VÝHODY A LIMITACE ORBITÁLNÍ PASTI V PROBLEMATICE DETEKCE A KVANTIFIKACE PESTICIDŮ V ROSTLINNÉM A JINÉM MATERIÁLU

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ADVANTAGES AND LIMITATIONS OF THE ORBITAL TRAP IN THE SCOPE OF DETECTION AND QUANTIFICATION OF PESTICIDES IN PLANT AND OTHER MATERIAL FROM AGRICULTURAL TERRAINS

HRMS INSTRUMENT: Q EXACTIVE FOCUS (THERMO)

Background of our project

- The constant growth of agricultural food production is inextricably linked to the necessary use of pesticides. Their effective analysis in various materials - parts of plants, soil or even in the bodies of insect pollinators is key to setting the safe use of such substances in agricultural ecosystems. The degree of effectiveness of the analytical system used for this purpose lies in the ability to capture representatives of this **huge group of many chemical classes, usually in trace amounts of their residues (ppb).** Regarding the use of a mass spectrometer based on the principle of orbital ion trap, we were able to see that even non-targeted analysis of pesticides is absolutely useful and prospective
- Results of these analyzes should maybe gradually contribute to a deeper understanding the European problem of mass extinction of bee colonies and other pollinators in the last decade of this century.
- Finally in the majority of cases we were satisfied with the basic full scan of the exact mass (full scan mode).

Honey Plants

- angelica zahradní, chrpa, zvonek zahradní, modrá phacelia, bílá hořčice, pohanka, východní třapatka nachová, trojlístek obecný, jetel karmínový, oregano, miláček, meduňka lékařská, náprstník obecný, brutnák lékařský, moldavská dračí hlava, šalvěj, volské oko sedmikráska, fialová viperova chyba a viperova chyba.

Svazenka vratičolistá - Phacelia tanacetifolia

Řepka olejka – Brassica napus L. (angl. RAPE, RAPESEED)

Pohanka setá – Polygonum fagopyrum

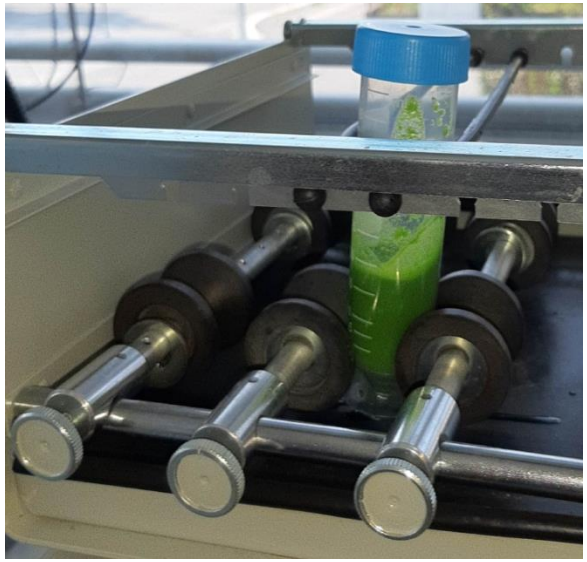
The Classification of Pesticide on the basis of Chemical Composition

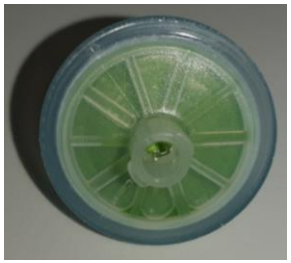
- more than 4600 registered preparations
- Fungicides: Fungicides are classified as aliphatic nitrogen fungicides (dodine), amide fungicides (carpropamid), aromatic fungicides (chlorothalonil), dicarboximide fungicides (famoxadone), dinitrophenol fungicides (dinocap) etc. Herbicides- The herbicides are anilide herbicides (flufenacet), phenoxyacetic herbicides (2, 4-D), quaternary ammonium herbicides (Paraquat), chlorotriazine herbicides (atrazine), sulfonylurea herbicides (chlorimuron), etc.

Classification of Pesticides in the perspective of Forensic Medicine and Toxicology

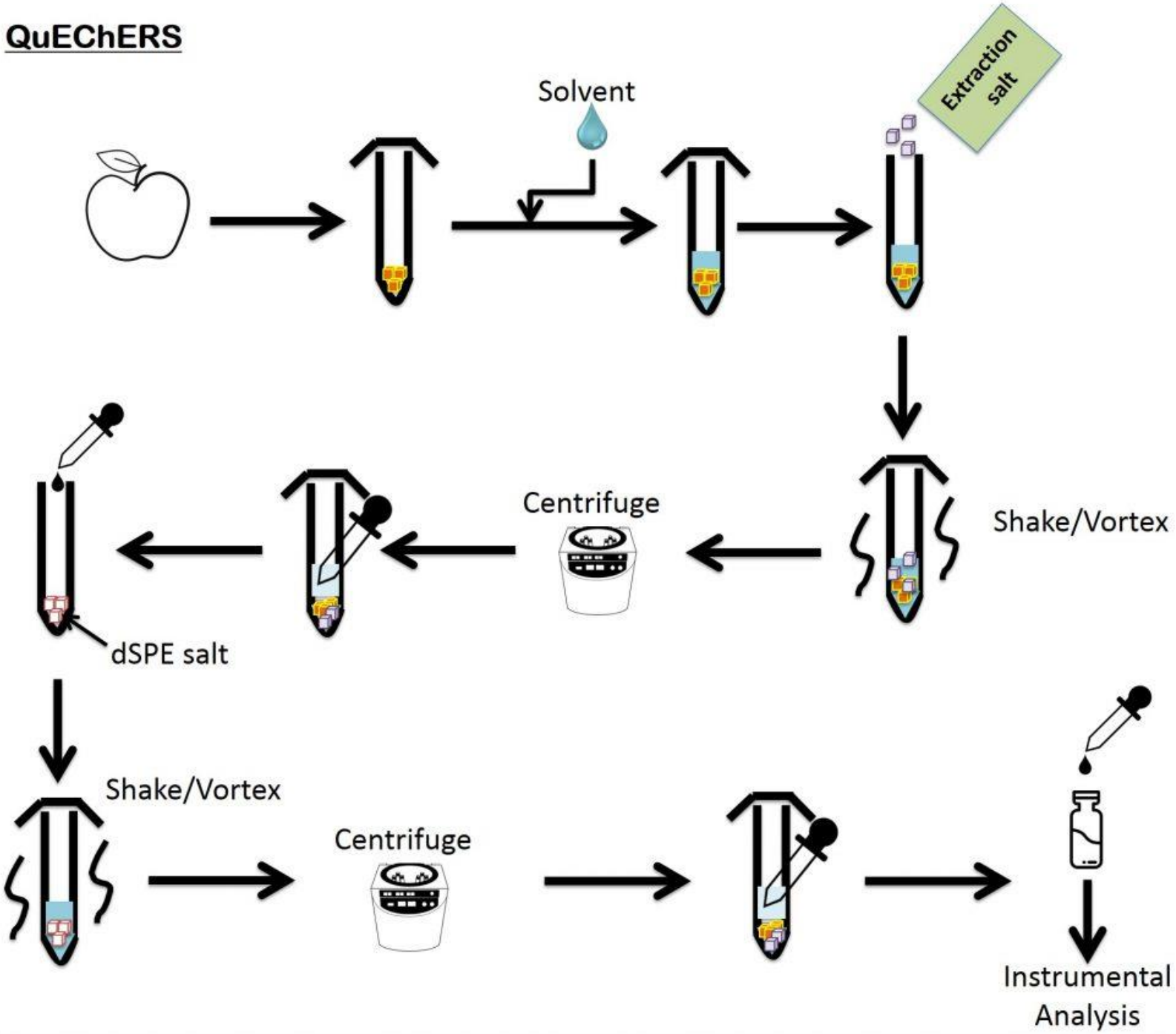
- *V. V. Pillay; Pesticides Chapter 34, Textbook of Forensic Medicine and Toxicology, 18th edition 2017, Paras Medical Publisher, Hyderabad. p. 645.*

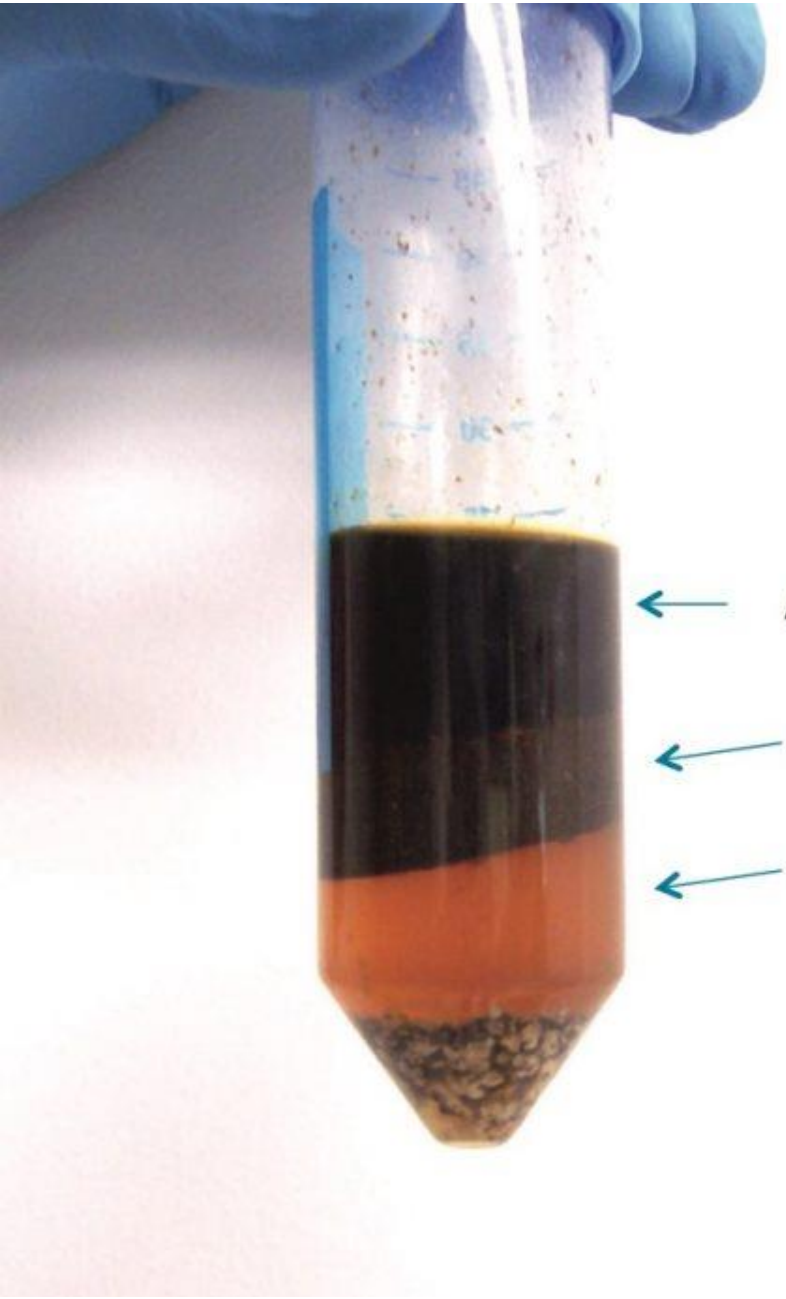
- 1. **Insecticides** – Compounds which kill or repel insects and related species. e. g. Organophosphates, Organochlorine, Carbamates etc. 2. **Herbicides** – Compounds which kill weeds/ prevent growth of undesirable herbs or weeds in the field. e. g. parquet, atrazine etc. 3. **Fungicides** – Compounds which kill fungi and moulds. e. g. Captan, Captofol etc. 4. Rodenticides – Compounds which kill rats, mice, moles and other rodents. E.g. anticoagulants, arsenic, strychnine etc. 5. Acaricides – Compounds which kill mites, ticks and spiders. e. g. azobenzene, chlorobenezilate etc. 6. Nematicides – Compounds which kill nematodes. e.g. Ethylene bromide 7. Molluscicides – Compounds which kill the molluscs such as snails and slugs. e. g. Metaldehyde. 8. Miscellaneous Pesticides – Compounds of lead, Copper, Mercury, nicotine etc.



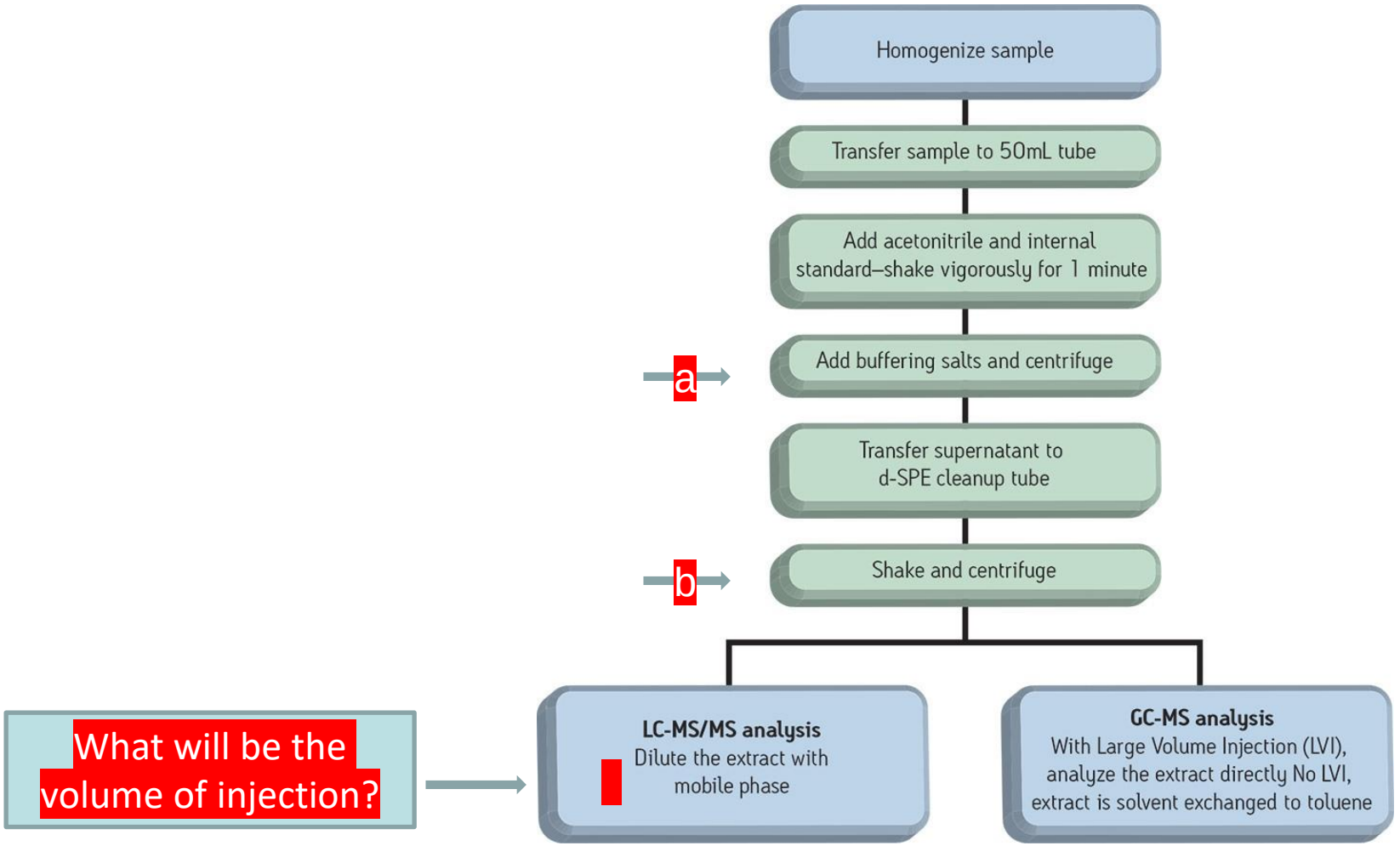


The Preparation of „smoothie“ sample (primary sample)


QuEChERS
Solvent
Extraction salt
Shake/Vortex
Centrifuge
dSPE salt
Shake/Vortex
Centrifuge
Instrumental Analysis


ACN layer (pesticides are here)
Tea solids
Aqueous layer (sugars and salts are here)

Schema from Waters Corp.:



Analytical Instrumental Equipment

- Mobile Phases, A: 0,1% HCOOH,D: MeOH/MeCN/HCOOH (50/50/0,1%)
- Column LUNA Omega-C18, 50mm x 2.1mm,1.6µm
- PAL Thermo
- Q Exactive Focus

Non-target gradient chromatography – „CONFPESTANAL“

	Start	time	flow	gradient	%A	%B
1.	0,00	60	0,30	Step	100	
2.	1,00	420	0,30	Ramp		100
3.	8,00	240	0,30	Step		100
4.	12,00	30	0,30	Ramp	100	
5.	12,50	90	0,30	Ramp	100	
6.	14,00	90	0,30	Step	100	

MS Parameters for Non-Target

Scan modes: Full MS, Full MS confirm
Chrom peak width: 6s.
Method duration: 14,00 min
Resolution: 70 000.
Scan range: 100 – 1000 m/z.
Autogain control(AGC targed): 1e6
H-ESI → Sheath Gas : 32

→ **Aux Gas:** 6
Cone (spray) voltage: 3,5 kV/2.2 kV for negatives
Capillary temperature: 290 °C
Vaporizer (Aux Gas Heater) temp: 200(temp labile compounds)-350°C
S-lens RF level: 55,0
1/ Vol of injection: 1.3 µl from dried sample reconstituted in 200 µl of MP D
2/ Vol of injection: 1.0 µl of 1.7 ml extract filtrated through 0.22 nylon membrane and diluted v/v by MPD

Salads/qualitative microinvestigation, 6collections (A-F), results below

Species

- Dubáček, 10A-F
- Ledový, 9A-F
- Lollo Rosso, 11A-F
- Lollo Biondo, 12A-F
- Římský,13A-F
- suspected use of three products at once: STOMP, GONDOLA, ALLIETE

Images





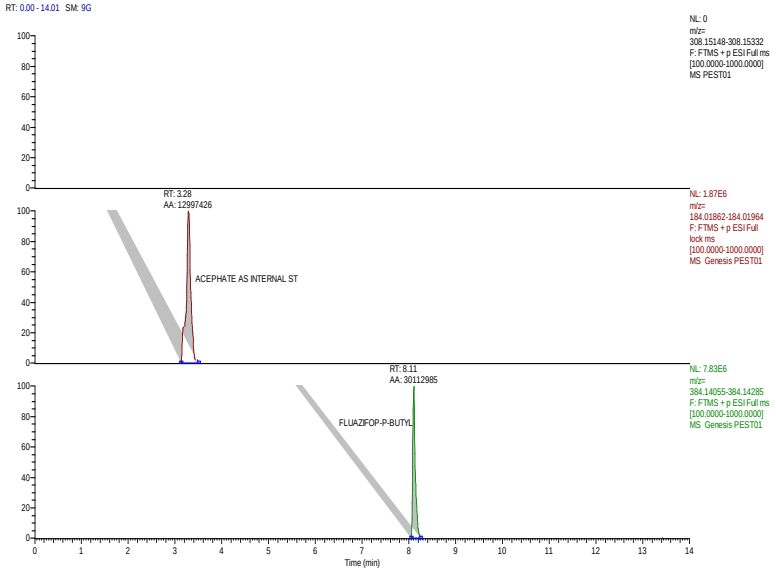

Some excerpts of qualitative results from pestanal monitoring in agricultural products – salads see above

- **9A – F: pendimethalin (STOMP)**
- **10A - F: pendimethalin,sulfoxaflor (GONDOLA)**
- **11A – F: pendimethalin,sulfoxaflor (GONDOLA)**
- **12A – F: pendimethalin (STOMP)**
- **13A – F: pendimethalin,sulfoxaflor (GONDOLA)**
- **The Use of ALIETTE has not be proven (active substance – fosetyl-Al)**

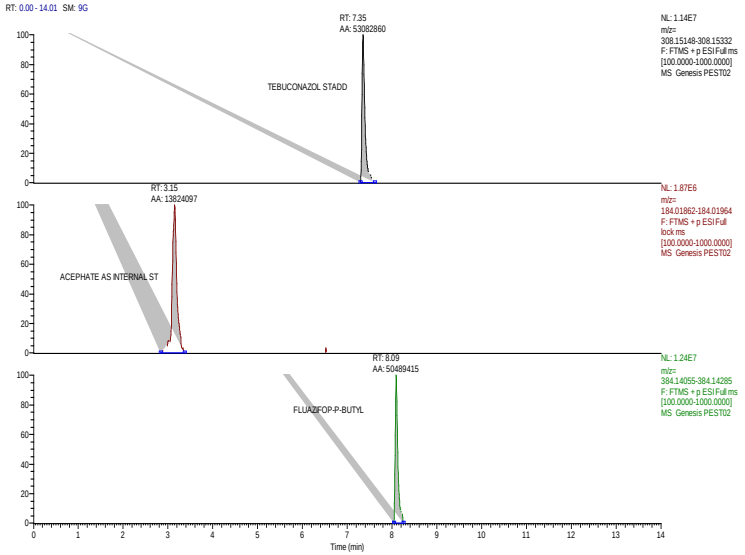
Note: Acephate was used as the control internal standard

Non- targeted screening and Accurate Mass Confirmation on the Focus HRMS instrument – contradictory samples

- Sample 1 free from an pesticide standard addition, positive fluazi



- Sample 2 with tebuco standard addition, positive fluazifop-p-bu



Quant results - excerpts

- **Svazenka:** Fluazifop-p-butyl 1-10-20-50ppb (4collection times)
- Acetamiprid 1-5-15-25 ppb (4collection times)

- **Pohanka:** Fluazifop-p-butyl 1-10-20-50ppb (4collection times)
- Acetamiprid 1-10-20-50 ppb (4collection times)

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Important Others:

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