EURL-FV

EUROPEAN UNION REFERENCE LABORATORY FOR PESTICIDES RESIDUES IN FRUITS AND VEGETABLES

IMPROVEMENT OF MULTIRESIDUE METHOD FOR PESTICIDE ANALYSIS WITH HIGH FAT AND PROTEIN CONTENT COMMODITIES BY USING MULTIPLE CLEAN UP STEPS BASED ON QUECHERS

EPRW 2016 **Limassol**

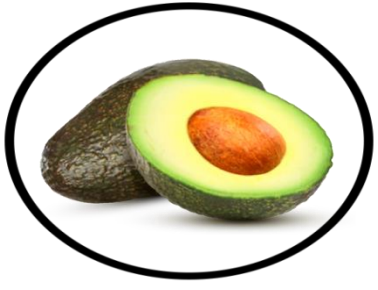
Victor Cutillas

Samanta Uclés, Amadeo Fernández-Alba

HIGH FAT AND PROTEIN CONTENT COMMODITIES

HIGH FAT CONTENT

20 – 30% Fatty Acids (Palmitic, oleic and linoleic) And triglycerides



≈99% Fatty Acids (Palmitic, oleic and linoleic)

PROTEIN CONTENT

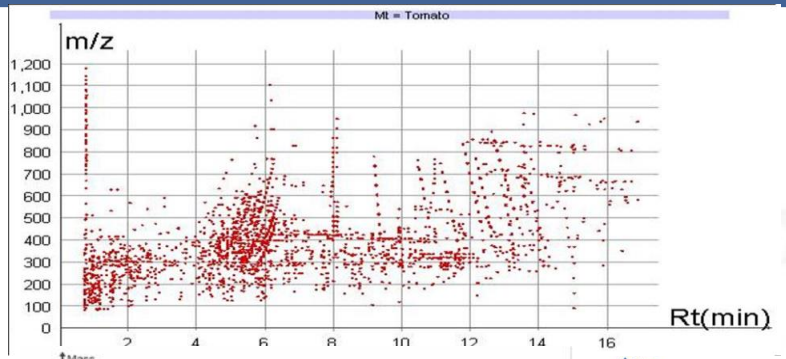
25% Proteins
5% Fat

25% Proteins

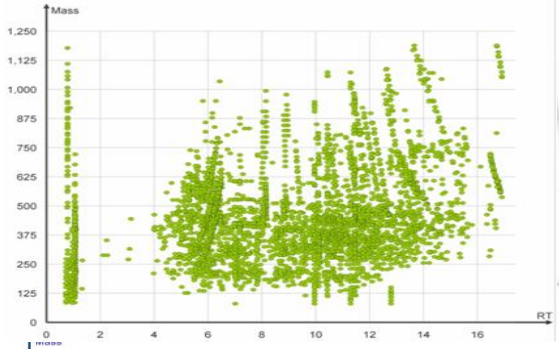
Co-extracted matrix components. LC-QTOF-MS

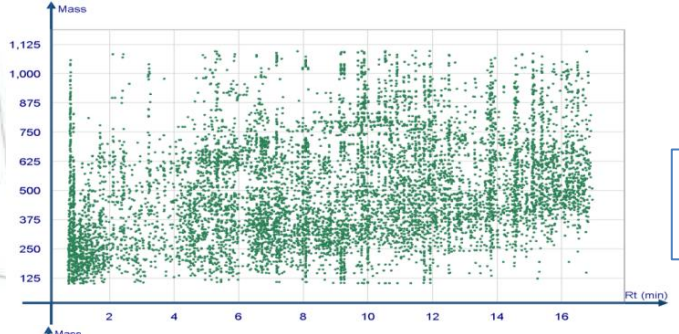
Injection volume: 4 µL

Tomato (1 g/mL)



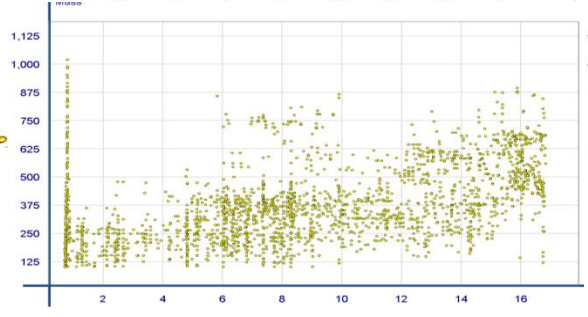
Avocado (0,5g/mL)

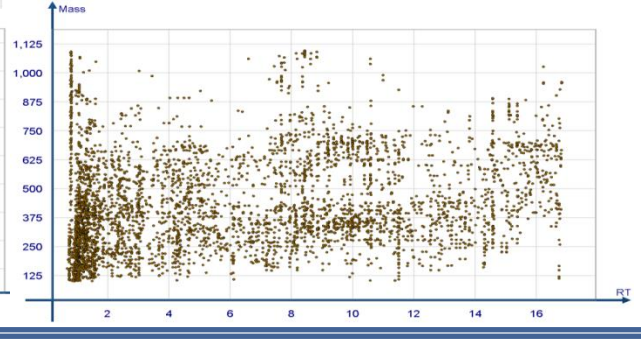




Bee Pollen (0,5g/mL)

Olive oil (0,2g/mL)





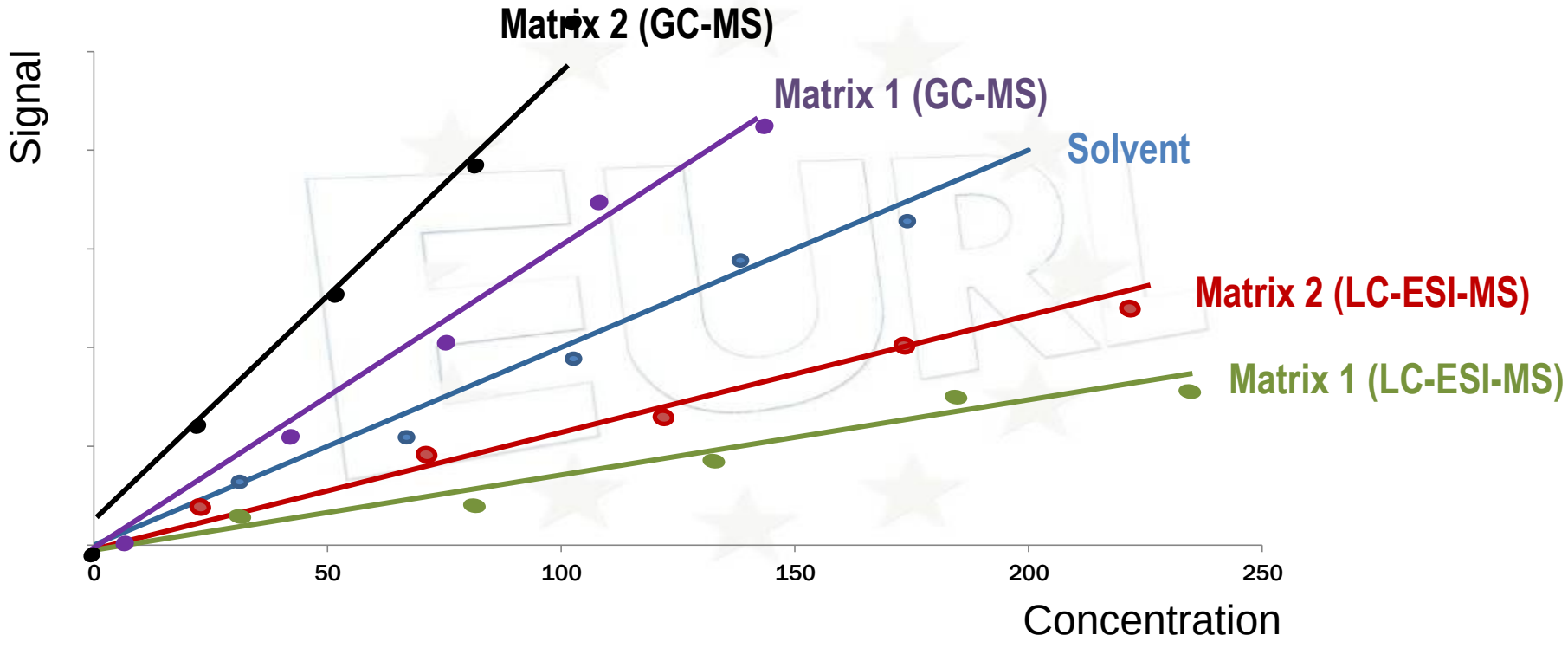
Lentils (0,2g/mL)

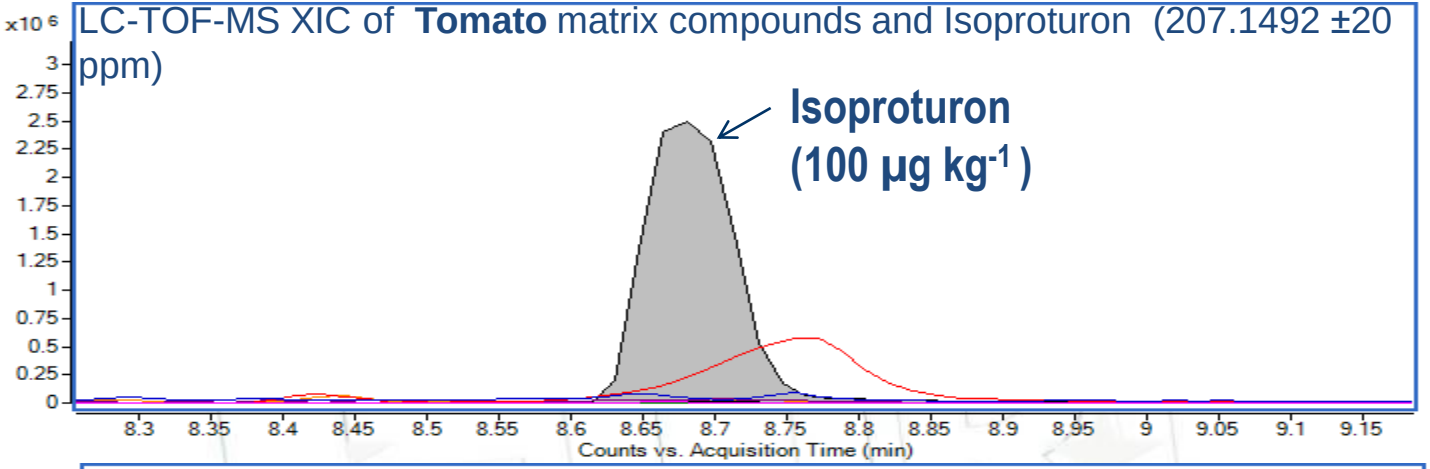
CONSEQUENCES OF «DIRTY» MATRICES

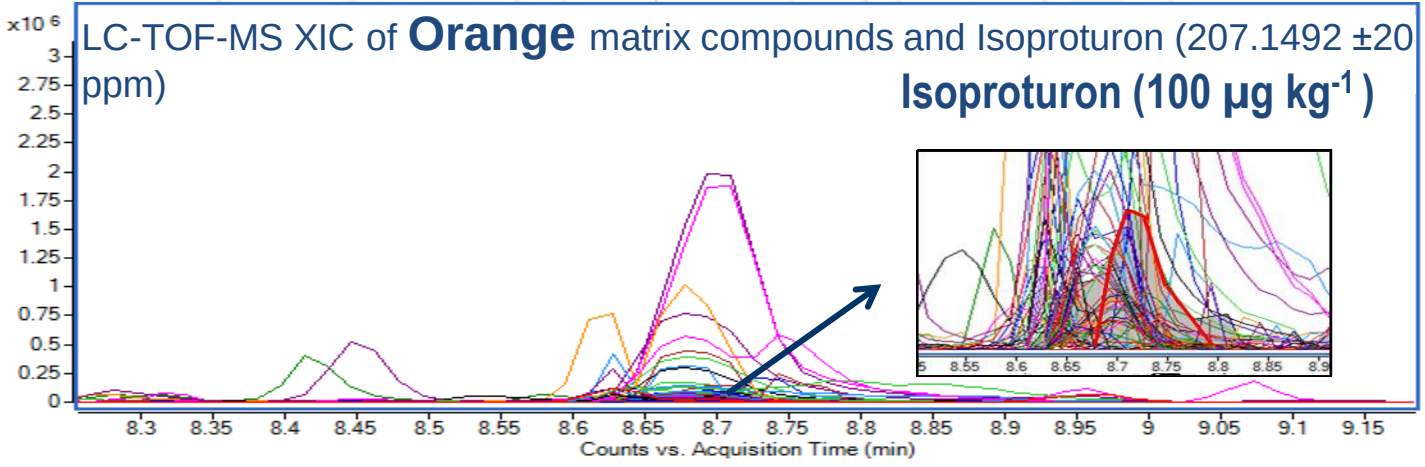
LC-QqQ-MS/MS
Skimer
After 30 injections

GC-Q-MS Liner after
40 injections

Injecting 1 g sample/mL

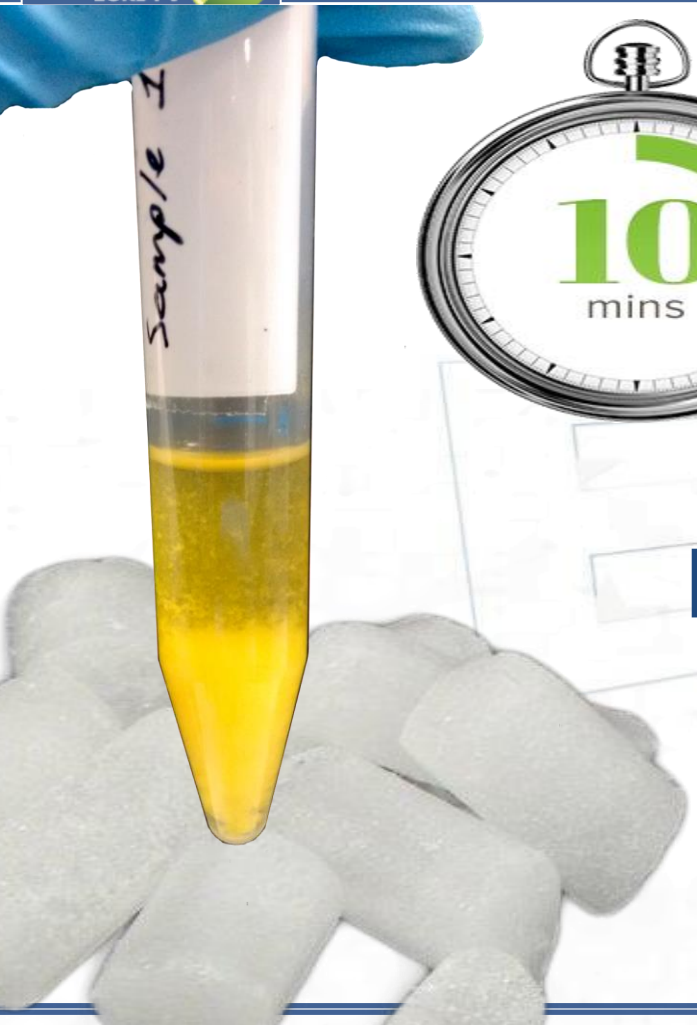

Matrix 2 (GC-MS)
Matrix 1 (GC-MS)
Solvent
Matrix 2 (LC-ESI-MS)
Matrix 1 (LC-ESI-MS)
Signal
0
50
100
150
200
250
Concentration


LC-TOF-MS XIC of **Tomato** matrix compounds and Isoproturon (207.1492 ±20 ppm)
Isoproturon
(100 µg kg-1)
x10 6
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
8.3 8.35 8.4 8.45 8.5 8.55 8.6 8.65 8.7 8.75 8.8 8.85 8.9 8.95 9 9.05 9.1 9.15
Counts vs. Acquisition Time (min)


LC-TOF-MS XIC of **Orange** matrix compounds and Isoproturon (207.1492 ±20 ppm)
Isoproturon (100 µg kg-1)
x10 6
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
8.3 8.35 8.4 8.45 8.5 8.55 8.6 8.65 8.7 8.75 8.8 8.85 8.9 8.95 9 9.05 9.1 9.15
Counts vs. Acquisition Time (min)

STUDIES

Fast freezing out and new sorbents (SPE and dSPE)



FAST FREEZING OUT

DRY ICE

-78ºC

EFFICIENT LIPID AND PROTEIN* REMOVAL BY PRECIPITATION

REDUCING TIME TO A FEW MINUTES

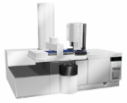
FREEZING OUT STEP REPRODUCIBILITY

SAME QUANTITY OF DRY ICE

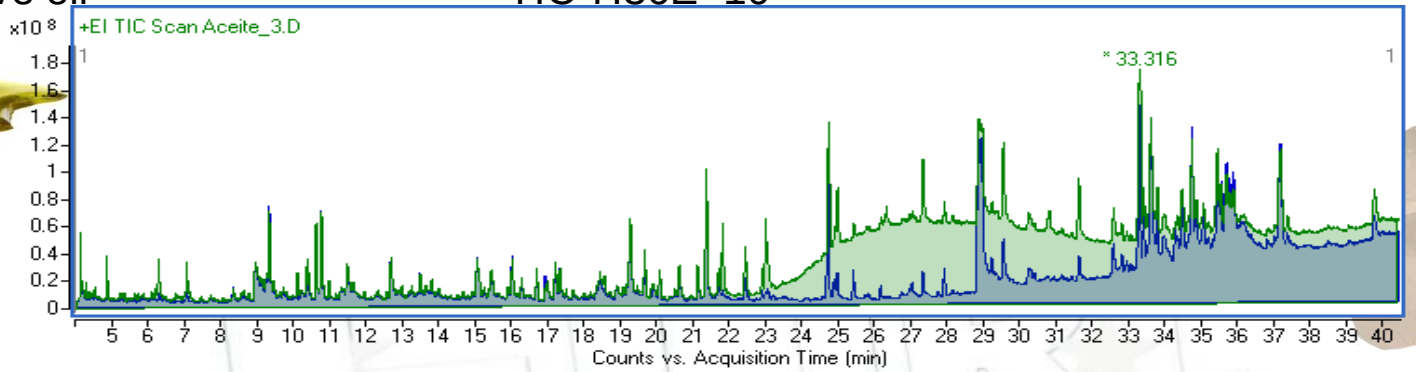
SAME TIME TO AN EQUAL VOLUME

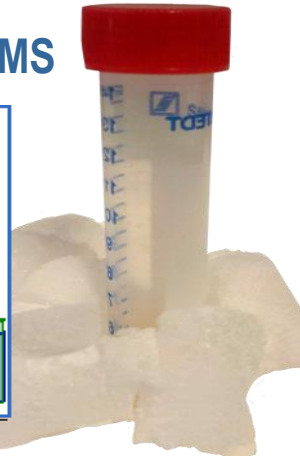
Olive oil with **Freezing out** TIC 4.21E+10

Olive oil TIC 7.36E+10



TIC Olive Oil GC-QTOF-MS

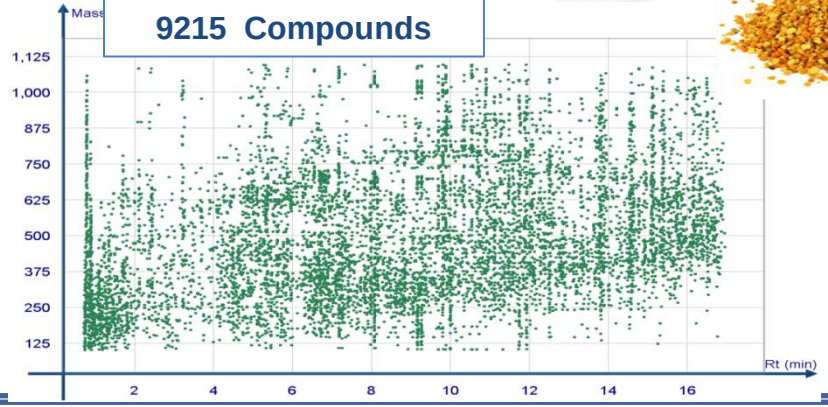




Co-extracted matrix components of Pollen LC-QTOF-MS

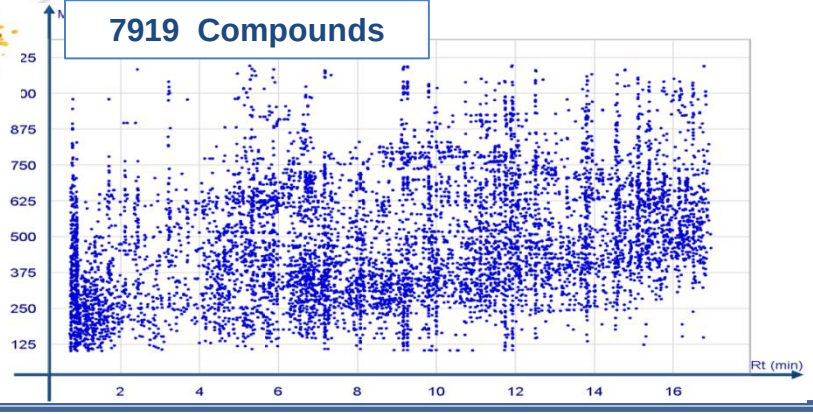
QuEChERS (Pollen)

9215 Compounds

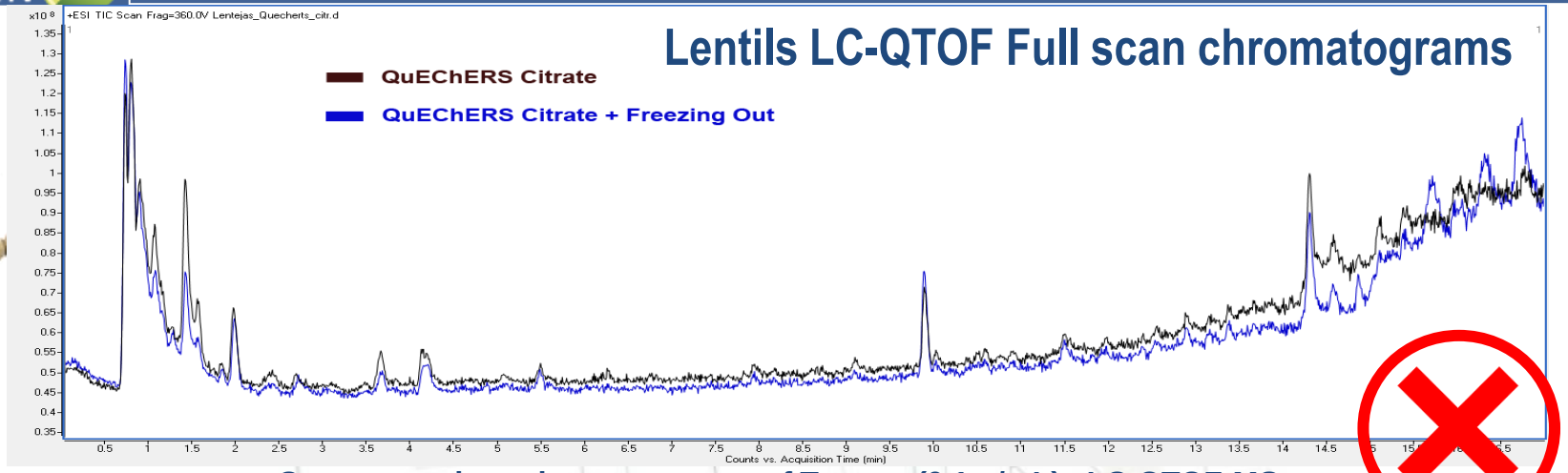


QuEChERS + Fast Freezing out CO_2

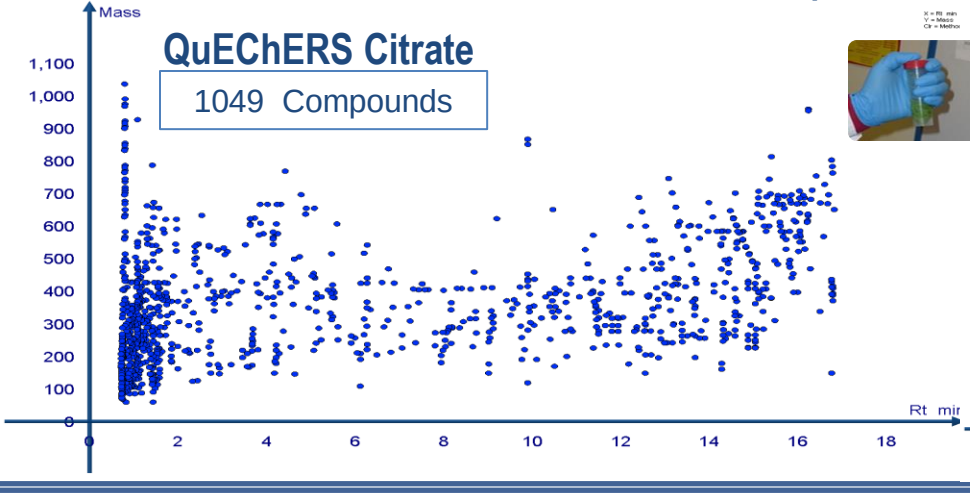
7919 Compounds

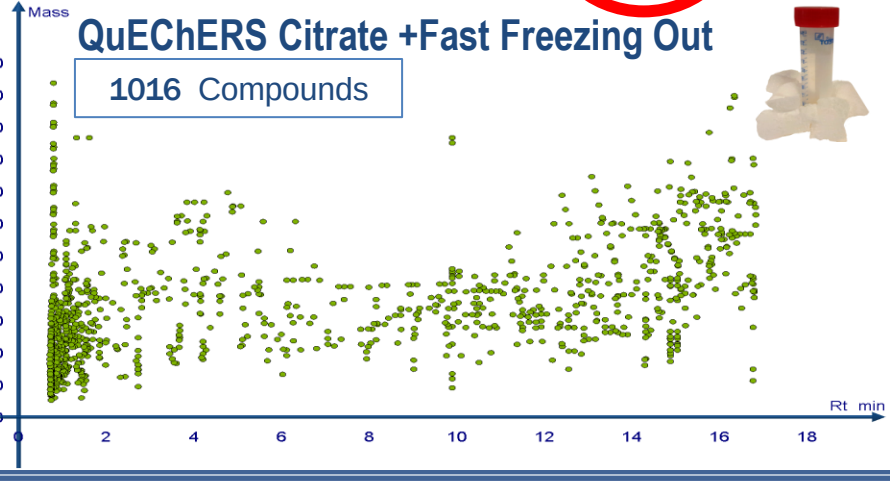


Lentils LC-QTOF Full scan chromatograms



Co-extracted matrix components of Tomato (0.1 g/mL). LC-QTOF-MS



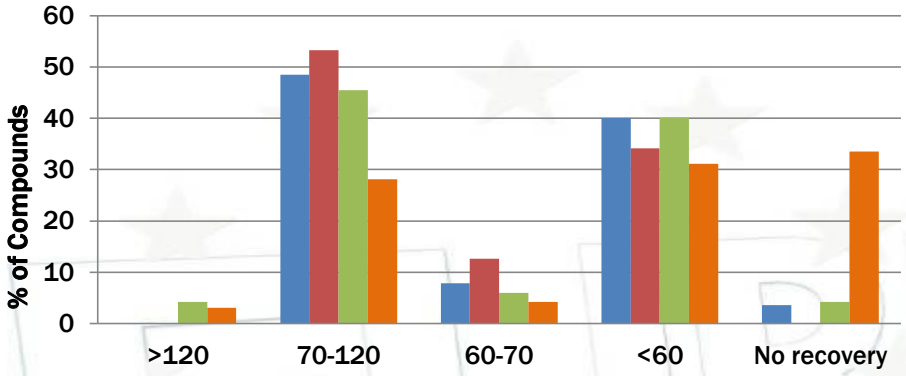


IN SOME COMMODITIES COEXTRATIVES REMOVAL IS NOT ENOUGH AND ADDITIONAL CLEAN UPS ARE NECESSARY

PSA + C18	dSPE
Z-Sep (ZrO_2+C18)	dSPE
	SPE
EMR	dSPE (2xsteps)

OLIVE OIL
Clean ups
After Freezing Out

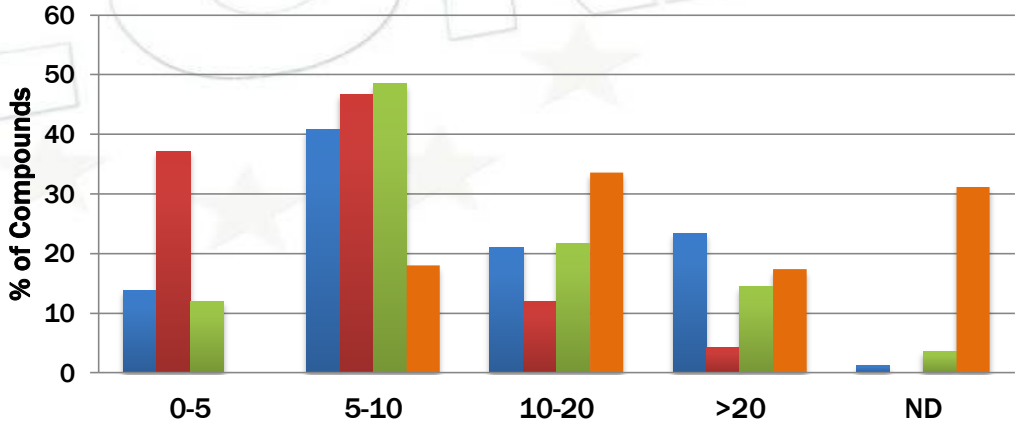
Recoveries (%) LC-MS/MS



PSA
EMR
ZrO_2-dSPE
ZrO_2-SPE

n=167

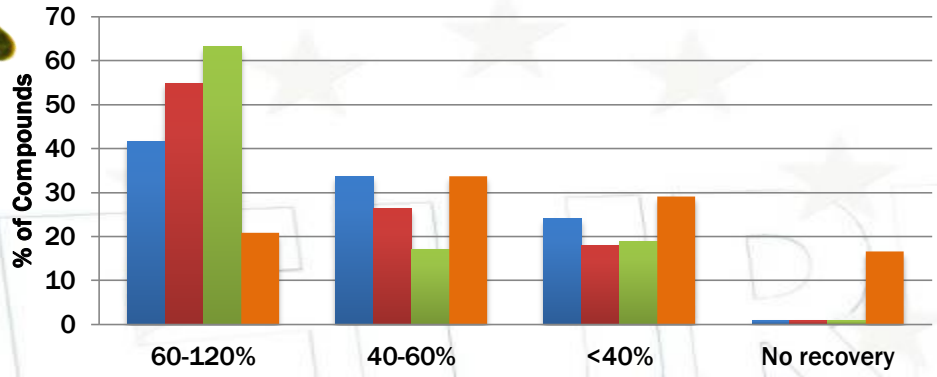
RSD (%)



LC

OLIVE OIL
Clean ups
After Freezing Out

Recoveries (%) GC-MS/MS



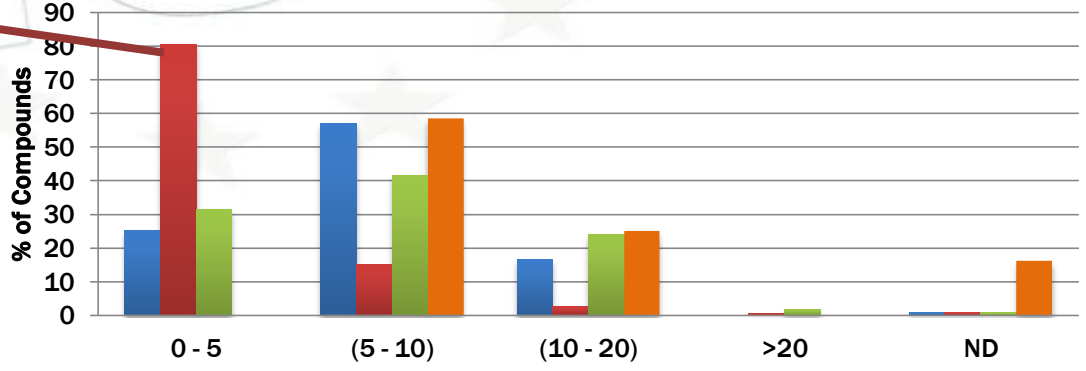
PSA
EMR
ZrO_2-dSPE
ZrO_2-SPE

n=213

EXCELENT REPRODUCIBILITY (EMR) 81% of Compounds

GC

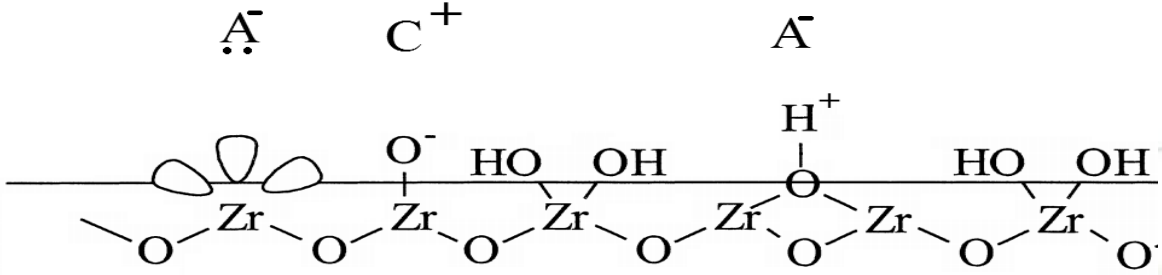
RSD (%)



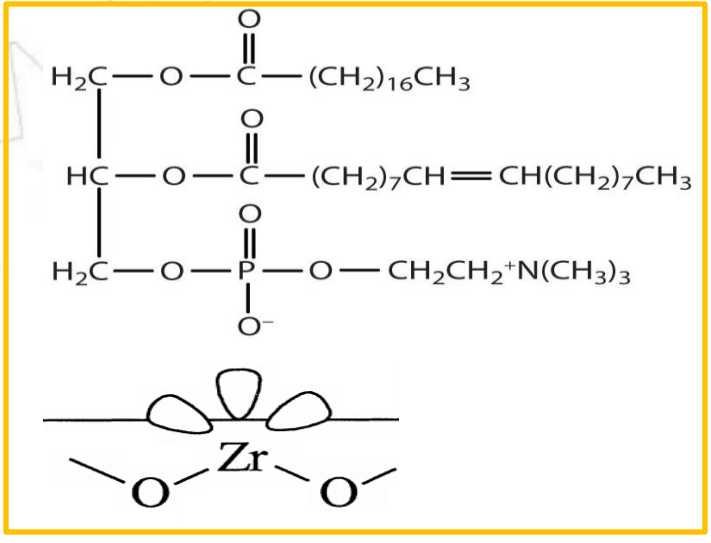
ZIRCONIUM DIOXIDE (Z-SEP)

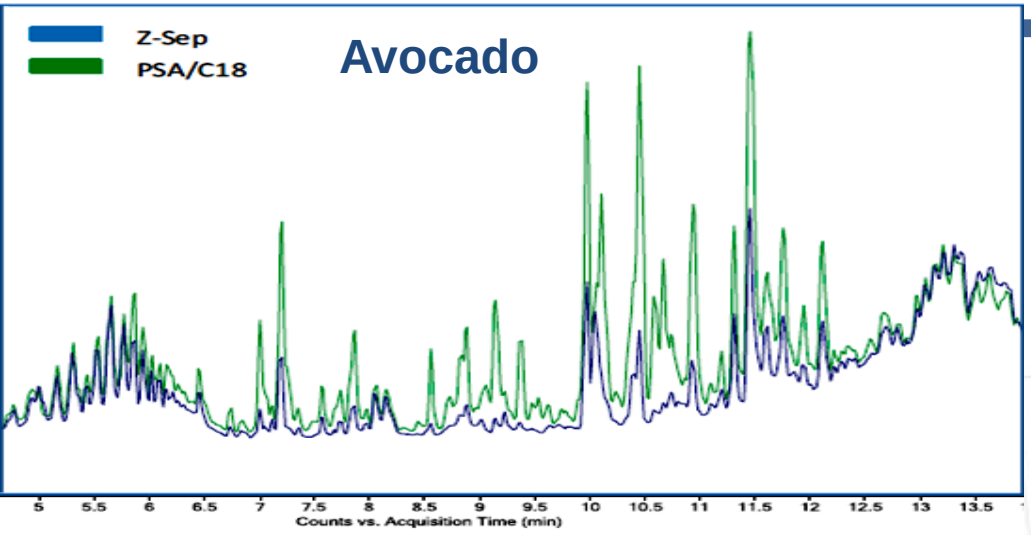
Zirconium dioxide surface acts as:

- **Brønsted acid (adsorption of anions in low pH via electrostatic interaction)**
- **Brønsted base (adsorption of cations in high pH via electrostatic interaction)**
- **Lewis acid (adsorption of Lewis bases via coordination bond with Zr atoms)**

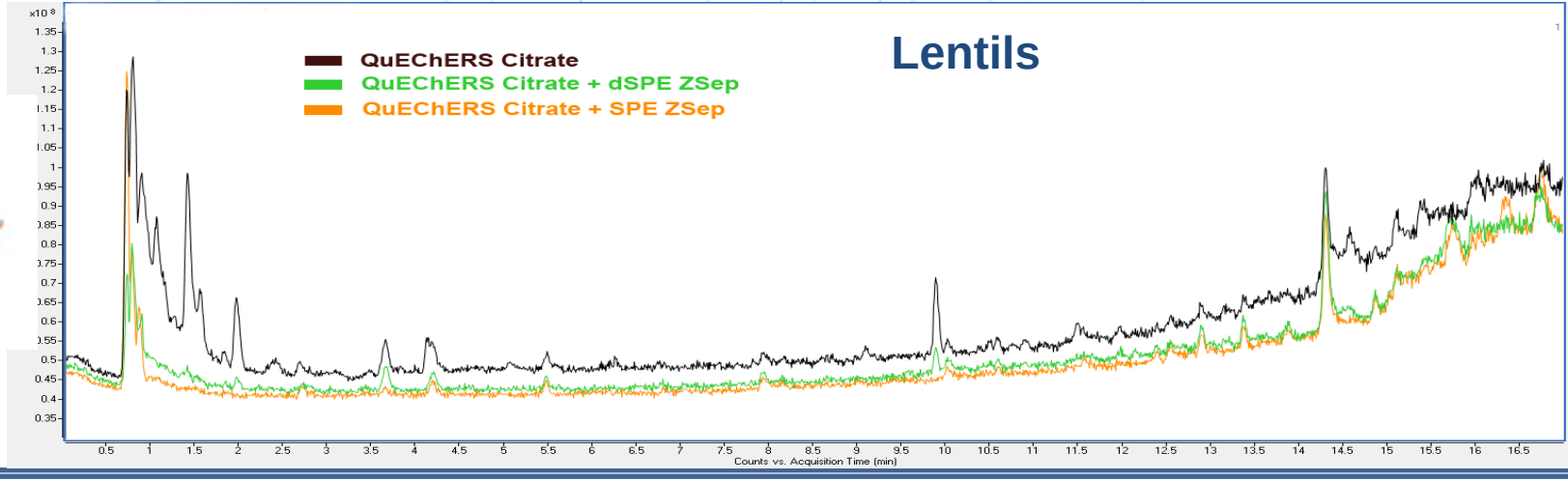


Interaction of phospholipid molecule with empty d-orbital of zirconium atom.

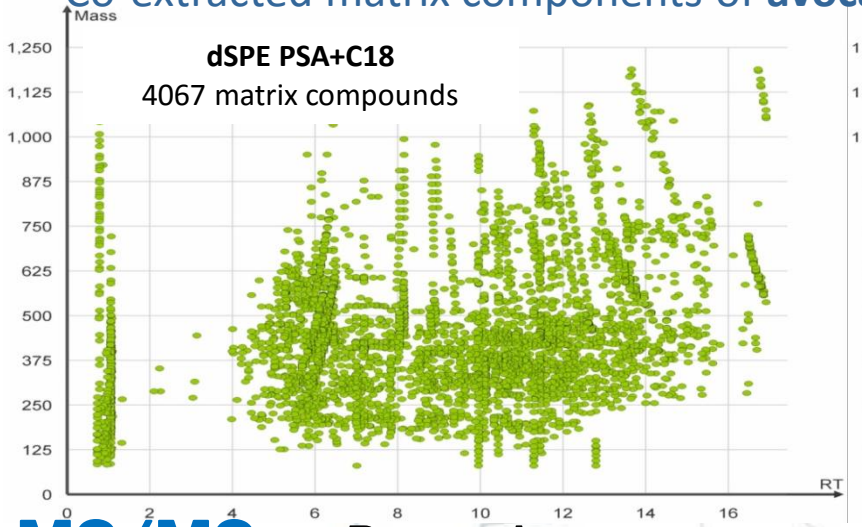


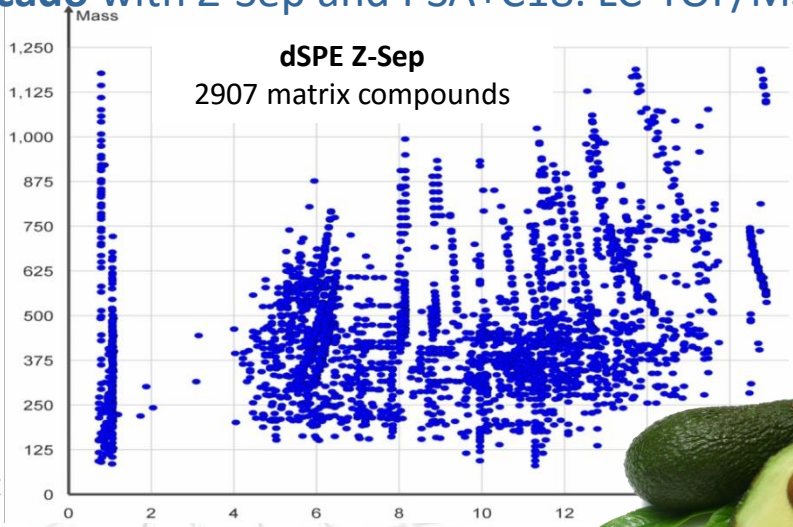


LC-QTOF Full scan chromatograms of avocado and lentils extracts with different sorbents

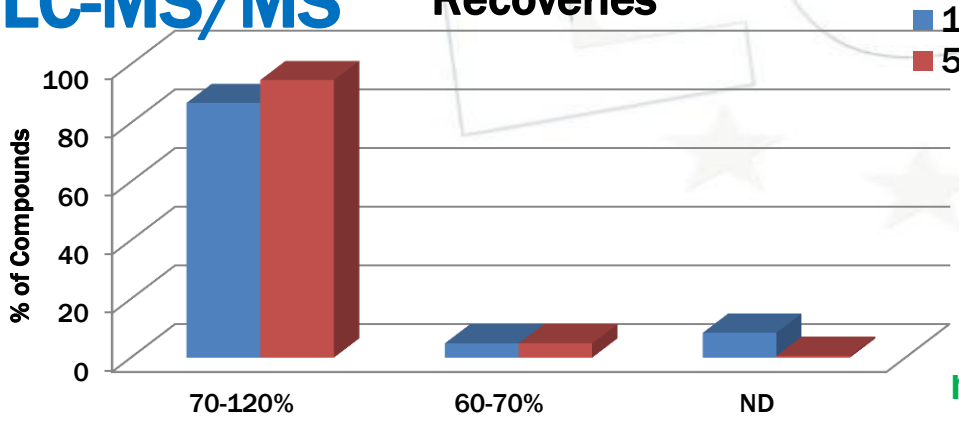


Co-extracted matrix components of **avocado** with Z-Sep and PSA+C18. LC-TOF/MS

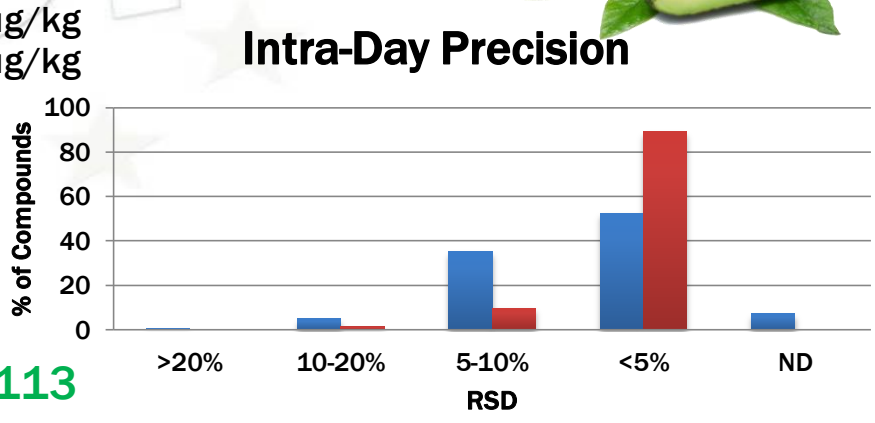




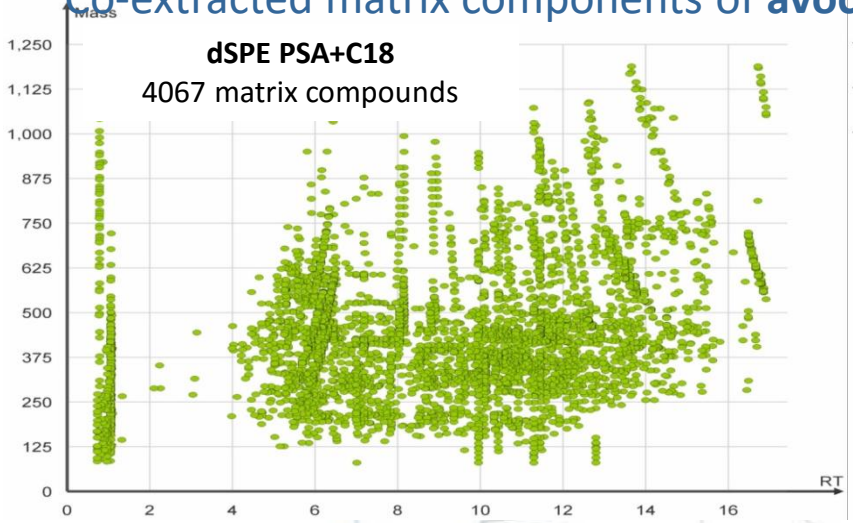
LC-MS/MS

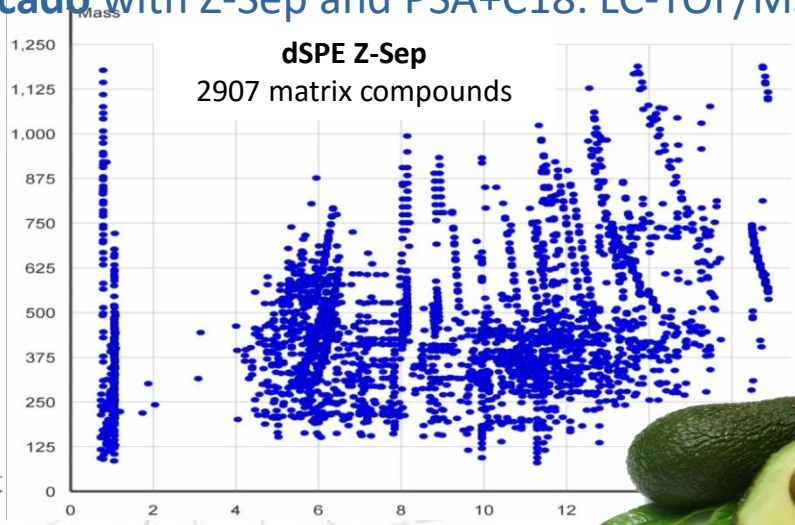


n=113



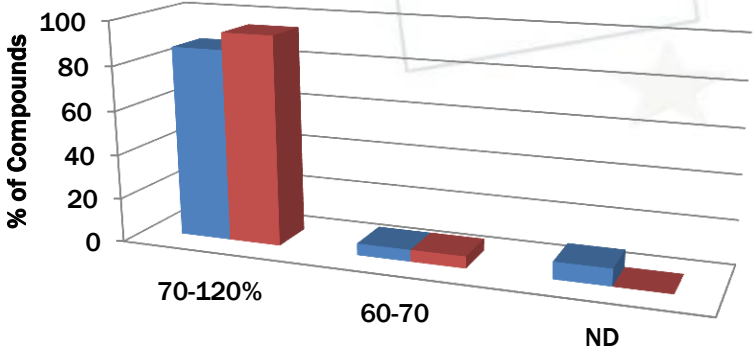
Co-extracted matrix components of **avocado** with Z-Sep and PSA+C18. LC-TOF/MS





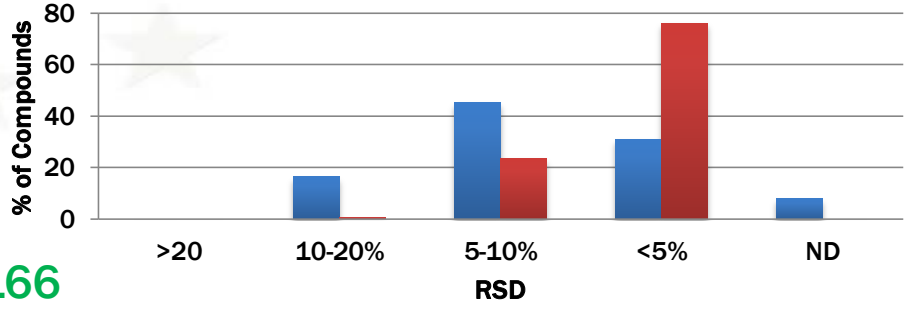
GC-MS/MS

Recoveries

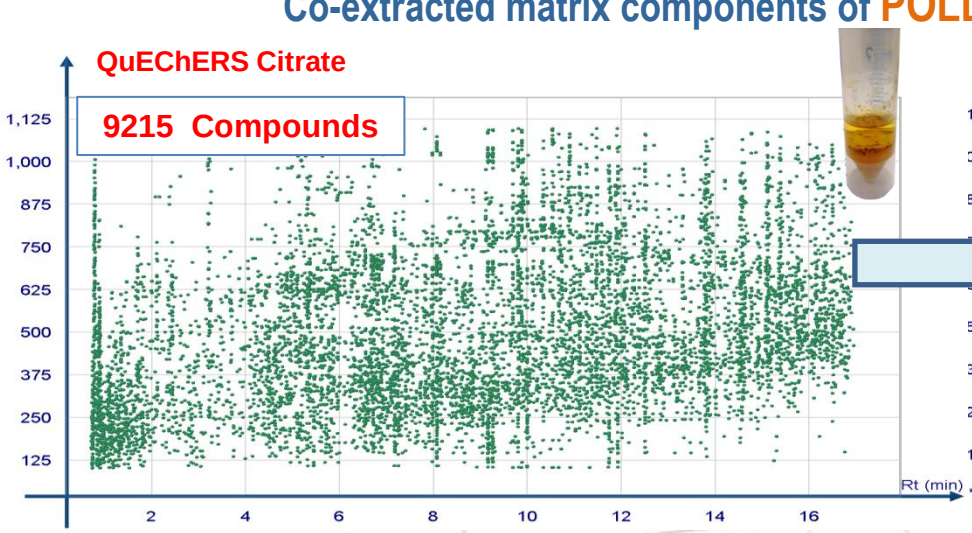


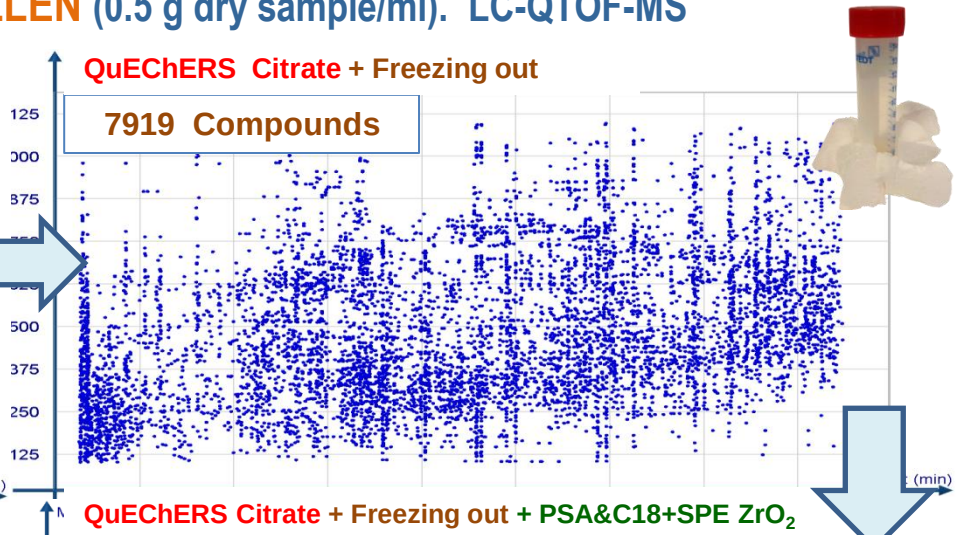
n=166

Intra-Day Precision



Co-extracted matrix components of POLLEN (0.5 g dry sample/ml). LC-QTOF-MS

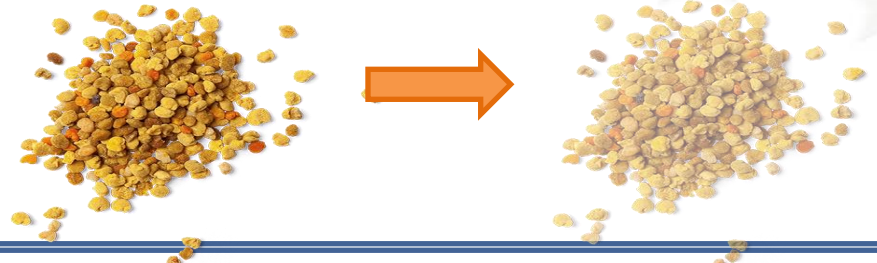


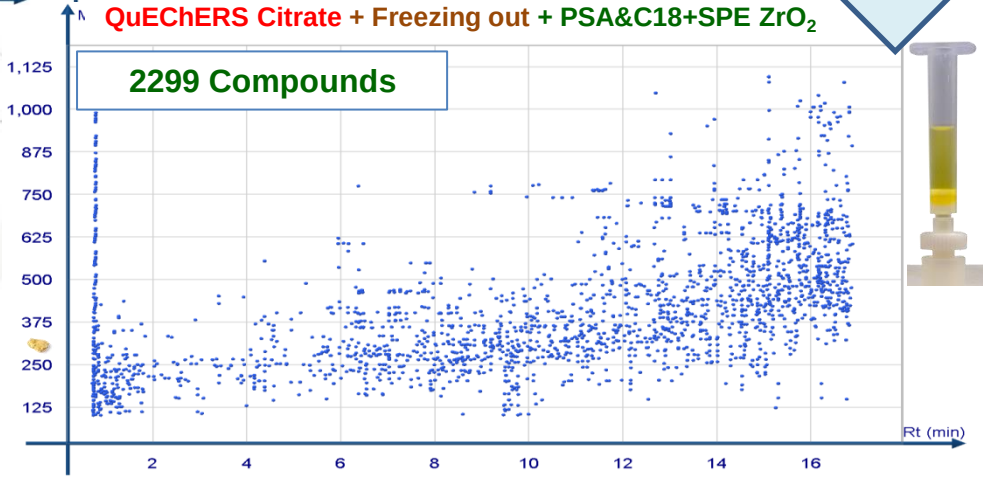


Multiple Clean up Steps:

- ≈ 7000 Compounds

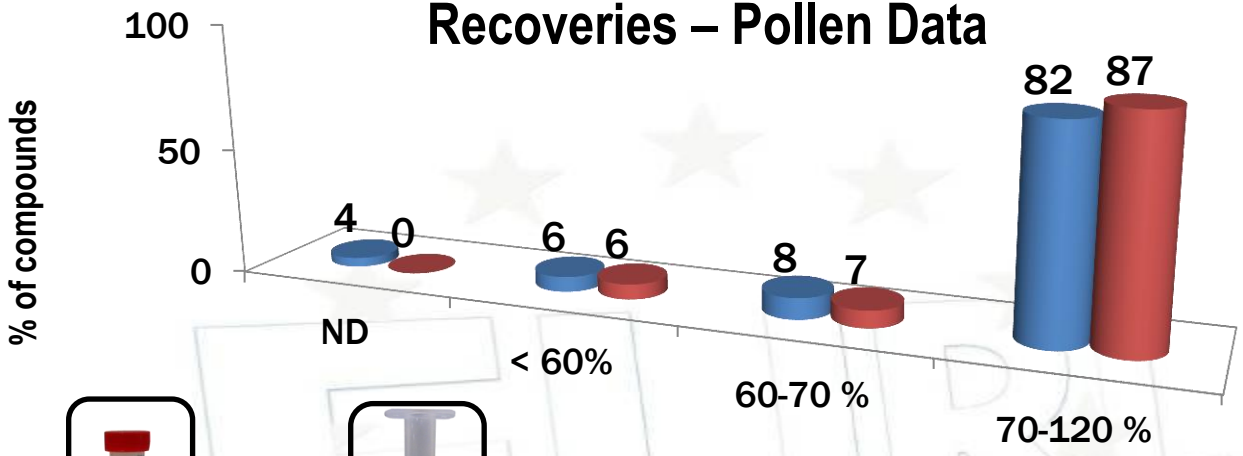
BEE POLLEN

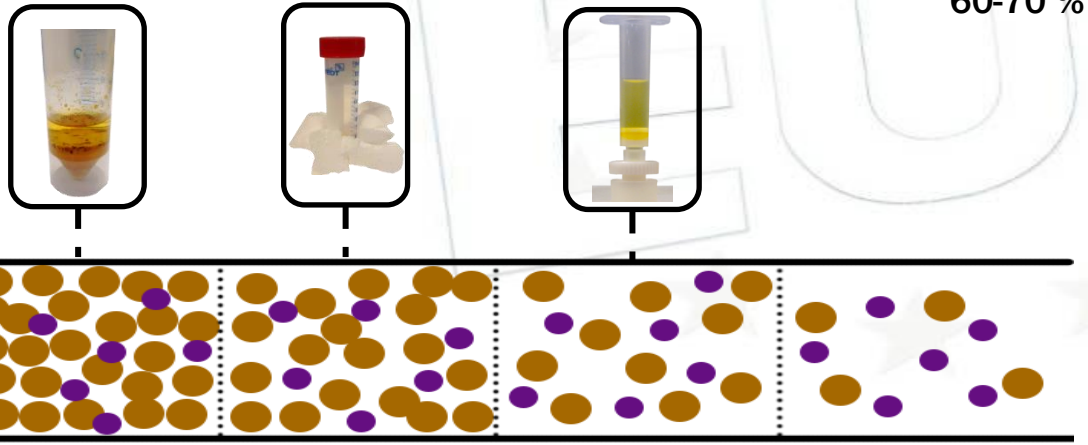




Recoveries – Pollen Data

n=251

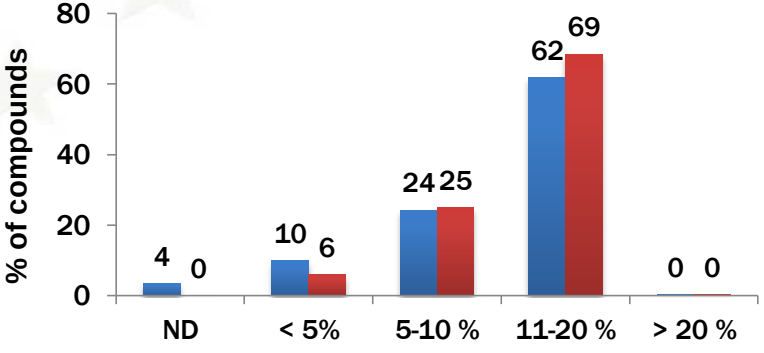




Matrix Compounds

Pesticides

Intra-day precision



CONCLUSIONS

- Sample extraction procedures should be adapted in the case of dealing with difficult commodities.
- Fast freezing out can remove a significant number of coextractives in a easy and quick way.
- Cleaner extracts were obtained by the implementation of different sorbents during the validation procedure.

www.eurl-pesticides.eu

EPRW
2016 Limassol

Thank You
for Your Attention

European Commission

EURL EUROPEAN UNION REFERENCE LABORATORY

EURL-FV

EUROPEAN UNION REFERENCE LABORATORY FOR PESTICIDES RESIDUES IN FRUITS AND VEGETABLES

IMPROVEMENT OF MULTIRESIDUE METHOD FOR PESTICIDE ANALYSIS WITH HIGH FAT AND PROTEIN CONTENT COMMODITIES BY USING MULTIPLE CLEAN UP STEPS BASED ON QUECHERS

EPRW 2016 **Limassol**

Victor Cutillas

Samanta Uclés, Amadeo Fernández-Alba