Joint EURLs/NRLs-Workshop for pesticide residues

Evaluation of Hydrogen as an Alternative Carrier Gas for GC-MS/MS Analysis of Pesticides

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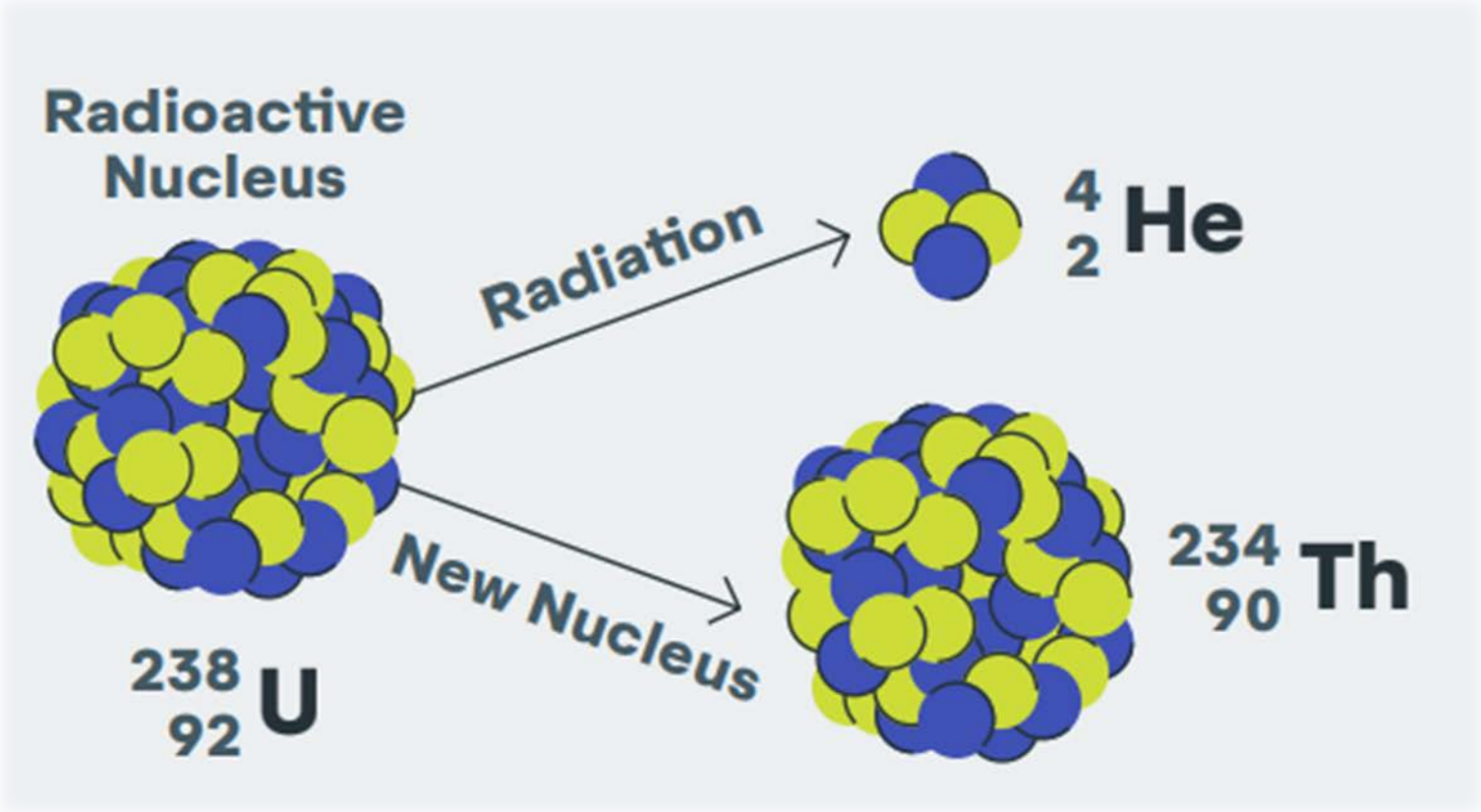
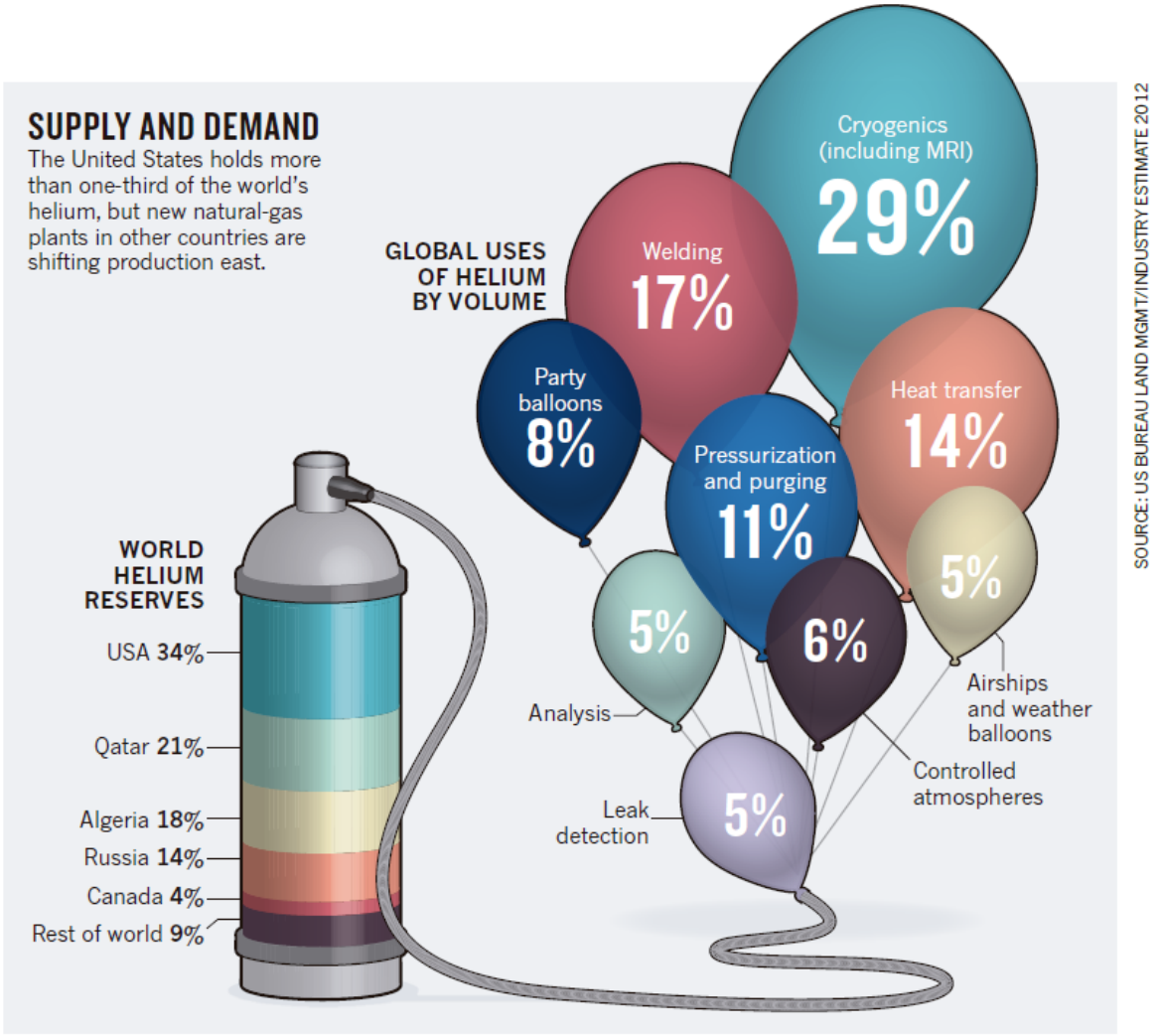
The majority of helium originates from the radioactive decay of uranium and thorium. This gas is located under the Earth's crust, alongside other natural gases. When the helium concentration surpasses 0.3%, it is commercially extracted from natural gas.



Helium – A gas facing extinction. ACS Green Chemistry institute

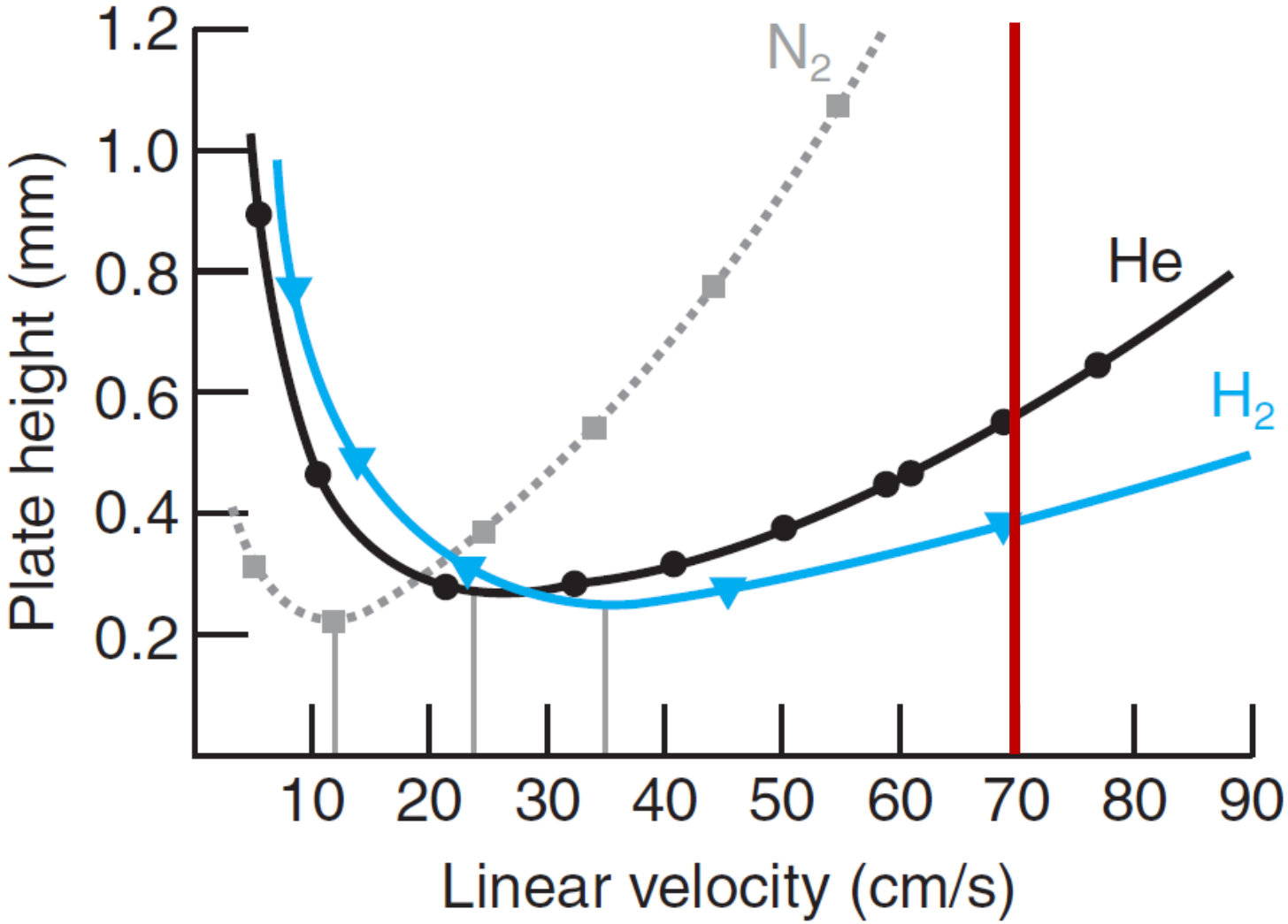
Helium shortage

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



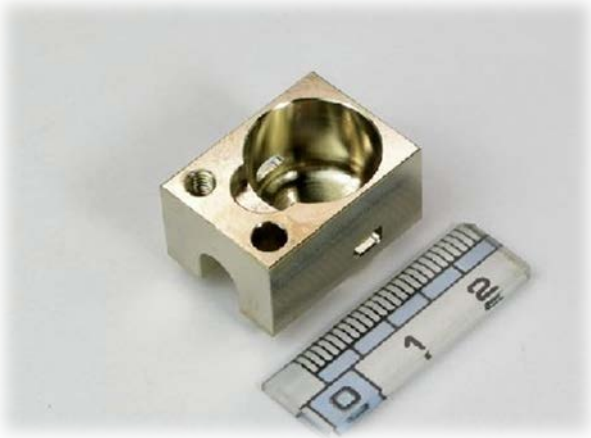
Quantitative Chemical Analysis, Daniel C. Harris, 8th Edition

	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



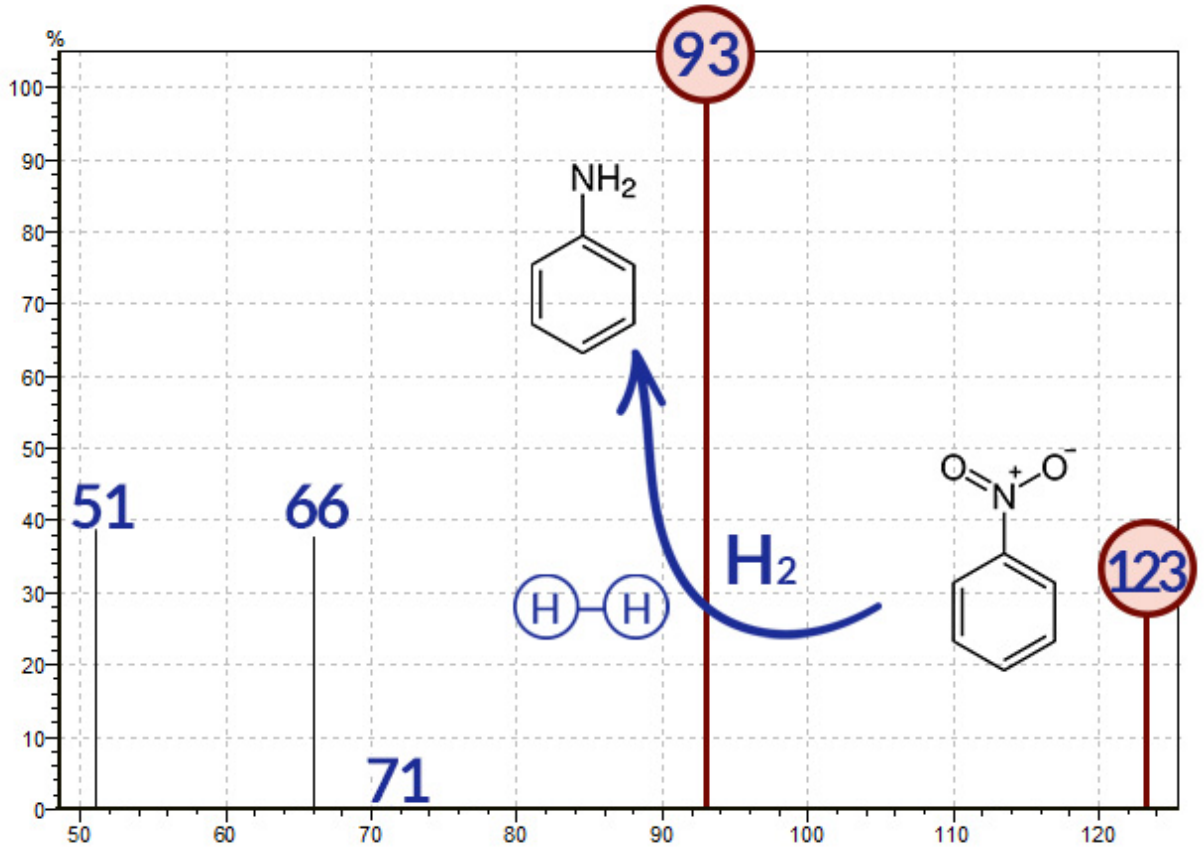
Vacuum performance

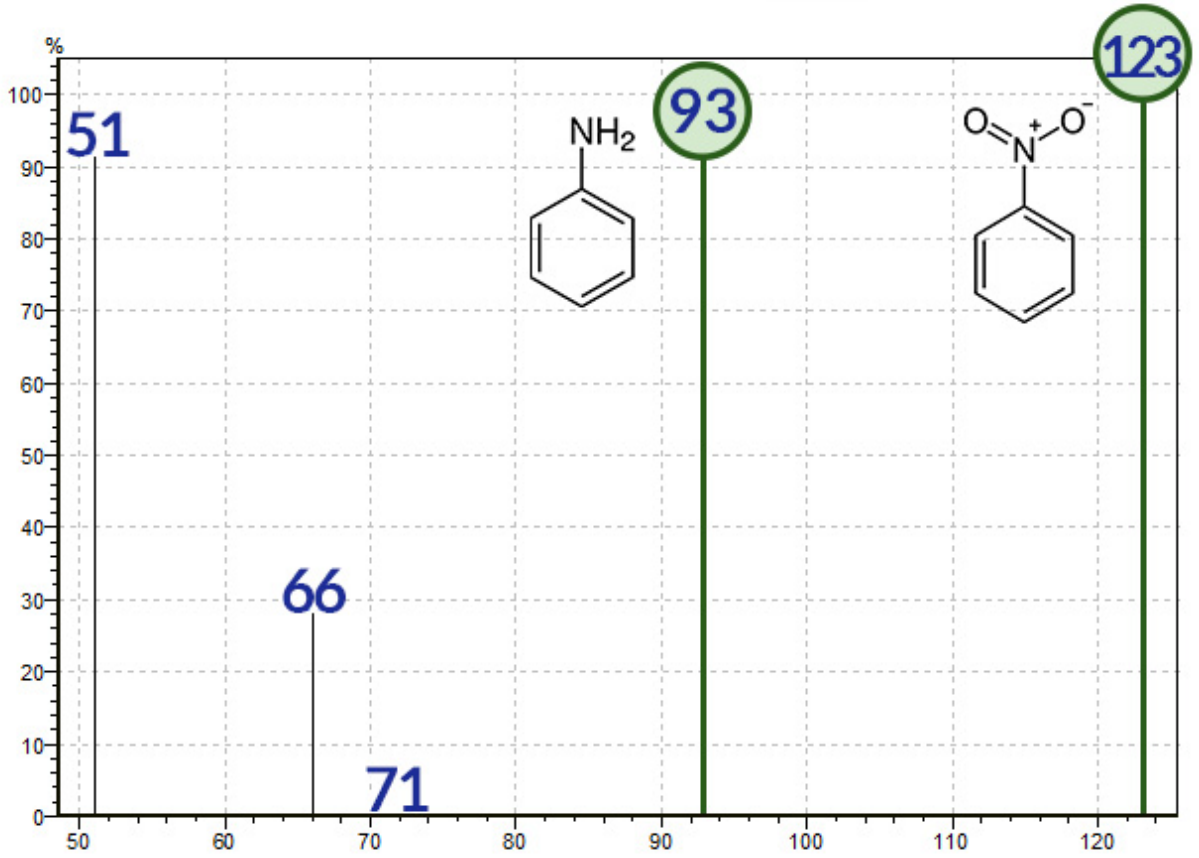
Use narrow-bore chromatographic columns (0.15-0.18 mm) and low carrier gas flow rates.

INERTNESS

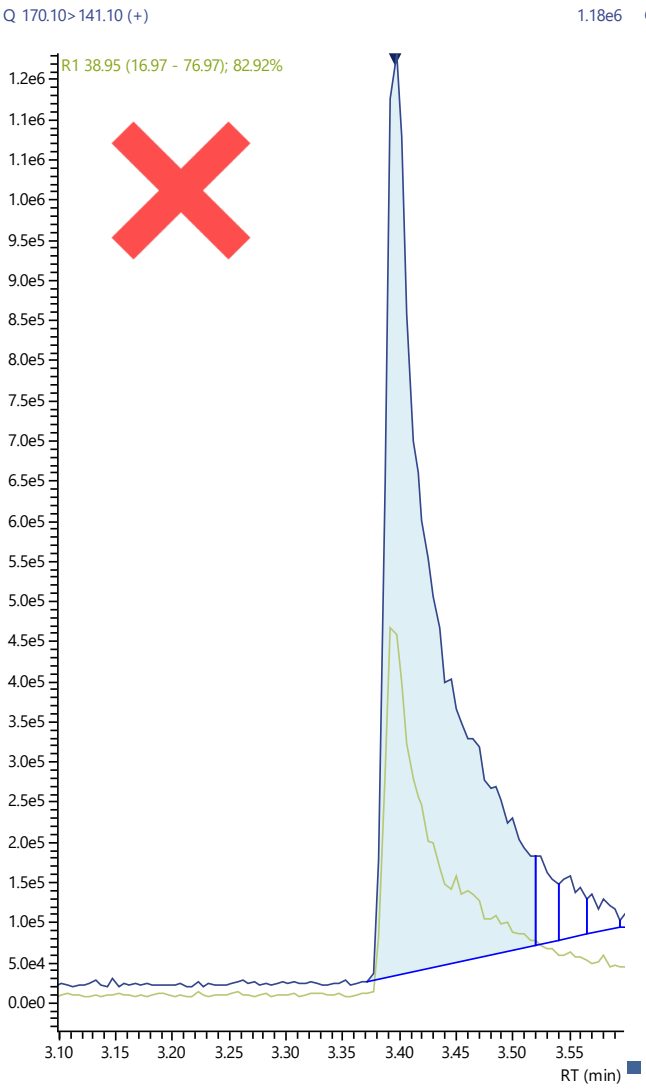
NITROBENZENE TEST

1ppm Nitrobenzene standard

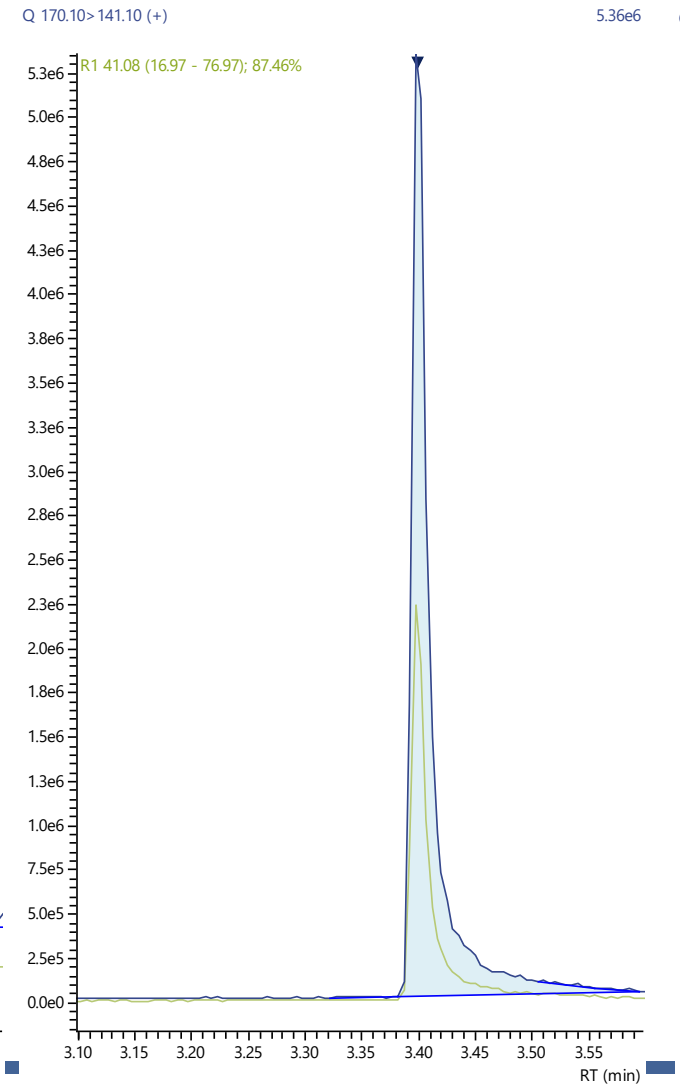




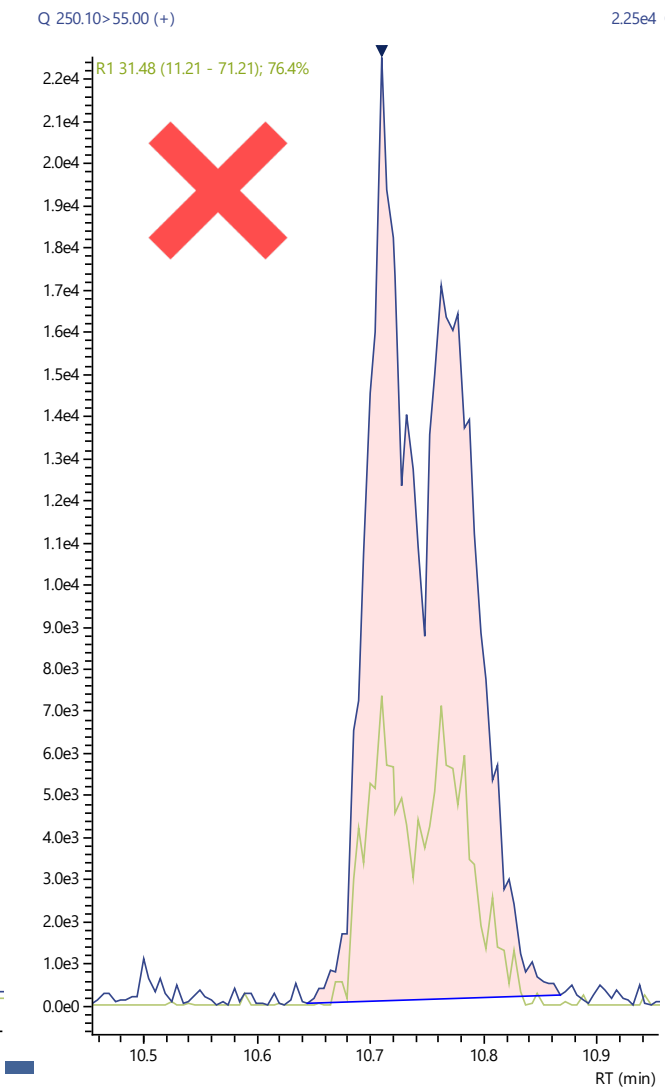
2-Phenylphenol HYDROGENATION



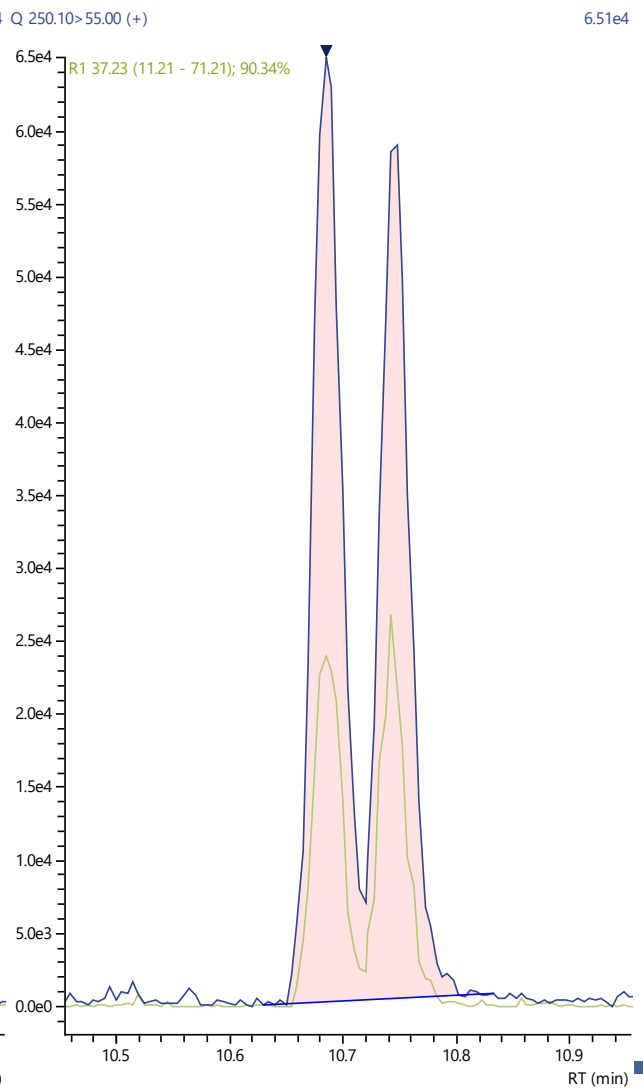
2-Phenylphenol

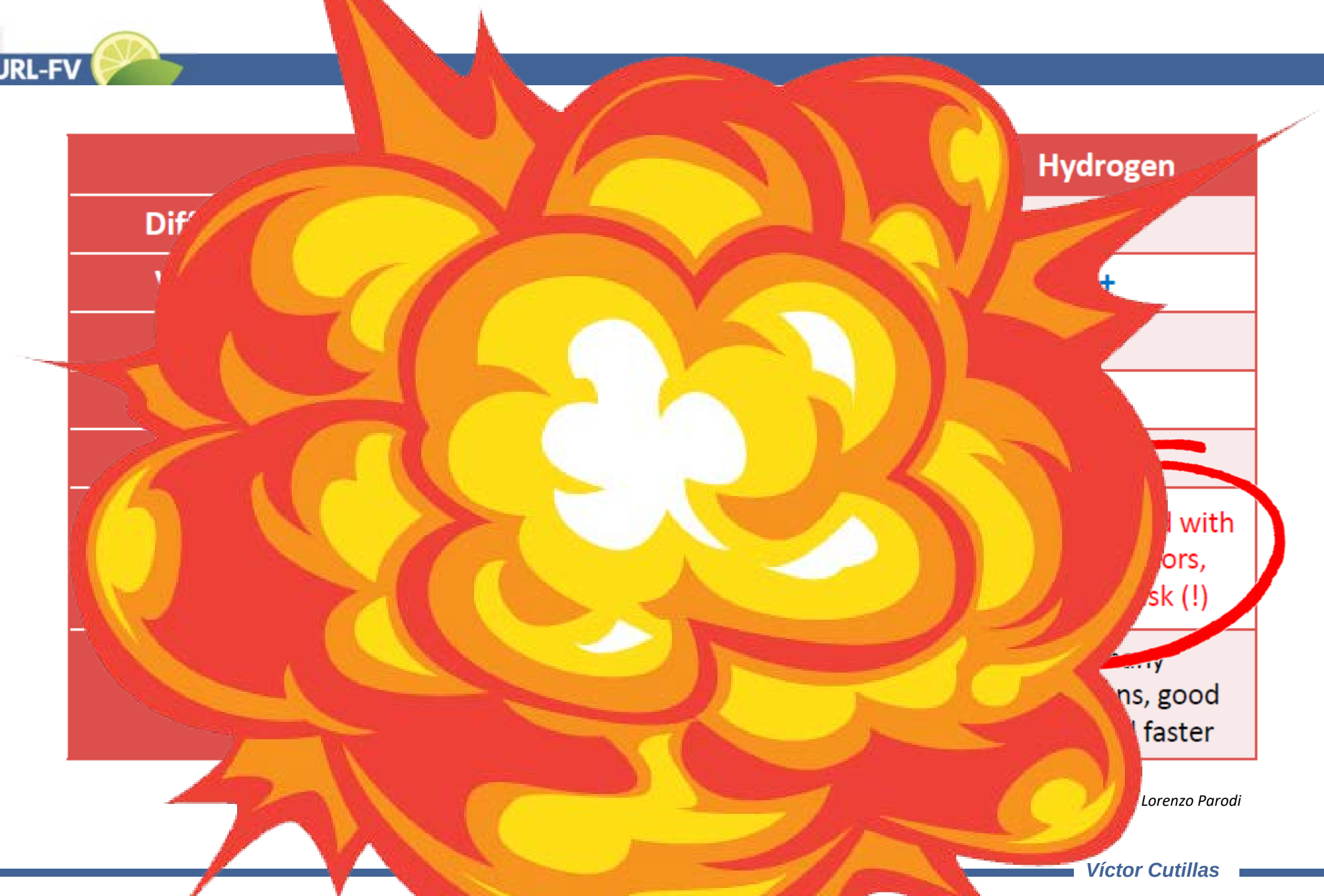


Tau-Fluvalinate HYDROGENATION

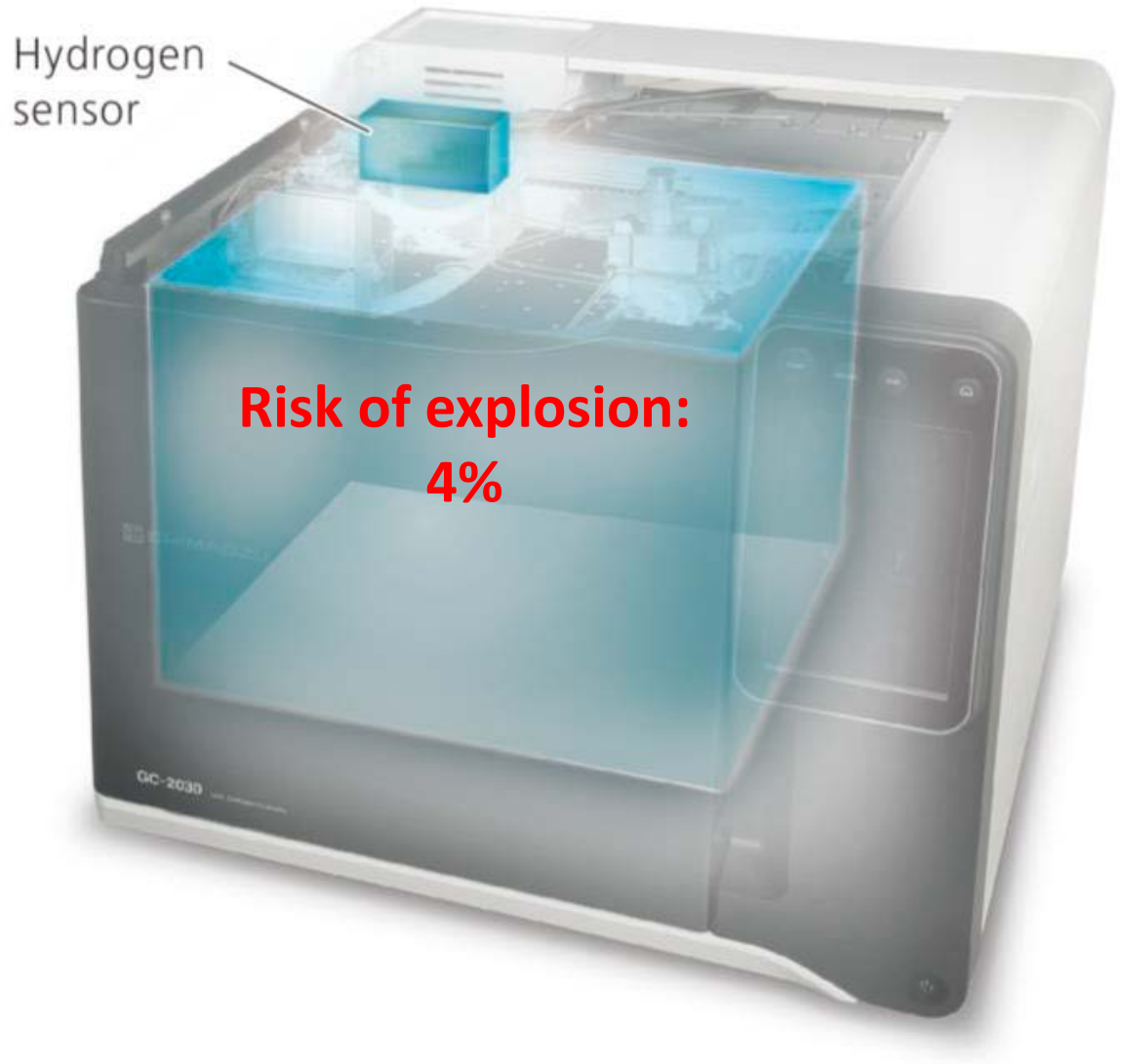


Tau-Fluvalinate





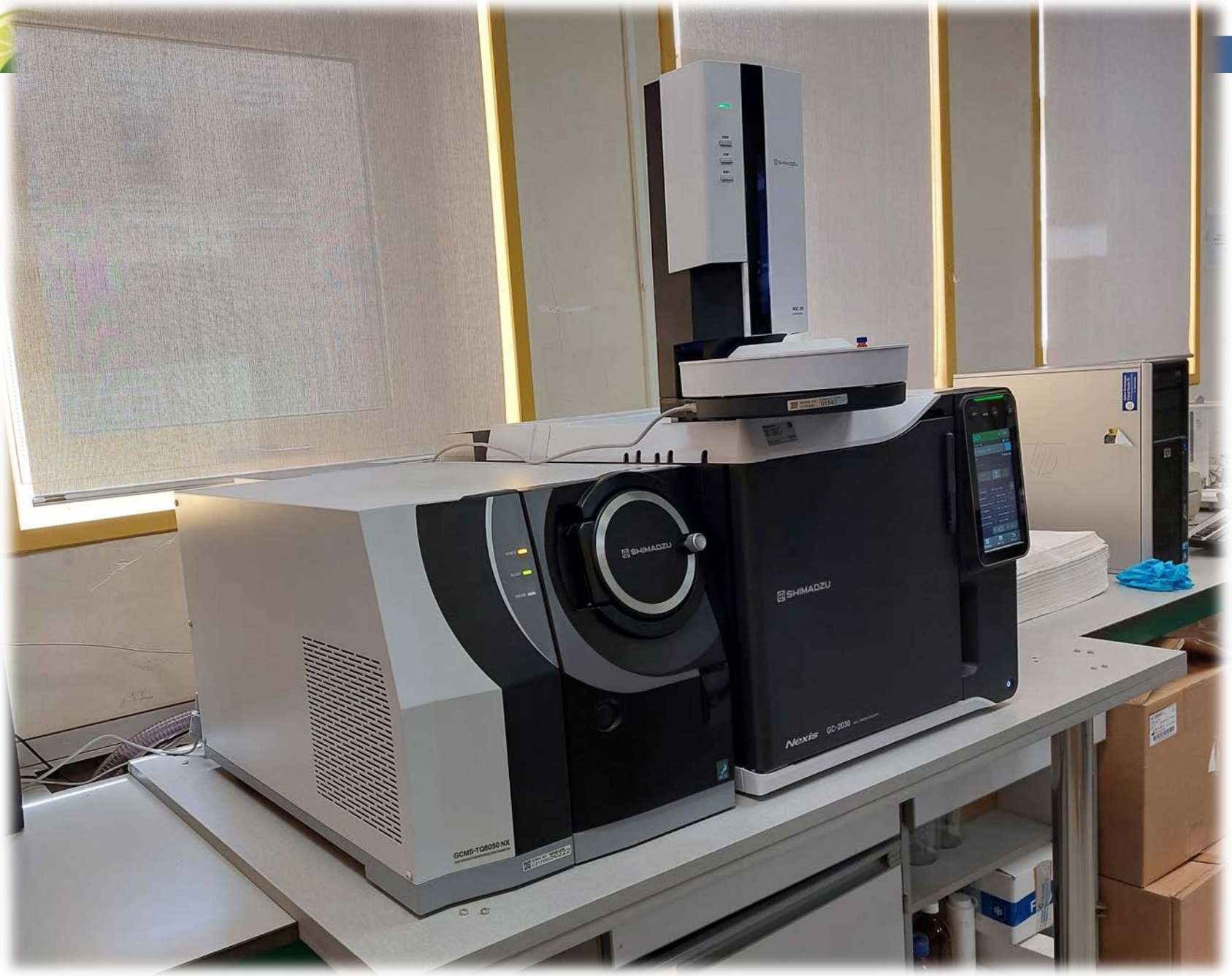
Lorenzo Parodi



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


SHIMADZU
SHIMADZU
Nexis GC-2030
GCMS-TQ8050 NX

INJECTION VOLUME

DETECTOR VOLTAGE

ION SOURCE TEMPERATURE

GCMS-TQ8050

Chromatograph:

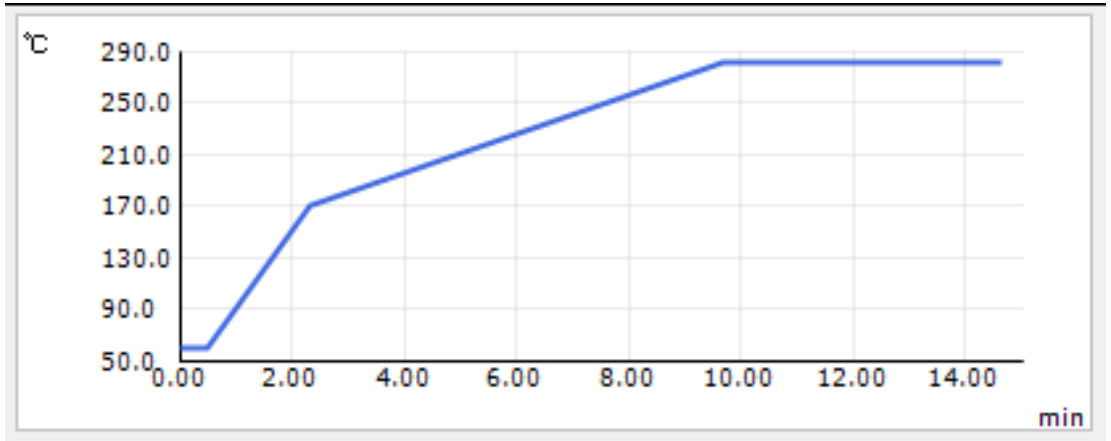
2030 PTV injector
Injection program temperature: 70ºC->280ºC (350ºC/min)
Injection volume: 1µL
Splitless mode
Column: Shimadzu SH-I-5 MS (20m, 0.18 mm, 0.15 µm)
Linear velocity: 70 cm/s
Equilibration time: 0.5 min

Mass spectrometer:

MRM acquisition mode
Ion source temperature: 280ºC
Interface temperature: 280ºC
Solvent cut time: 2 min
Detector voltage 1.6kV

Column oven temperature program:

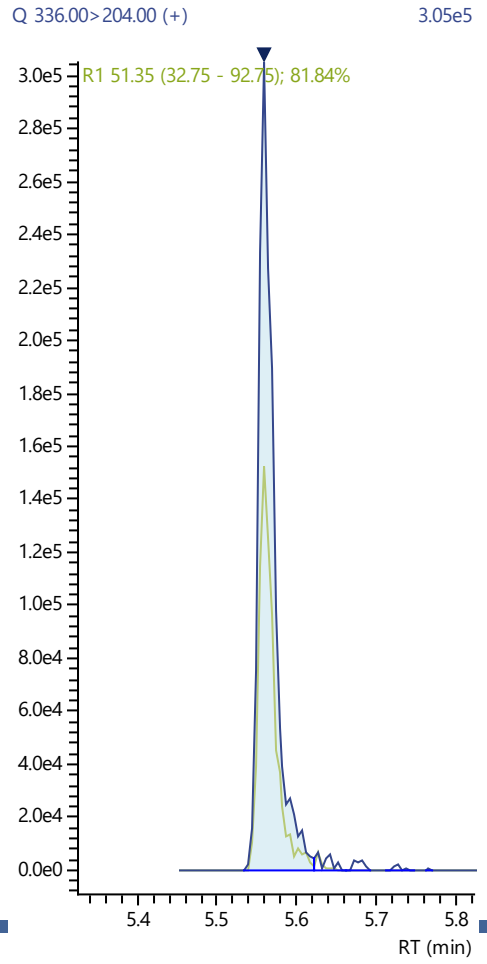
Rate	Temperature	Hold Time
-	60	0.5
60	170	0
15	280	5



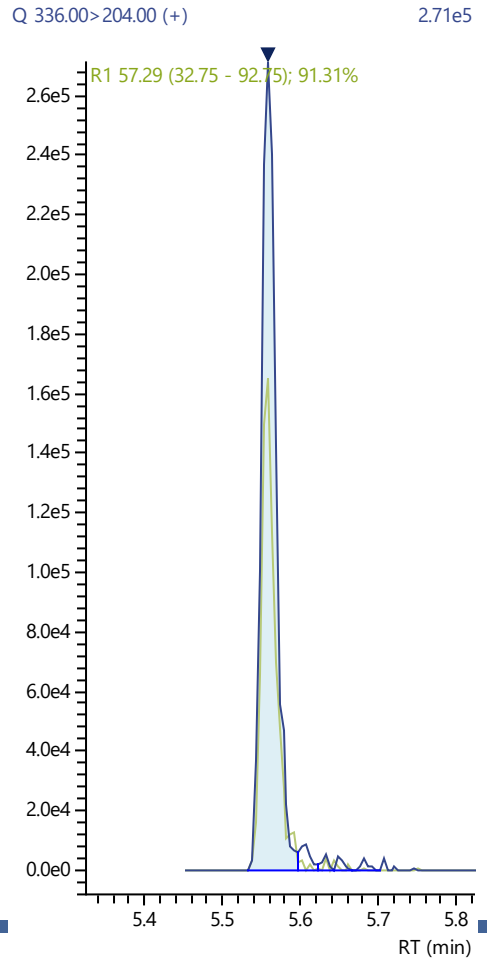
ID: 1.5mm; OD: 3.5 mm
Length: 95mm

Tetraconazole (100 µg/Kg Tomato)

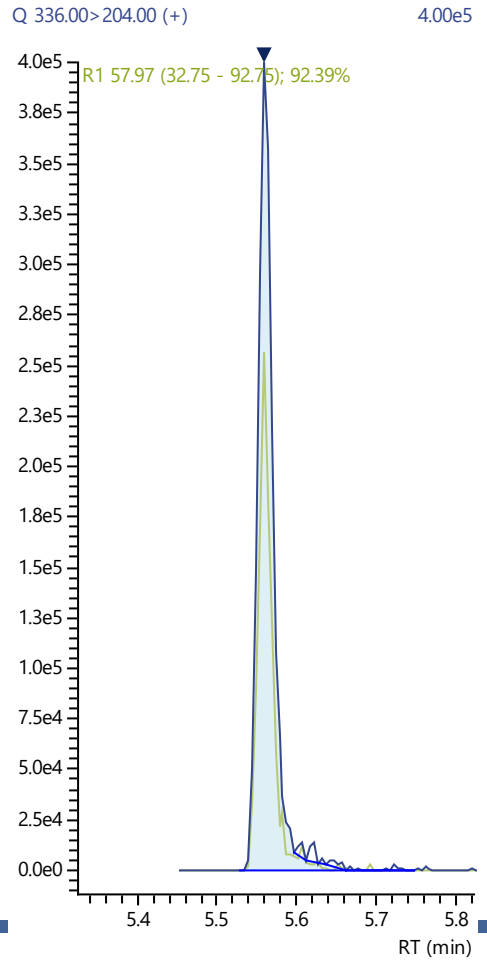
Restek Topaz Wool



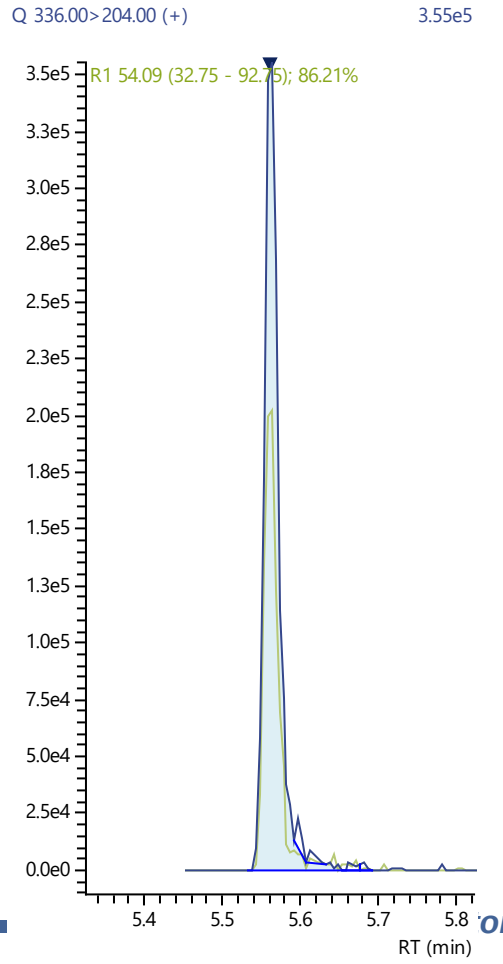
Shimadzu Based deact. Wool



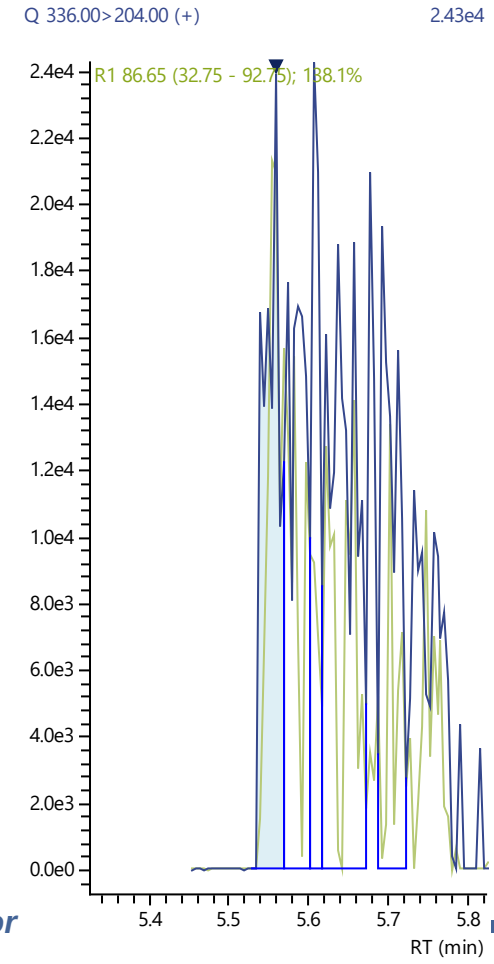
Shimadzu IP deact. Wool



Shimadzu Siltek deact. Wool



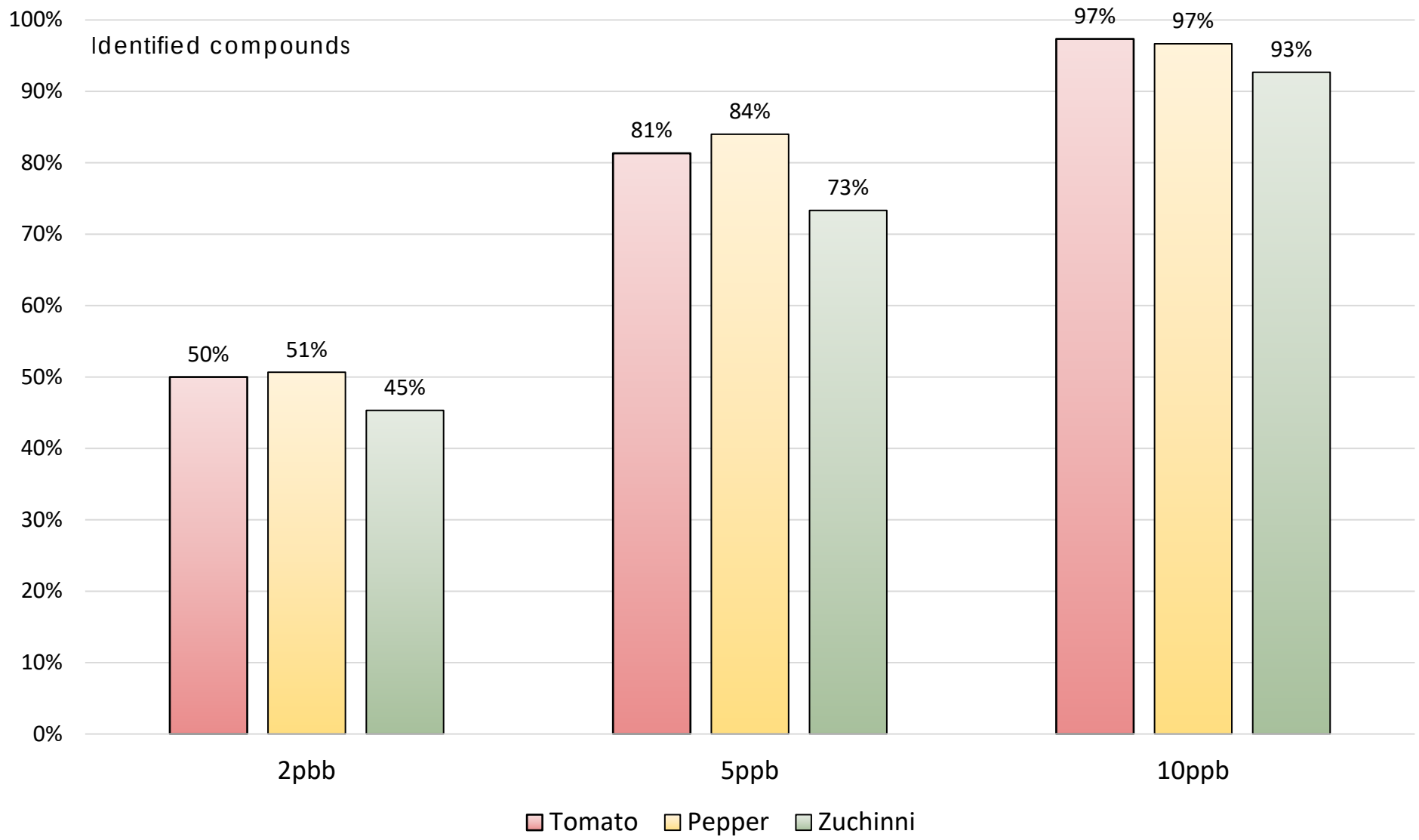
Restek Topaz No Wool



150 Pesticides
100 µg/Kg
Tomato

SENSITIVITY

150 Pesticides



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				

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.

http://www.eurl-pesticides.eu

Thank You for Your Attention

EURL EUROPEAN UNION REFERENCE LABORATORY

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- **Is helium an abundant element?**

  -Yes, it is abundant and easily recyclable.
  -No, the main reserves of helium are located under the Earth's crust.

- **Which carrier gas provides better chromatographic performance using GC-MS/MS?**

  - Helium

  - Hydrogen

  - Nitrogen

- **What is the main reason for the lower sensitivity of hydrogen compared to helium?**

  -The lack of inertness of hydrogen, as well as its small molecular size.

  -Its viscosity and diffusion coefficient values.

- **How should the explosion risk associated with hydrogen use be managed?**

  - Every step should be monitored carefully during batch injection to avoid any explosion.

  - The system will manage it. The chromatograph and hydrogen generator are equipped with sensors.

  (Remember, common sense and care are essential, as with any other system.)