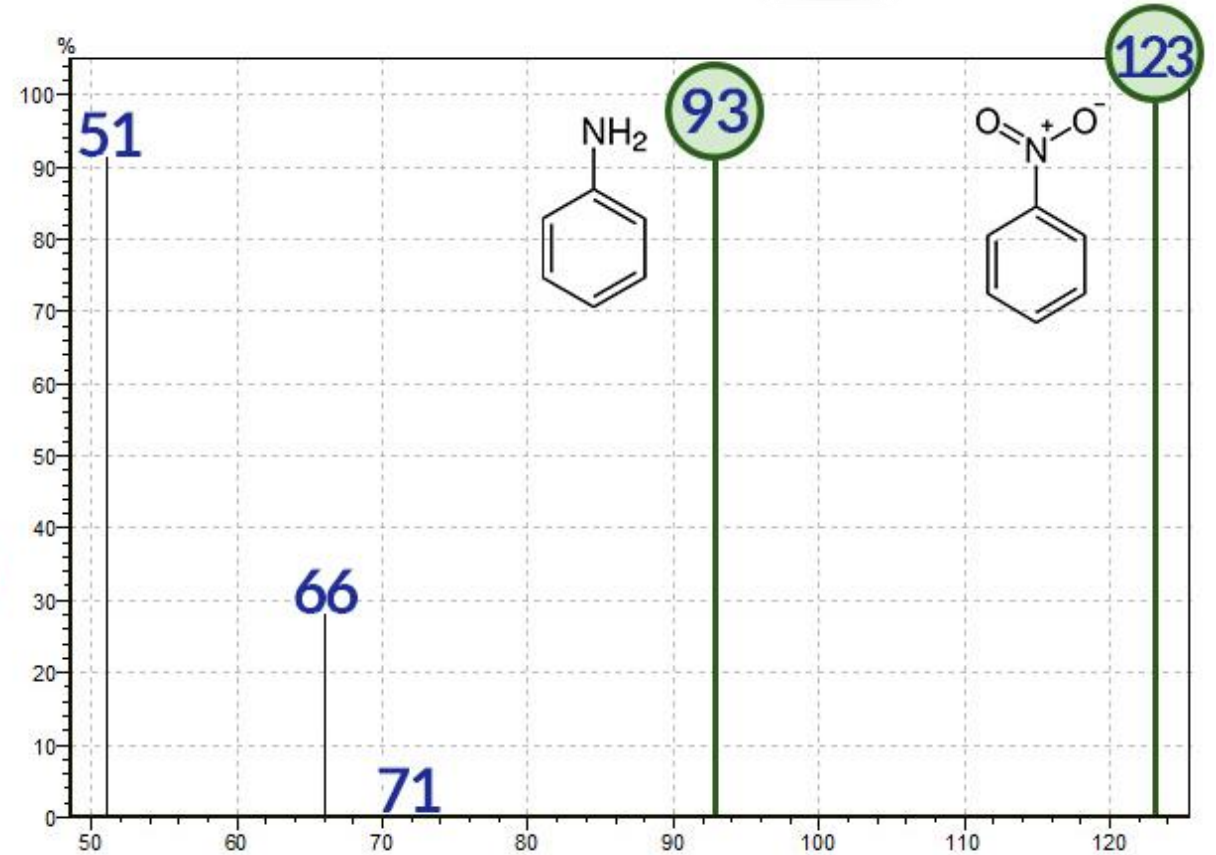
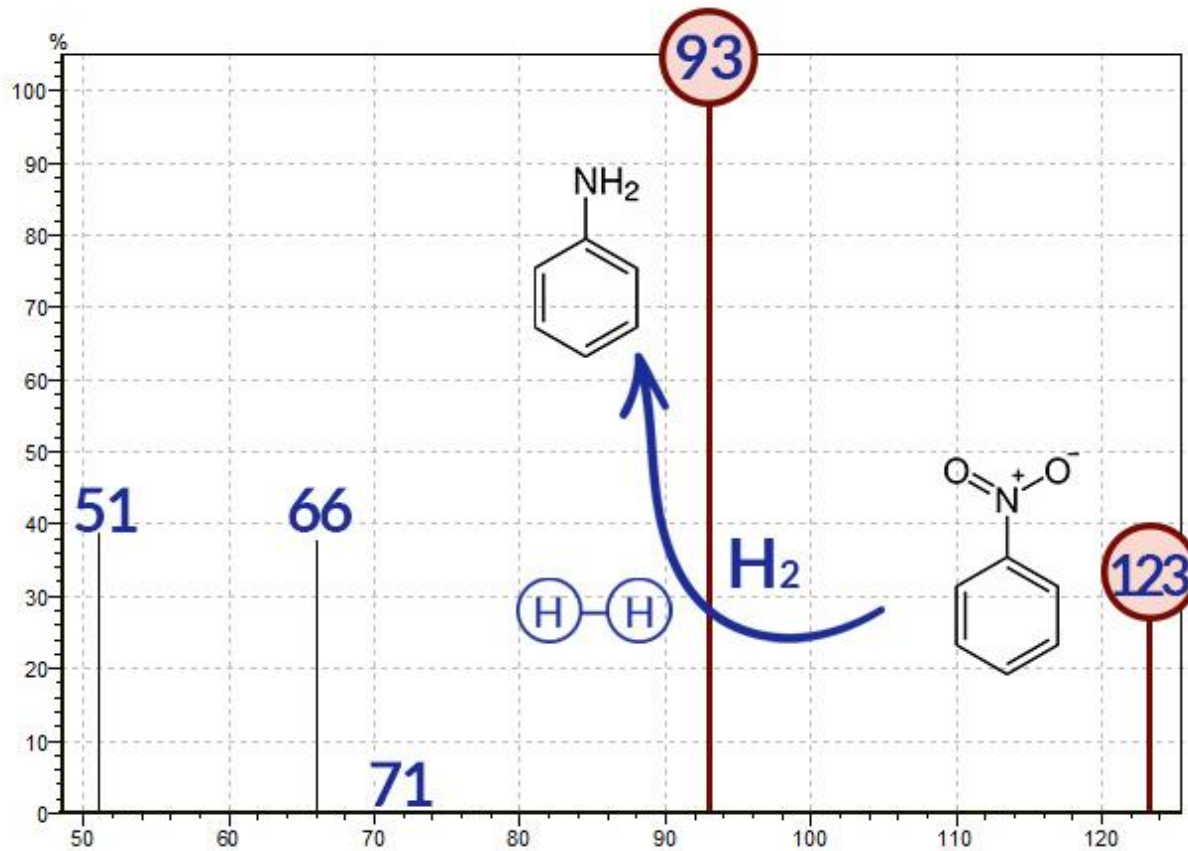
Use narrow-bore chromatographic columns (0.15-0.18 mm) and low carrier gas flow rates.



INERTNESS

NITROBENZENE TEST

1 ppm Nitrobenzene
standard

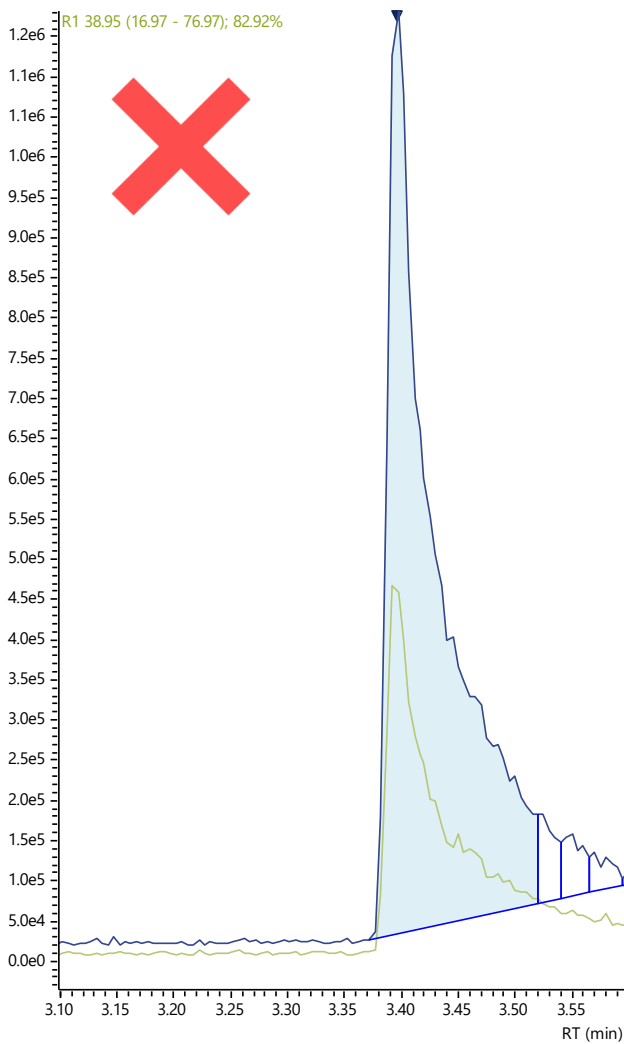


2-Phenylphenol HYDROGENATION

Q 170.10>141.10 (+)

1.18e6

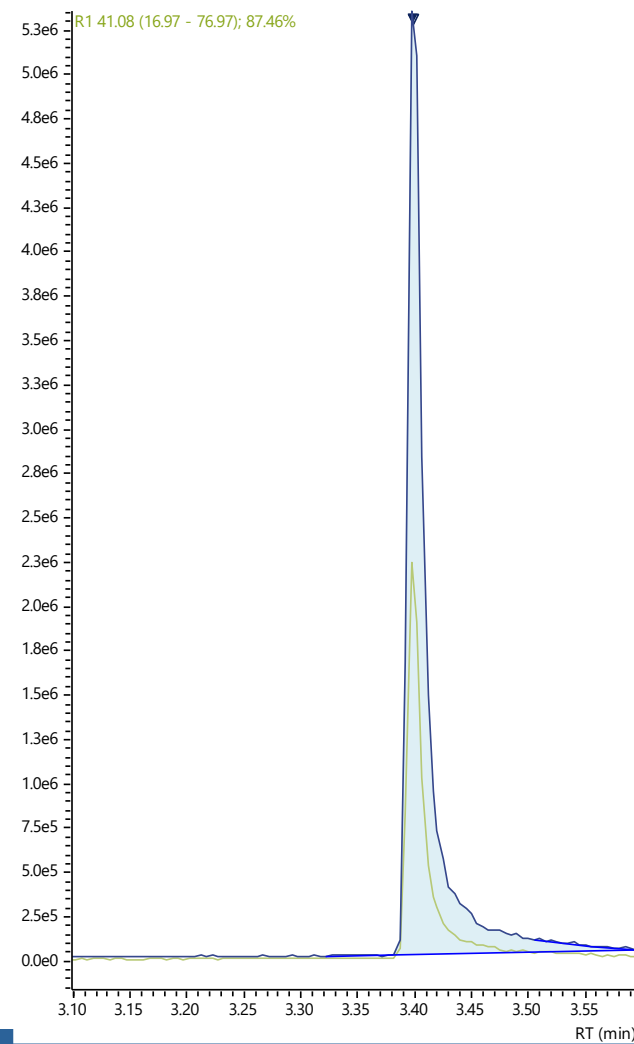
Q 170.10>141.10 (+)



2-Phenylphenol

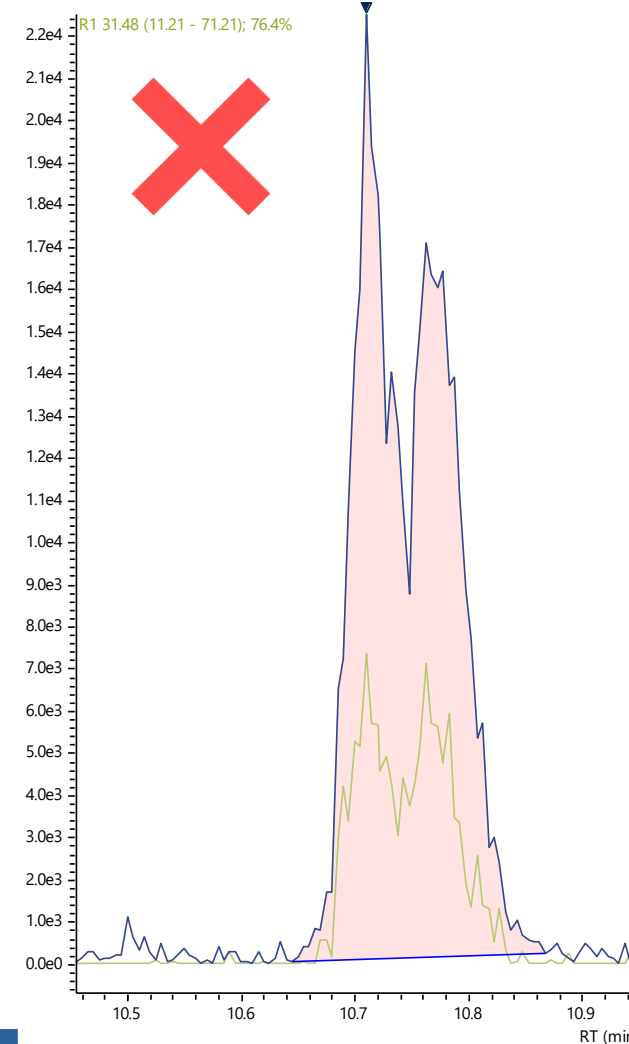
5.36e6

Q 170.10>141.10 (+)



Tau-Fluvalinate HYDROGENATION

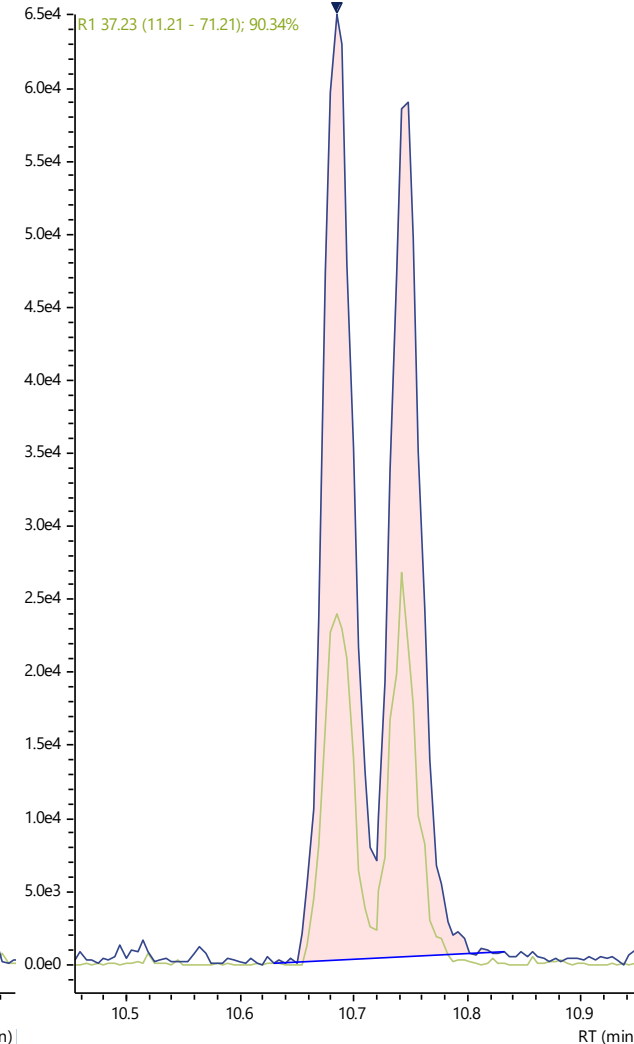
Q 250.10>55.00 (+)



Tau-Fluvalinate

2.25e4 Q 250.10>55.00 (+)

6.51e4



Hydrogen	
Dif	
	+
	l with ors, sk (!)
	erry ns, good faster

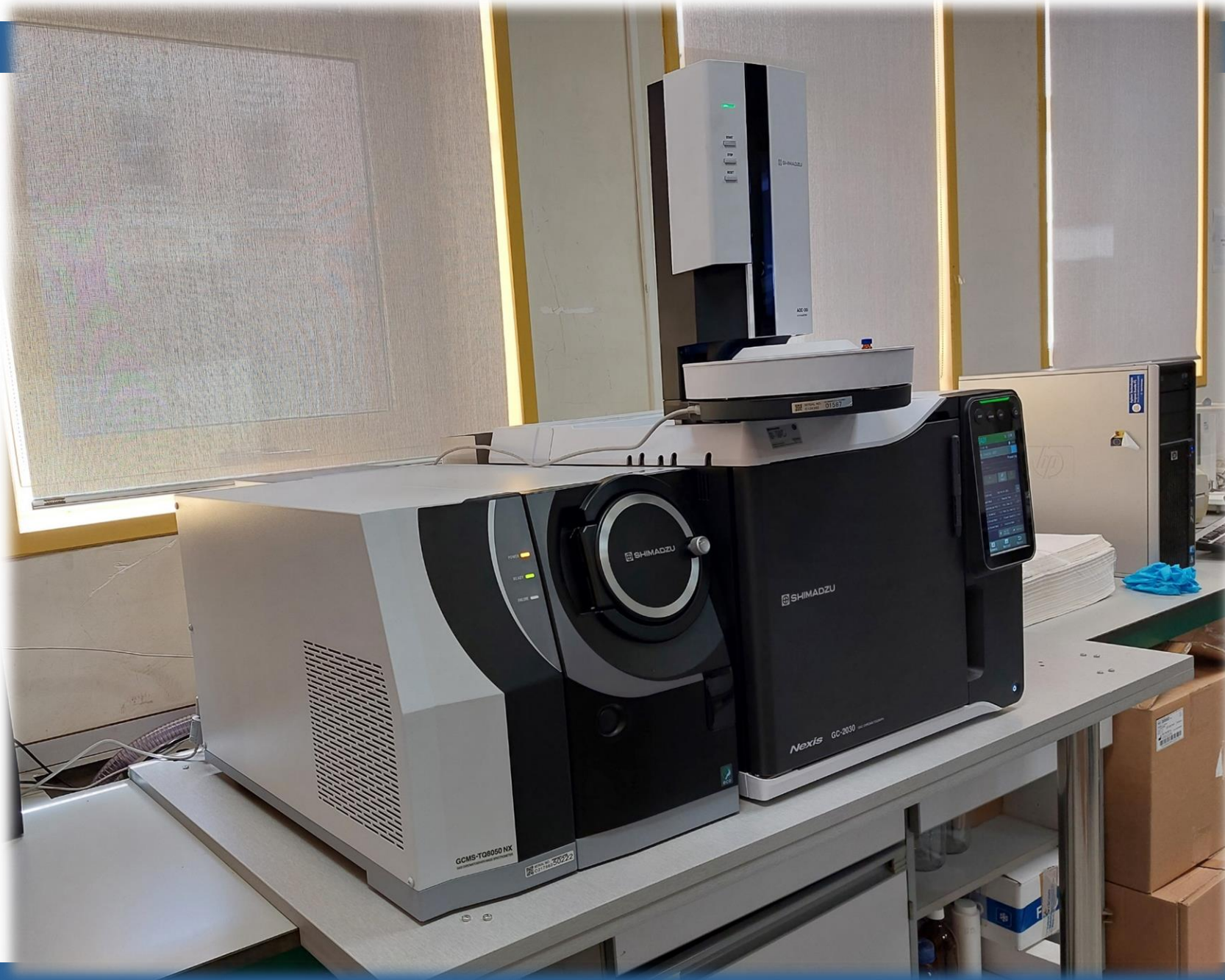
Lorenzo Parodi



Fast responding AFC automatically identifies hazardous leaks but, in addition, GC-2030 is built with a hydrogen sensor

Hydrogen concentration in GC oven:
1 % - Error Message, AFC flow stop
2 % - System shuts down

Usual oven capacity 20L
Average Flow: 1-1.5 mL/min



**DETECTOR
VOLTAGE**

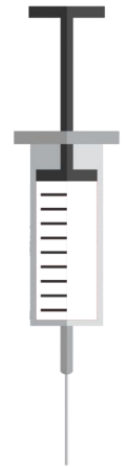
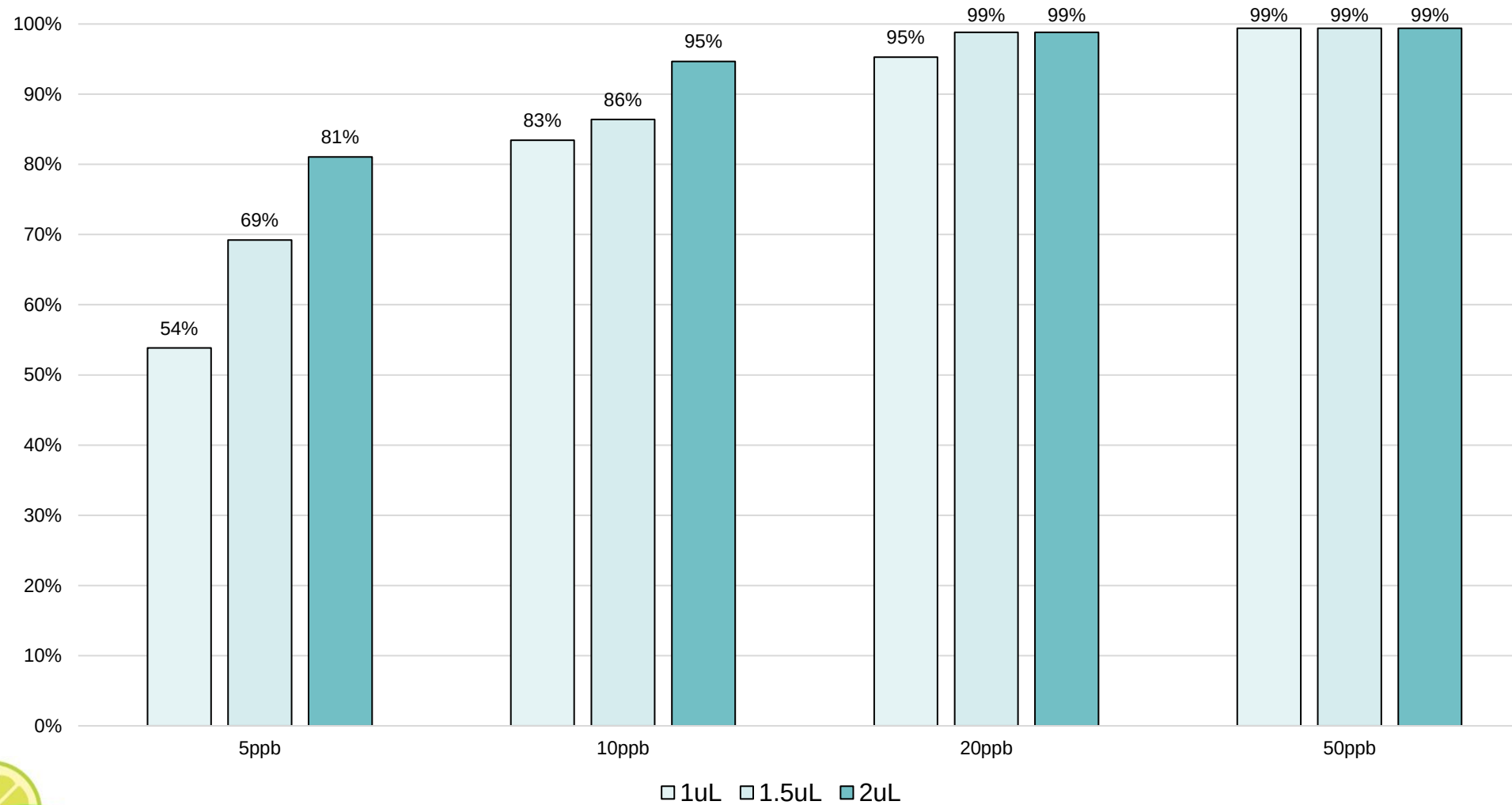
**INJECTION
VOLUME**



**ION SOURCE
TEMPERATURE**

INJECTION VOLUME

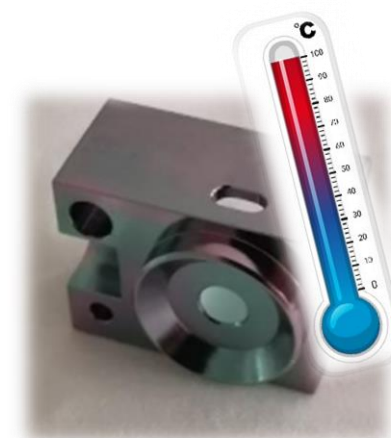
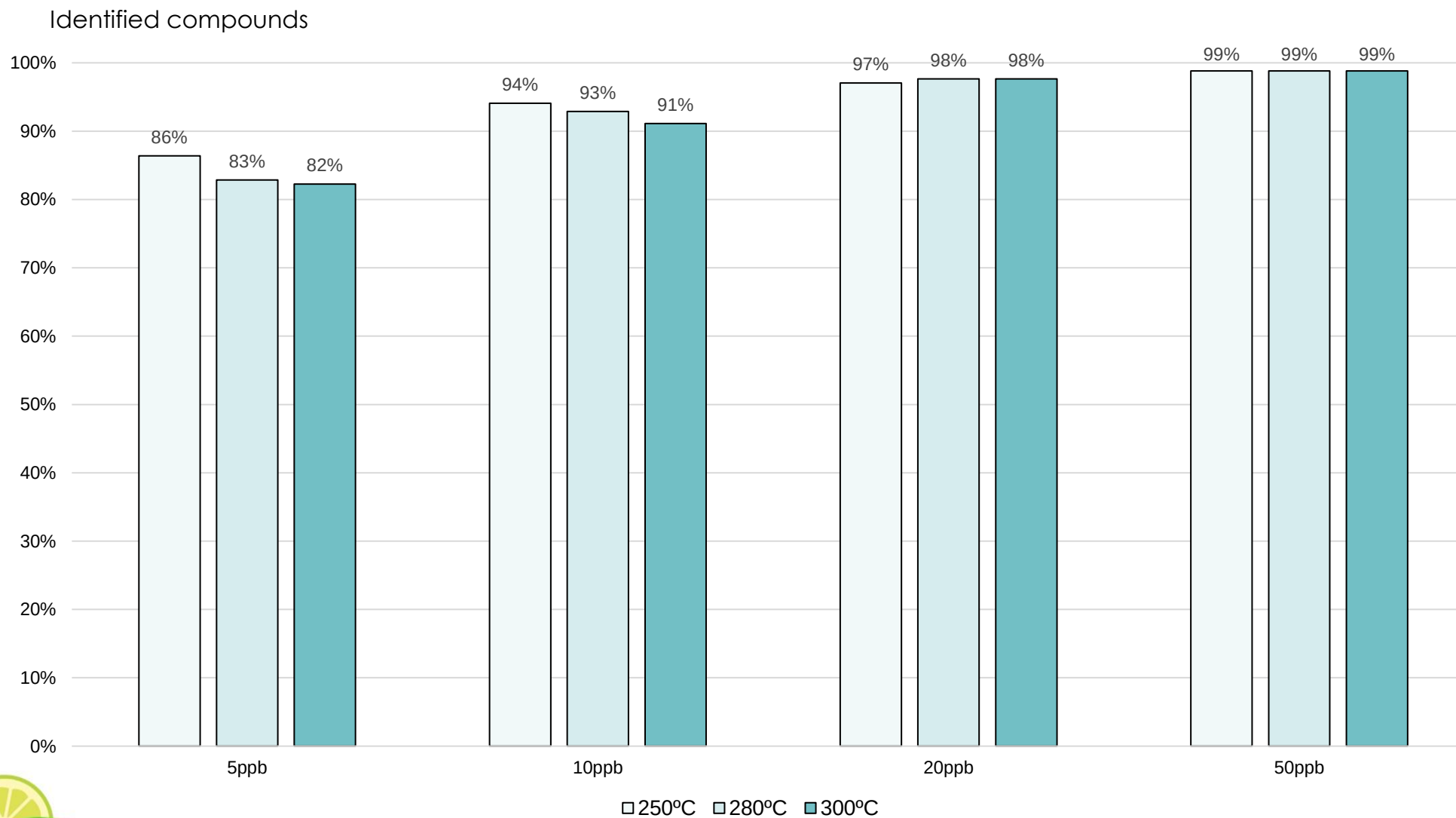
Identified compounds



Amount of matrix

Liner backflush

ION SOURCE TEMPERATURE

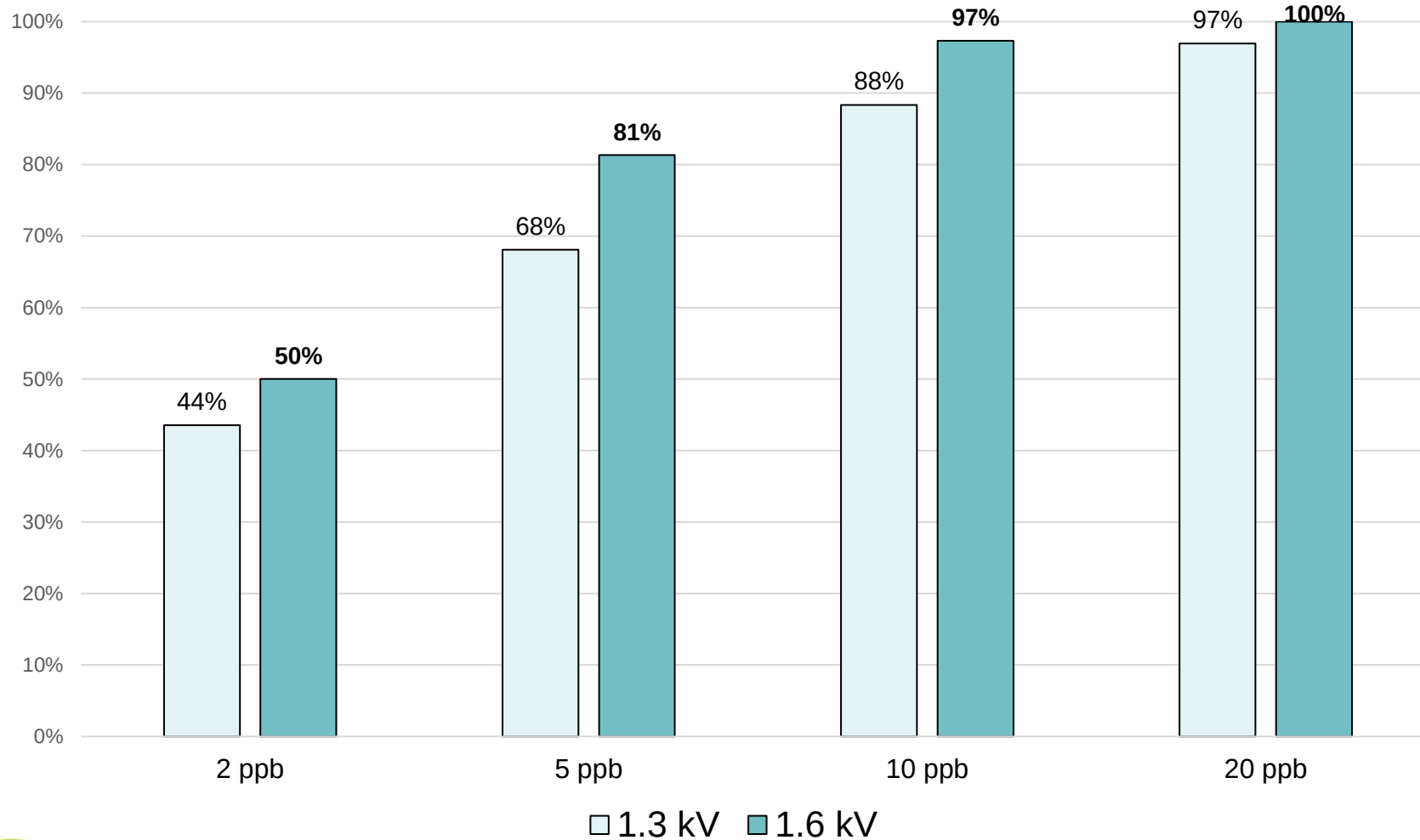


There are no major differences

DETECTOR VOLTAGE



Identified compounds



>1.6kV
SATURATION OF
SOME COMPOUNDS:
Pebulate
Molinate
Hexachlorobenzene
Tefluthrin

Voltage for MRM up to 2kV

GCMS-TQ8050

Chromatograph:

2030 PTV injector

Injection program temperature: 70°C->280°C (350°C/min)

Injection volume: 1 µL

Splitless mode

Column: Shimadzu SH-I-5 MS (20m, 0.18 mm, 0.15 µm)

Linear velocity: 70 cm/s

Equilibration time: 0.5 min

Mass spectrometer:

MRM acquisition mode

Ion source temperature: 280°C

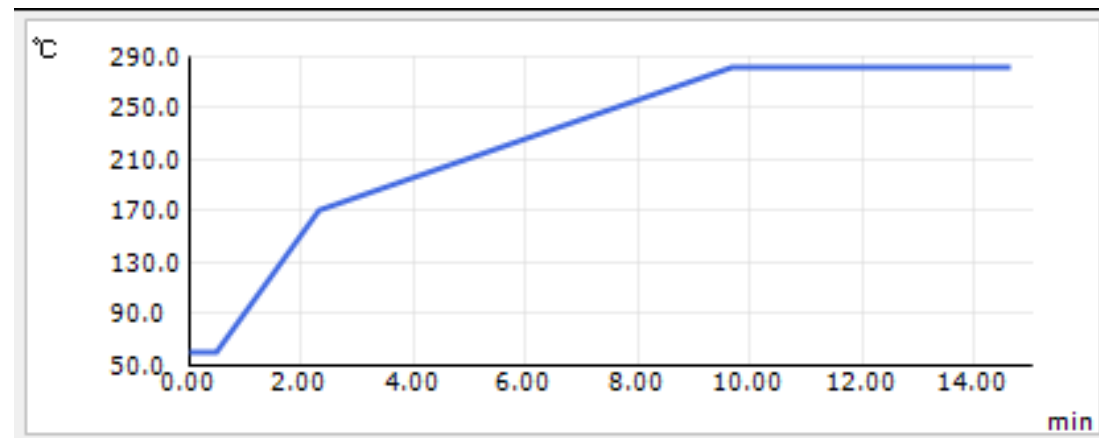
Interface temperature: 280°C

Solvent cut time: 2 min

Detector voltage 1.6kV

Column oven temperature program:

Rate	Temperature	Hold Time
-	60	0.5
60	170	0
15	280	5



ID: 1.5mm; OD: 3.5 mm
Length: 95mm
Restek
Topaz
Wool

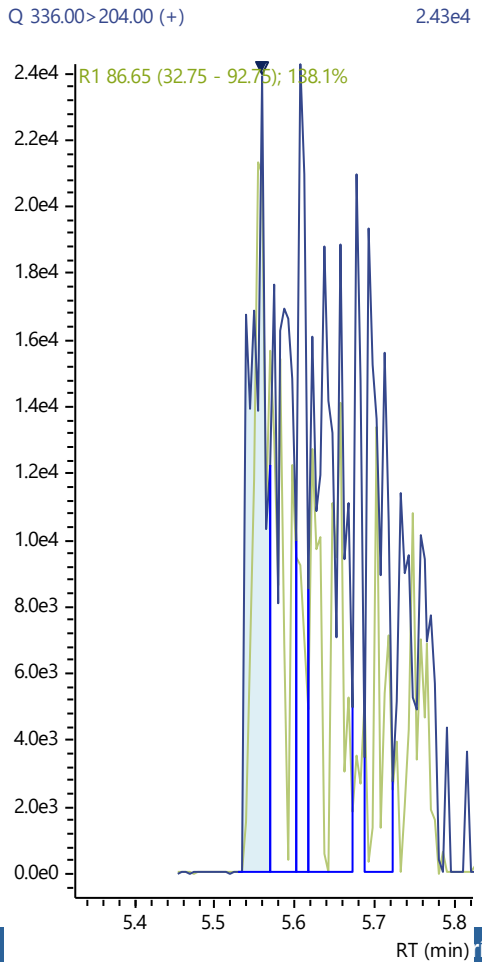
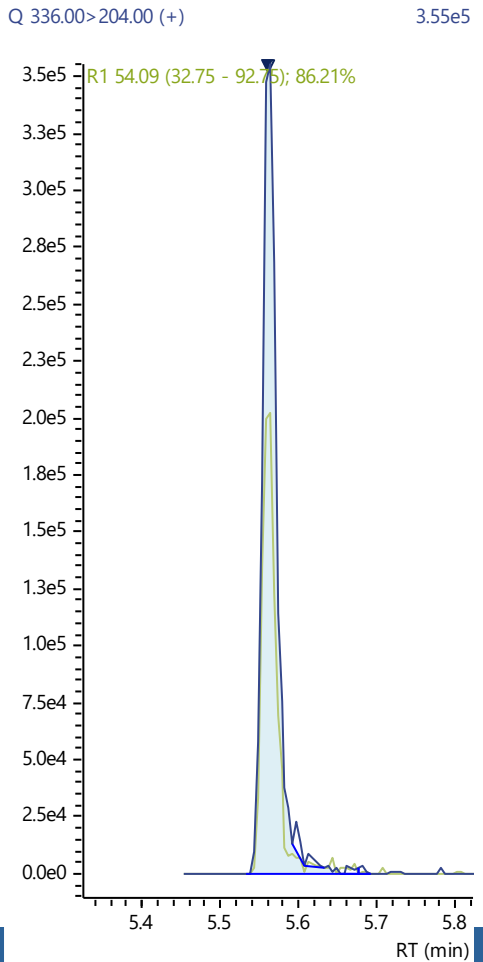
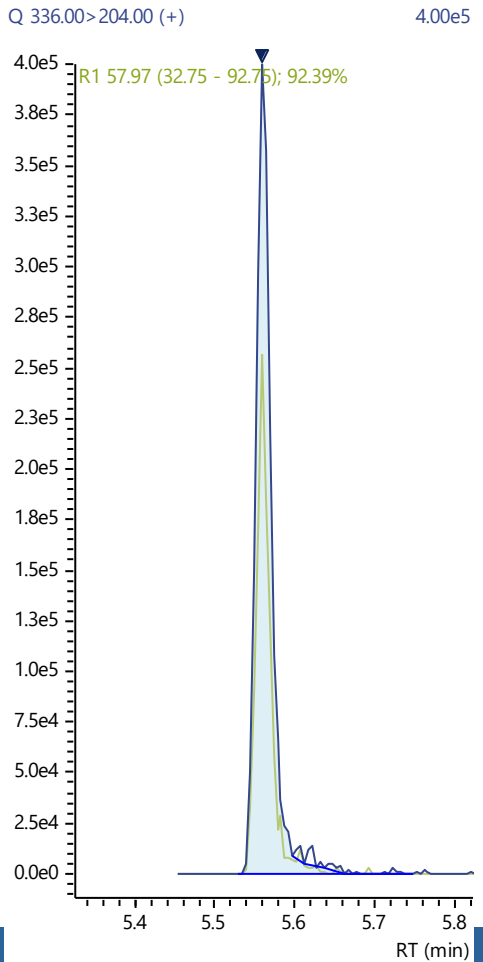
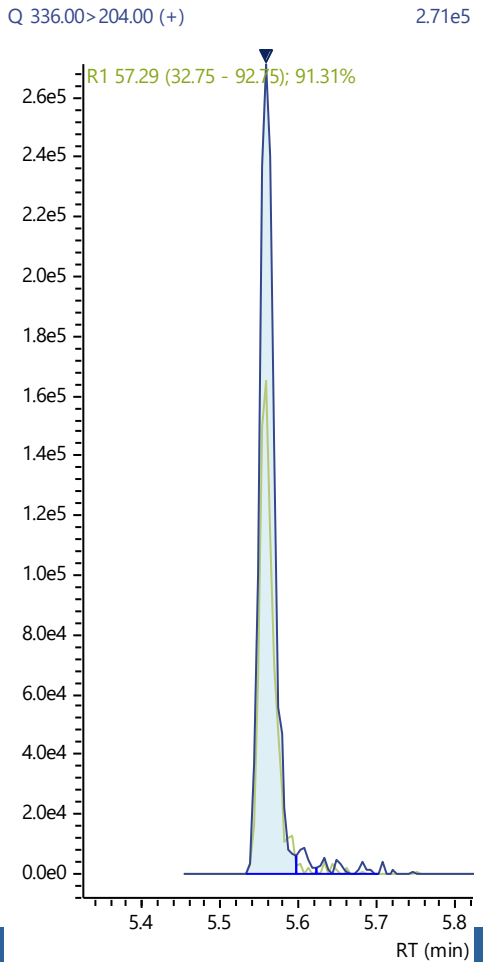
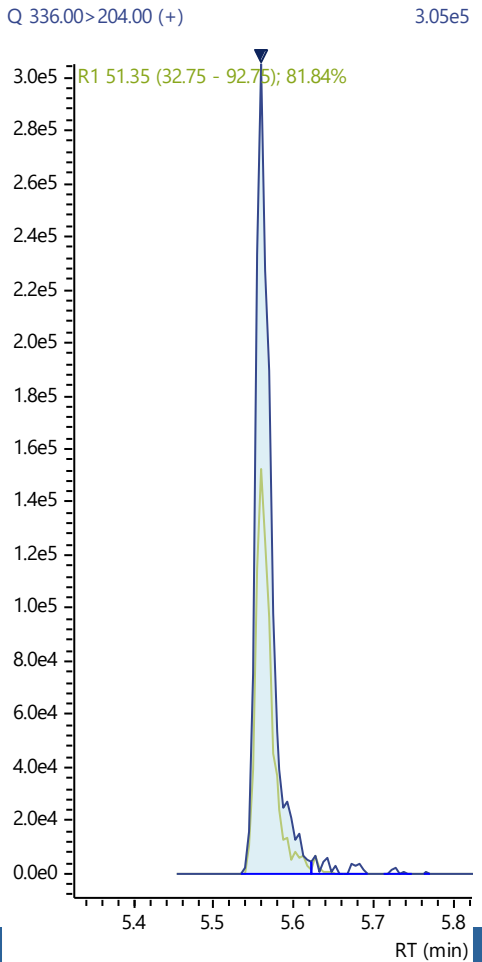
Tetraconazole (100 µg/Kg Tomato)

Shimadzu
Based deact.
Wool

Shimadzu
IP deact.
Wool

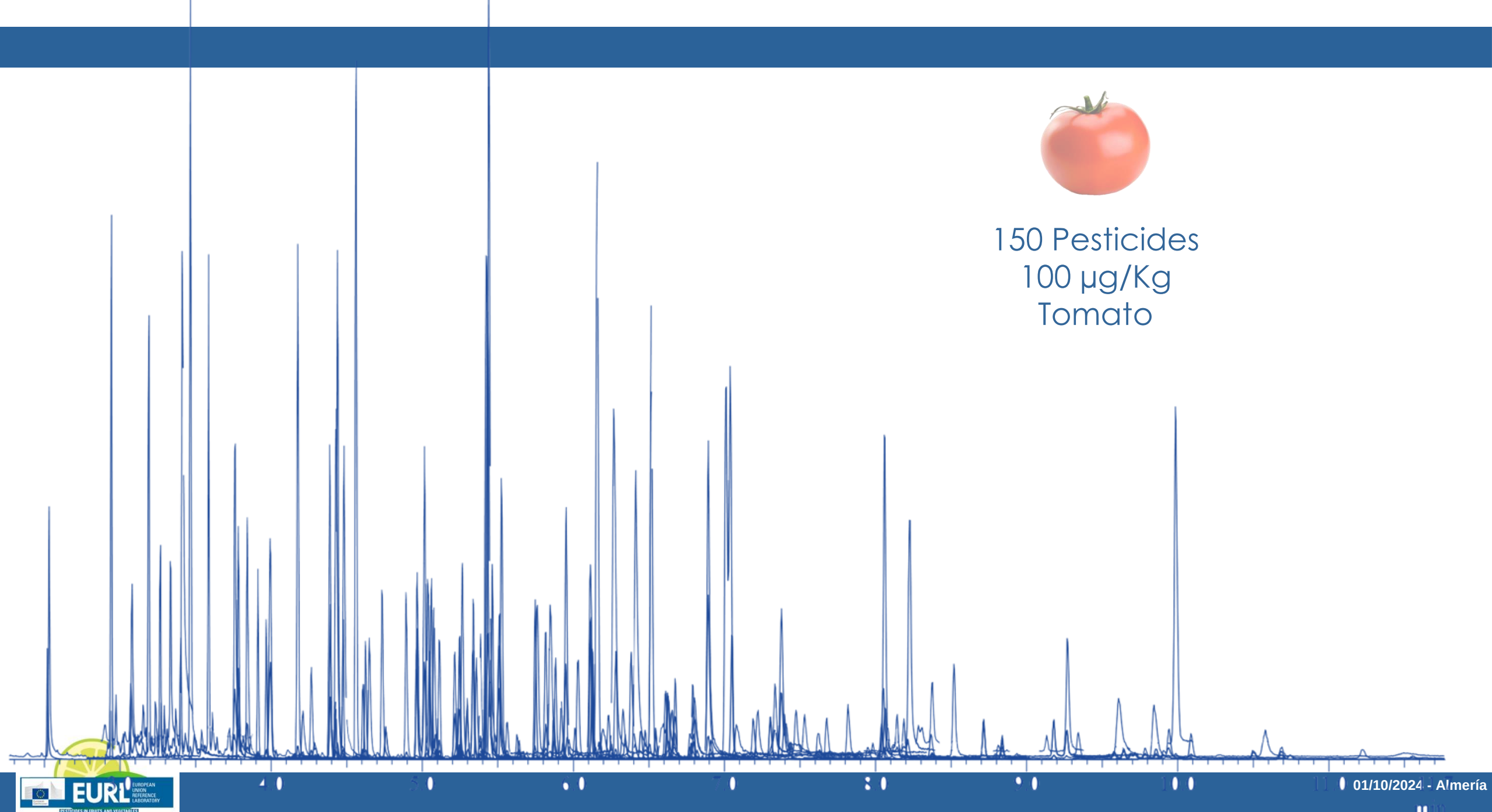
Shimadzu
Siltek deact.
Wool

Restek
Topaz
No Wool



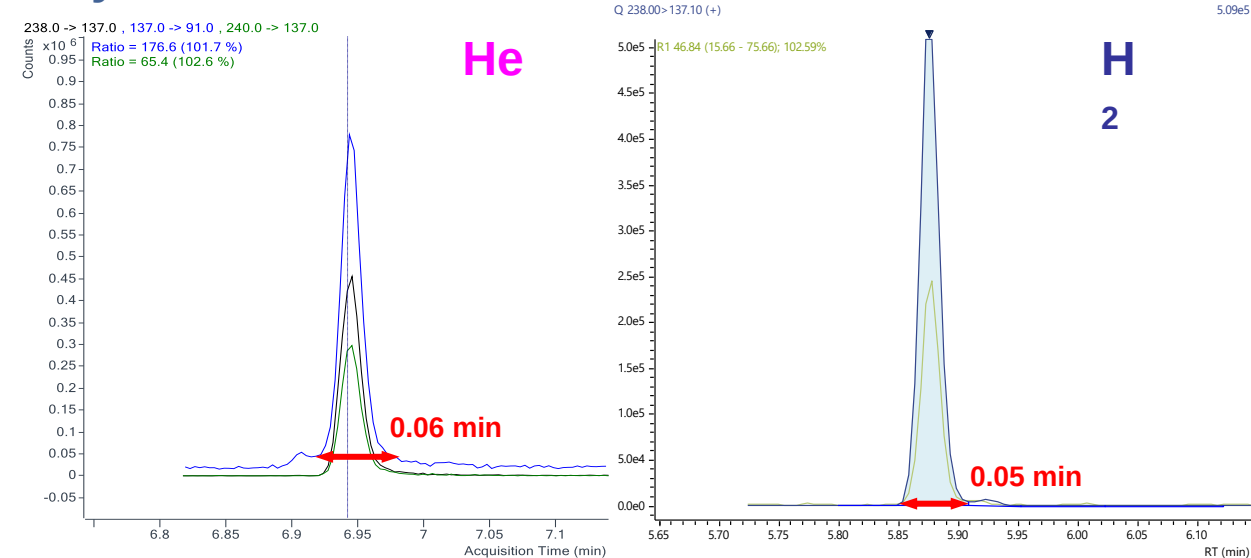


150 Pesticides
100 µg/Kg
Tomato

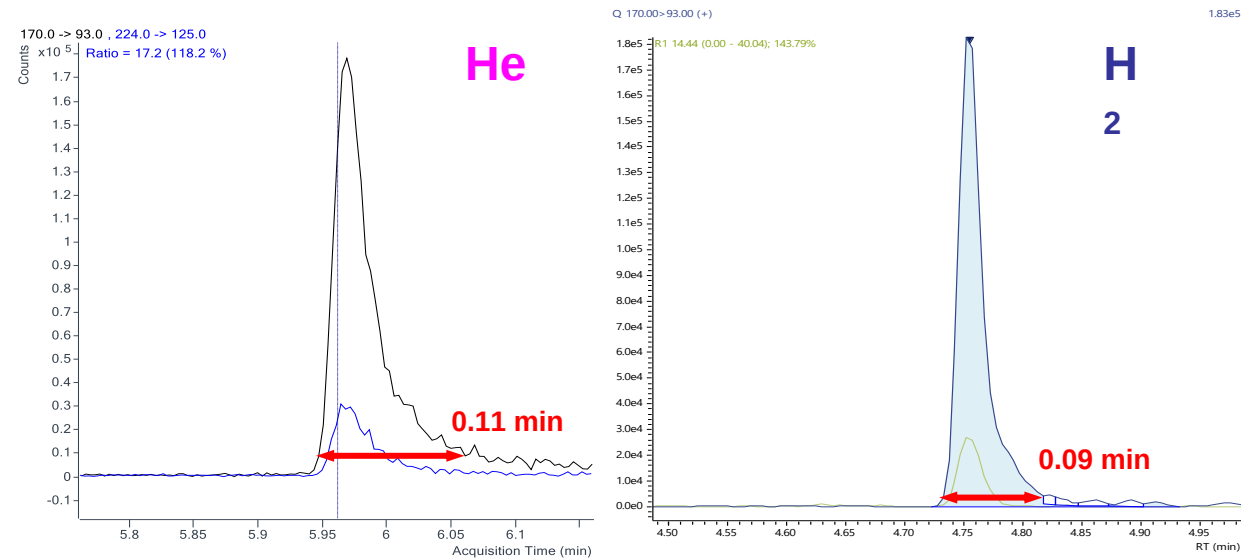


He (30m column) H₂ (20m column)

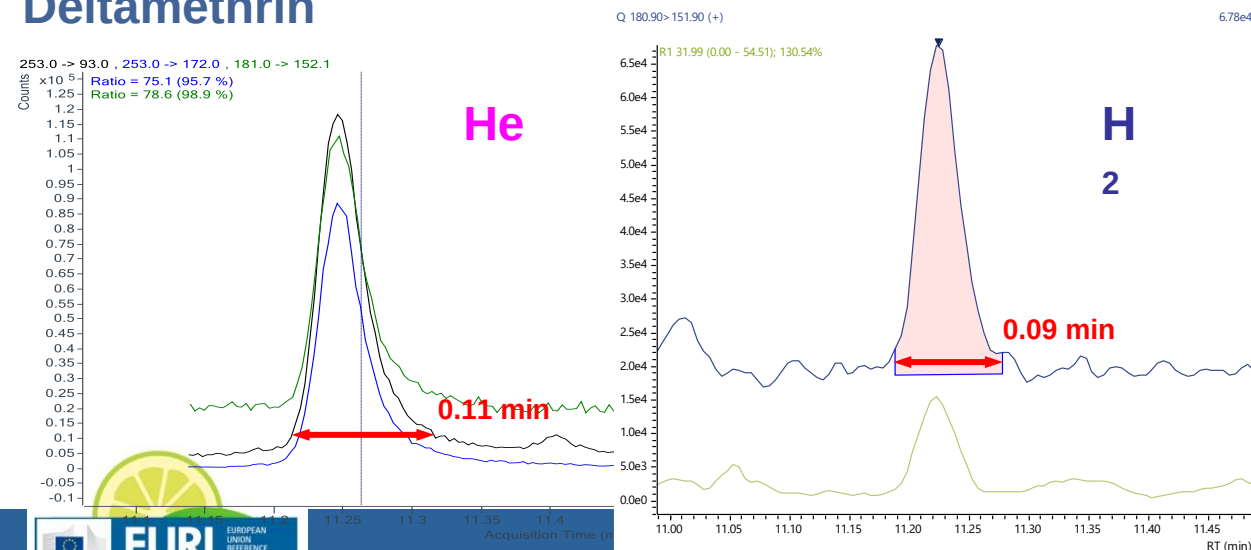
Tolyfluamid



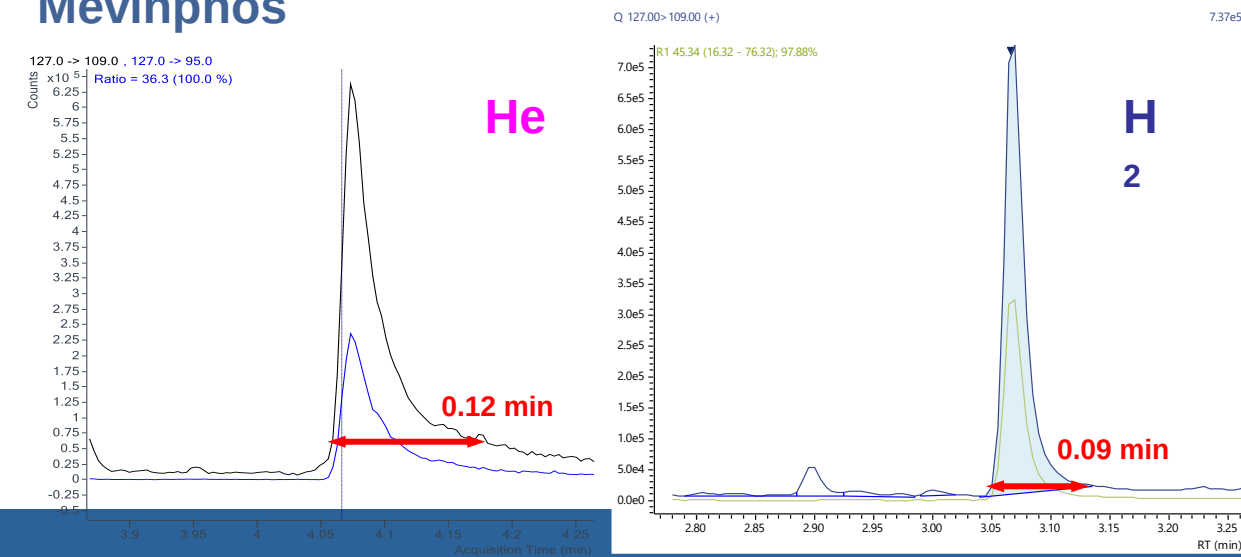
Formothion



Deltamethrin

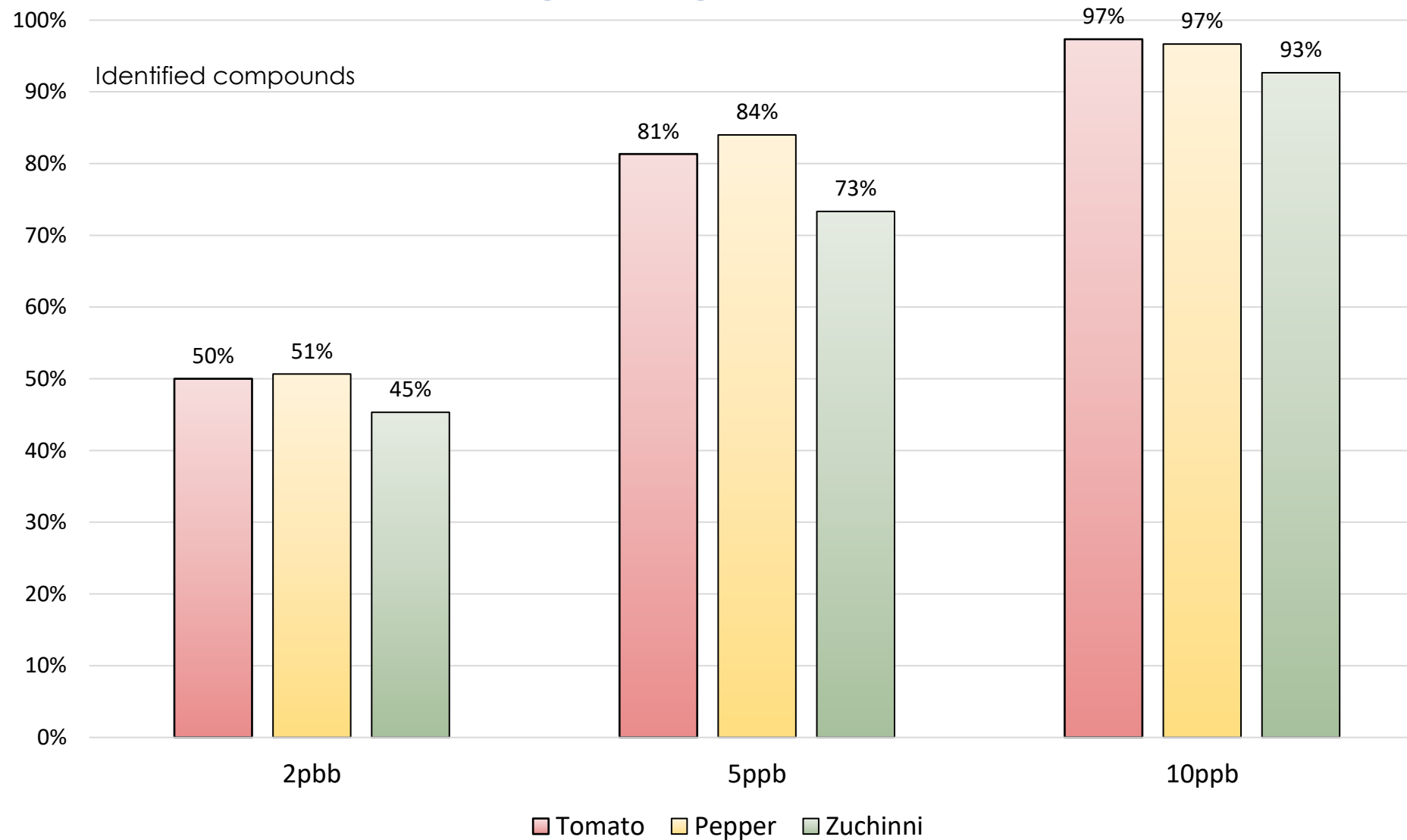


Mevinphos



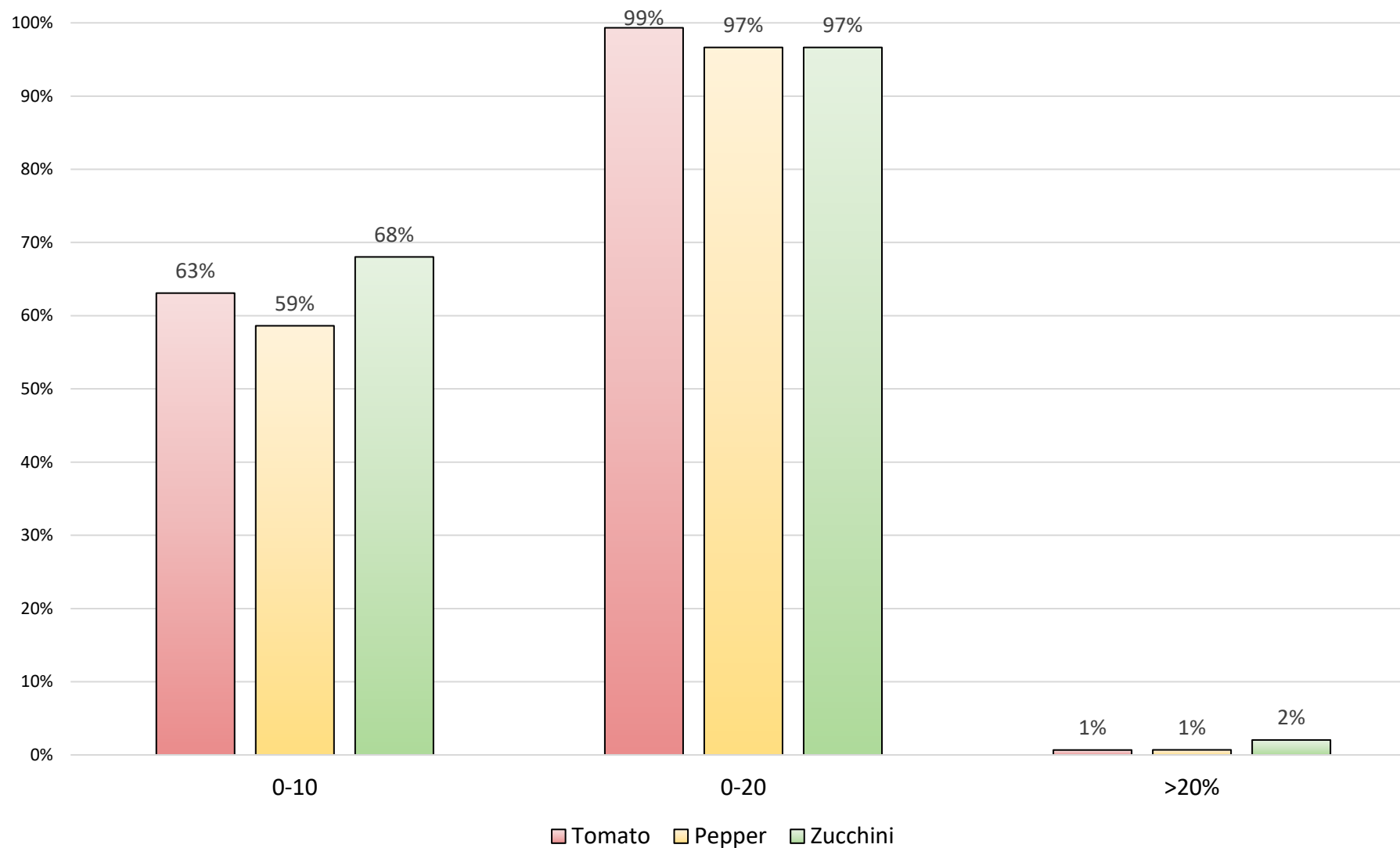
SENSITIVITY

150 Pesticides

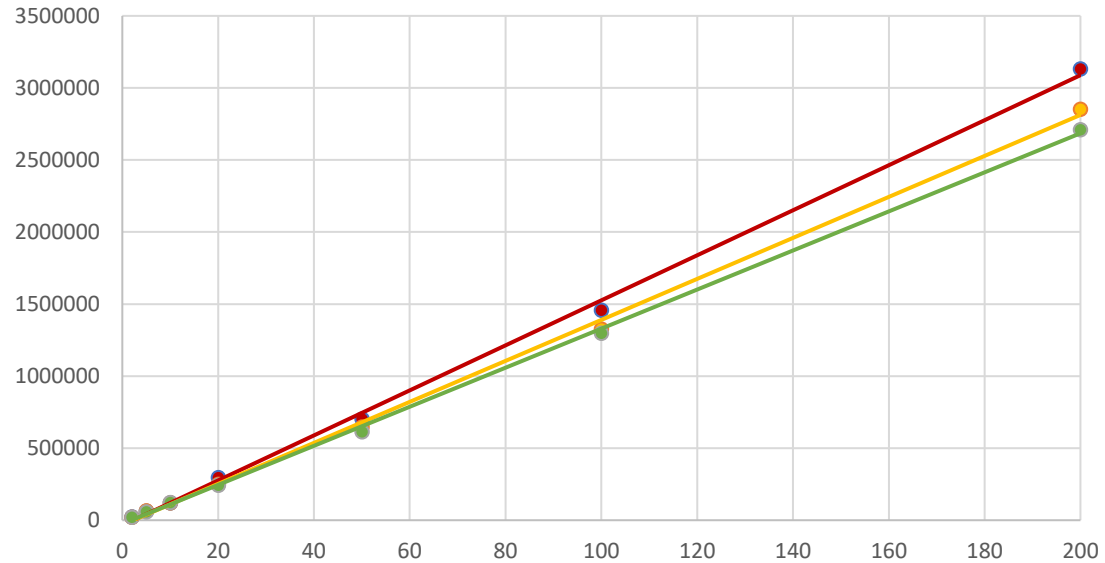


REPRODUCIBILITY – RSD(%)

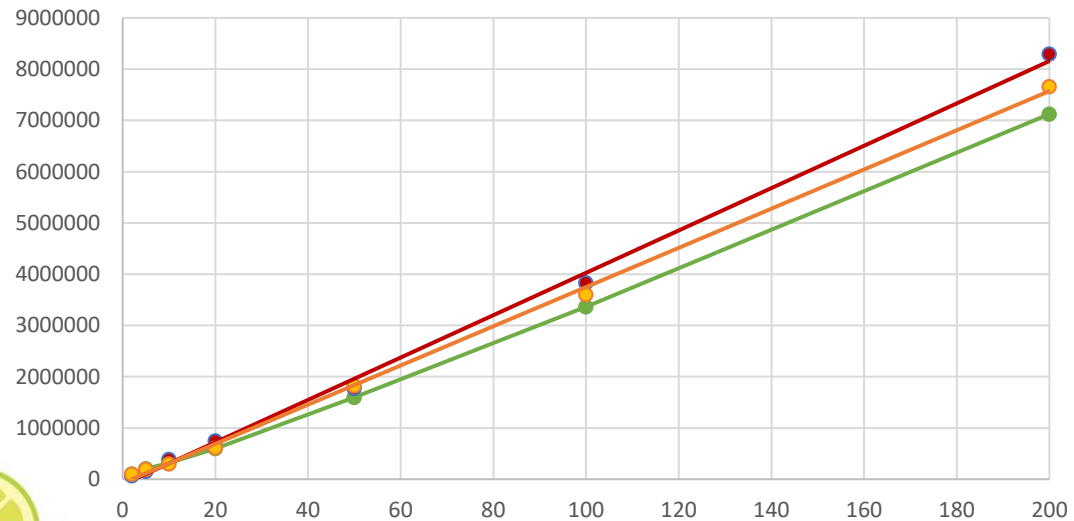
150 Pesticides
10 µg/Kg



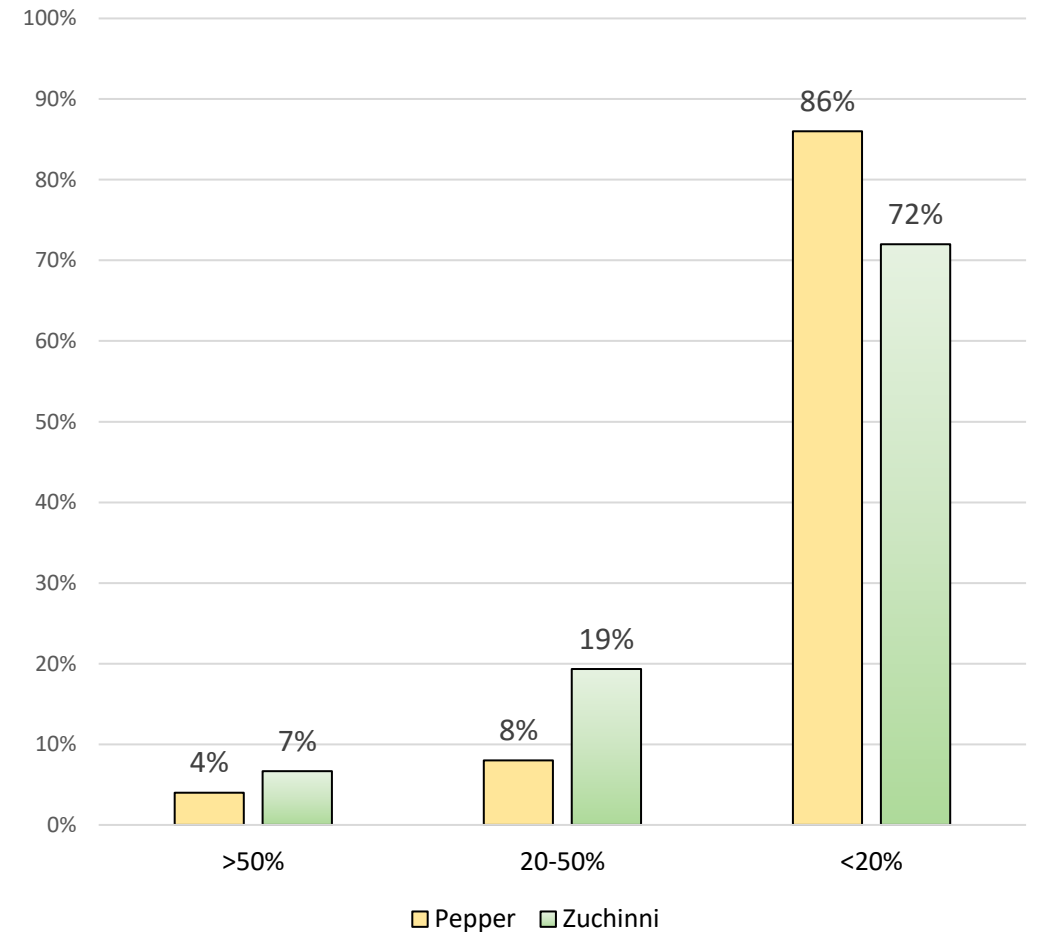
Chlorpyrifos



Cyprodinil



MATRIX EFFECTS





REAL SAMPLES



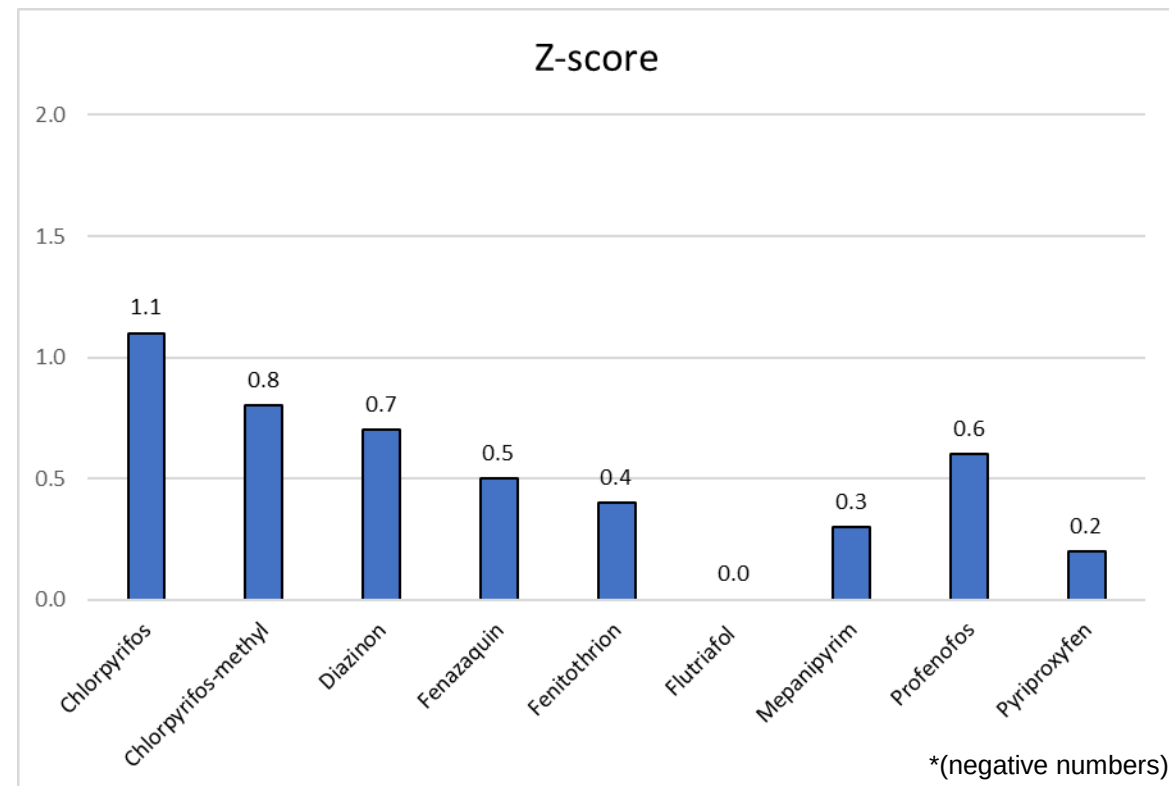
Matrix	Boscalid		Cypermethrin		Cyprodinil		Flutolanil		Lambda-Cyhalothrin		Pyrimethanil		Pyriproxyfen	
	Hydrogen	Helium	Hydrogen	Helium	Hydrogen	Helium	Hydrogen	Helium	Hydrogen	Helium	Hydrogen	Helium	Hydrogen	Helium
Potato							0.024	0.031						
Spinach			0.008	0.011										
Lemon											0.009	0.011	0.014	0.018
Peach					0.015	0.017								
Pear					0.058	0.07								
Grape	0.036	0.046			0.232	0.289								
Orange													0.009	0.014
Nectarine					0.106	0.137								
Tomato									0.109	0.111				

Proficiency test

EURLFV-25

(melon)

GCMS/MS-Hydrogen	EURLFV Sample results	Robust Mean X* (mg/kg)
Chlorpyrifos	0.004	0.005
Chlorpyrifos-methyl	0.072	0.090
Diazinon	0.086	0.104
Fenazaquin	0.069	0.078
Fenitothrion	0.076	0.085
Flutriafol	0.301	0.304
Mepanipirim	0.075	0.081
Profenofos	0.099	0.117
Pyriproxyfen	0.232	0.245



CONCLUSIONS

- Hydrogen is no longer considered a safety risk in the lab due to the numerous safety measures modern systems incorporate.
- While the diffusivity and viscosity values of hydrogen surpass those of helium, its lack of inertness must be monitored.
- Sensitivity is sufficient to identify 80% of compounds at 5 ppb.
- The optimized method displays strong reproducibility and minimal matrix effects.

In summary, using hydrogen as a carrier gas in GC-MS/MS appears to be a viable alternative to helium for the analysis of pesticide residues.

**Thank You
for Your Attention**

