

AUTOMATISATION OF THE CLEANUP STEP OF MULTIRESIDUE METHODS IN LC-MS FOR HIGH FAT CONTENT COMMODITIES



EURL

EUROPEAN
UNION
REFERENCE
LABORATORY

PESTICIDES IN FRUITS
AND VEGETABLES

2024 ALMERIA



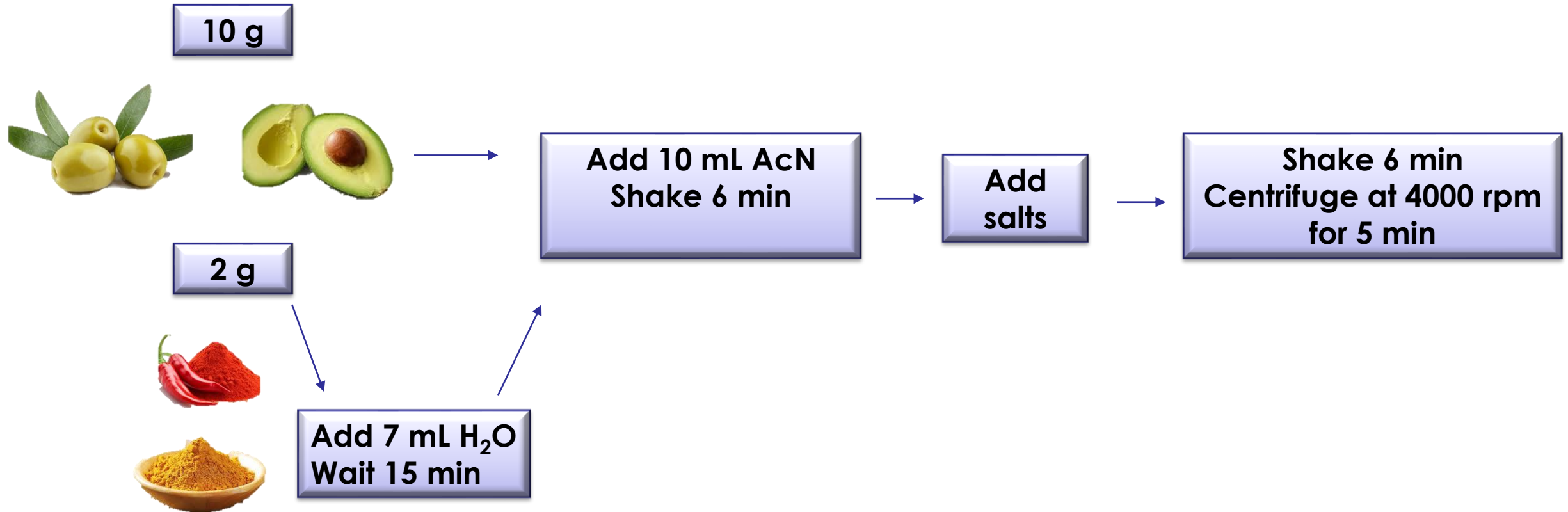
This study compared manual dSPE with automated μ SPE workflows for cleaning extracts of olives, avocado, and various spices (paprika and curry). Both methods employed QuEChERS extraction for a target list of 264 pesticides.



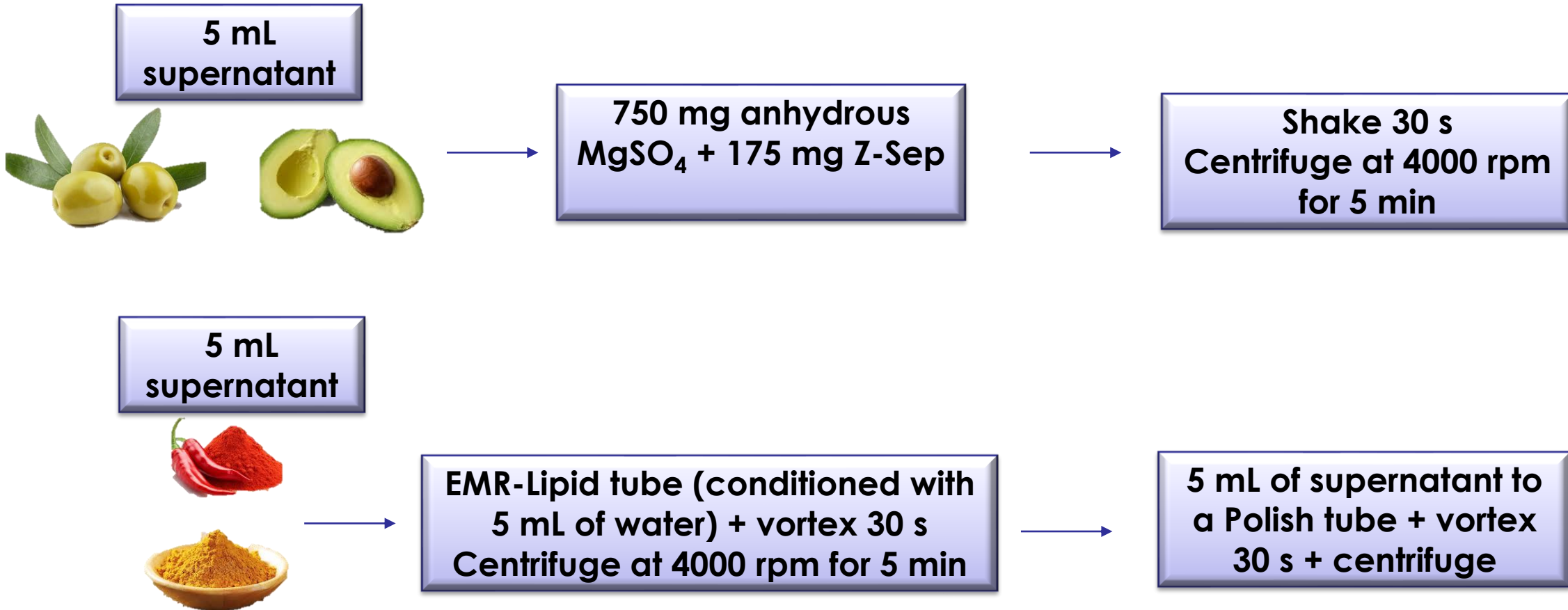
| Sorbent | Amount | Format | Automatisation |
|---|---|-------------------|----------------|
| anhydrous MgSO₄/PSA/C18/CarbonX | 20/12/12/1 mg | μ SPE | ✓ |
| EMR | 30 mg | μ SPE | ✓ |
| EMR | 15 mg | μ SPE | ✓ |
| C18 | 15 mg | μ SPE | ✓ |
| anhydrous MgSO₄/Zsep | 750/175 mg | dSPE (avocado) | |
| EMR-Lipid/EMR Lipid Polish | 1000 mg / 2000 mg (anhydrous MgSO ₄ /NaCl (4:1)) | dSPE (spices) | |

Spanish Food Composition Database. <https://www.bedca.net/bdpub/> (Access in May 2024)

Extraction Step: Citrate QuEChERS



dSPE



Automated μ SPE



200 μ L extract
without clean-
up + 50 μ L AcN

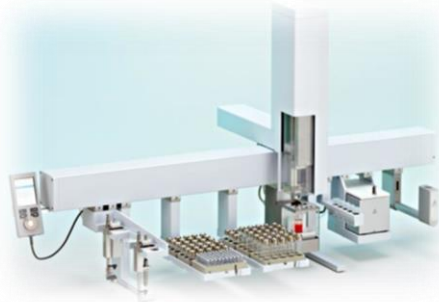


anhydrous $MgSO_4$ /PSA/C18/CarbonX

Condition with 100 μ L of AcN

Load
200 μ L of
sample

Elution with 100 μ L
of AcN (5% formic
acid)



150 μ L extract
without clean-
up + 50 μ L AcN



EMR 30 mg
EMR 15 mg



Condition with 100 μ L of AcN
(20% H_2O)

Load
150 μ L of
sample

C18



Condition with 100 μ L of AcN



Injection vials

anhydrous MgSO_4 /PSA/C18/CarbonX

100 μL clean-up extract

EMR 30 mg
EMR 15 mg

C18

71 μL clean-up extract
+ 29 μL AcN

400 μL water (dimethoate-d6)
900 μL water (dimethoate-d6)



dSPE

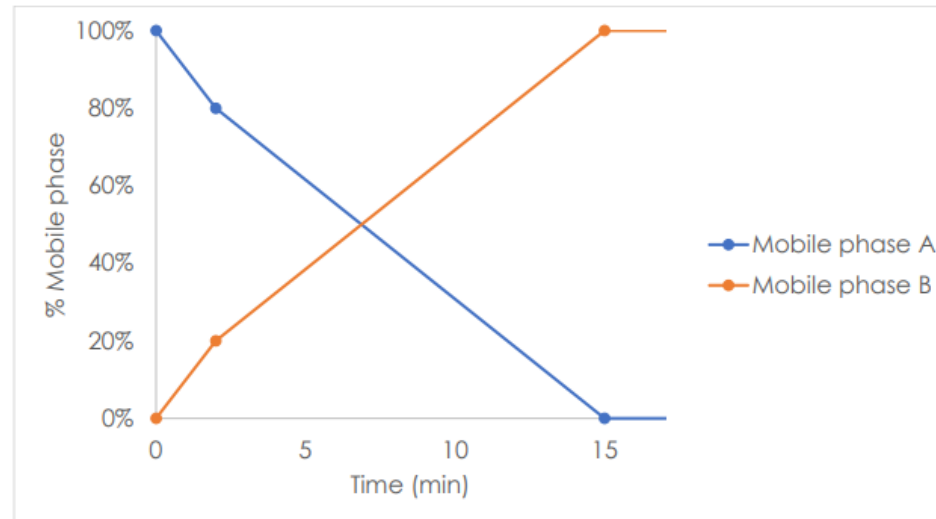
53 μL clean-up extract
+ 47 μL AcN



In this way, the matrix-solvent ratio remains consistent regardless of the cleaning method used

Analysis by LC-QqQ-MS/MS

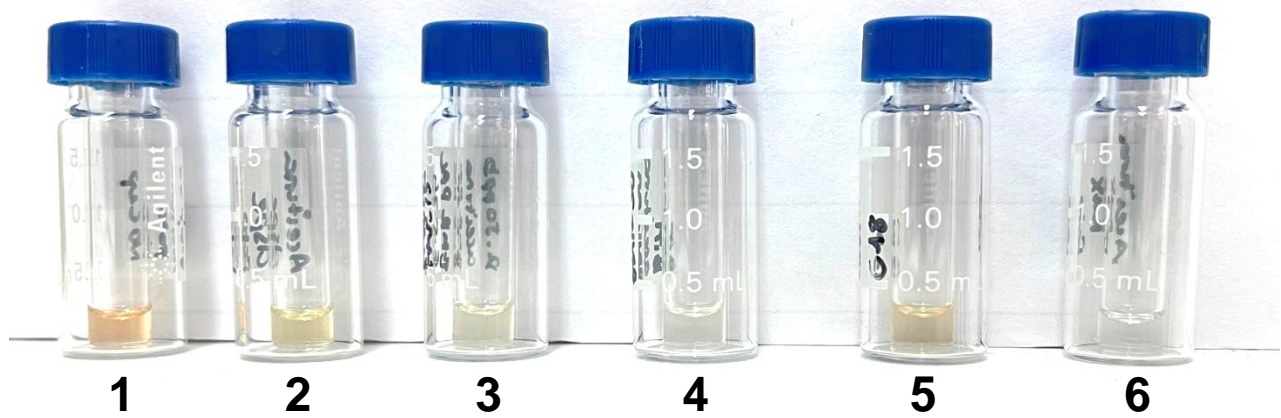
- Column: Zorbax Eclipse Plus C8 2.1x100 mm and 1.8 μm particle size
- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)
- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)
- Column temperature: 35 $^{\circ}\text{C}$
- Flow rate: 0.3 ml/min
- Injection volume: 5 μL
- Autosampler temperature: 12 $^{\circ}\text{C}$



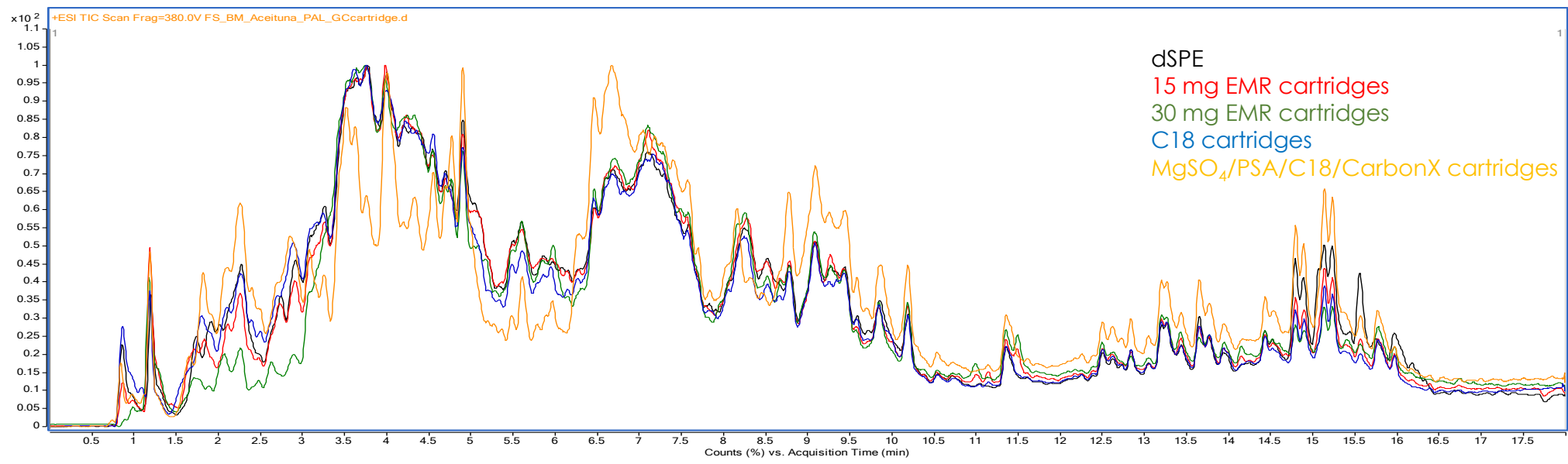
- Ionisation mode: Positive and negative
- Capillary (positive and negative): 3000 V
- Nebulizer: 45 psi
- Nozzel: 400 V
- Drying gas flow: 13 L/min
- Drying gas temperature: 120 $^{\circ}\text{C}$
- Sheat gas flow: 10 L/min
- Sheat gas temperature: 375 $^{\circ}\text{C}$
- High Pressure RF (Positive): 150 V
- High Pressure RF (Negative): 110 V
- Low Pressure RF (Positive): 60 V
- Low Pressure RF (Negative): 60 V

Results and discussion

- TIC's and extract appearance

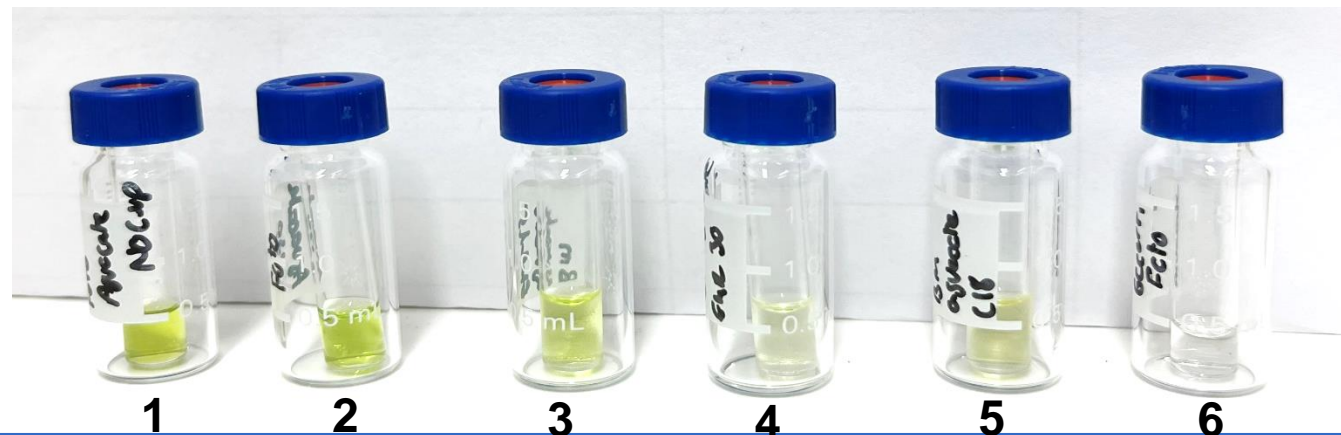


1. Not clean-up
2. dSPE
3. EMR 15 mg
4. EMR 30 mg
5. C18
6. MgSO₄/PSA/C18/Carbon X

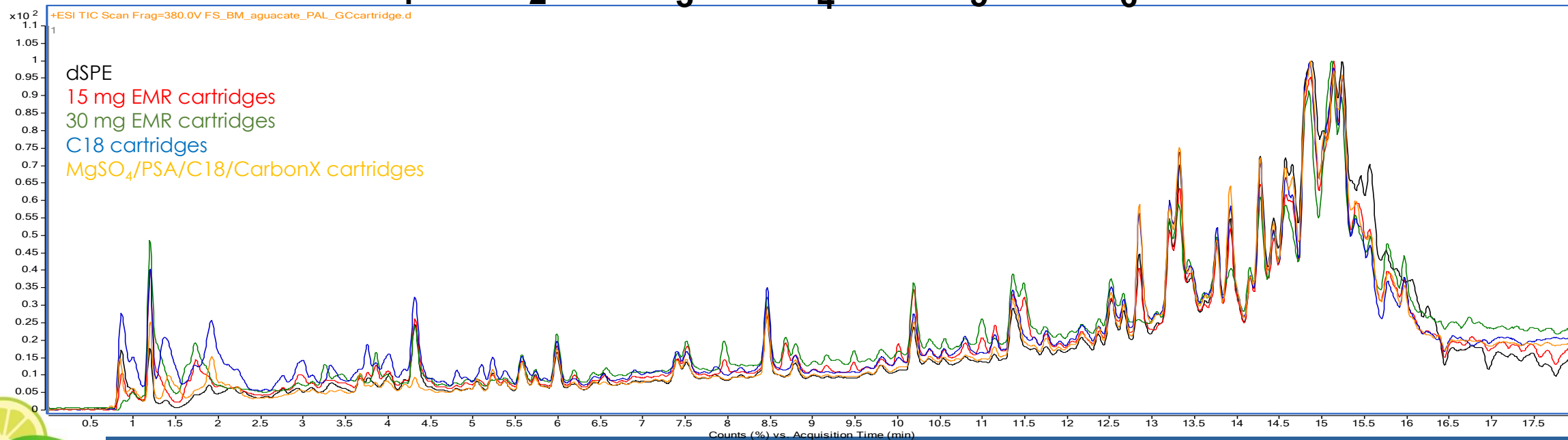


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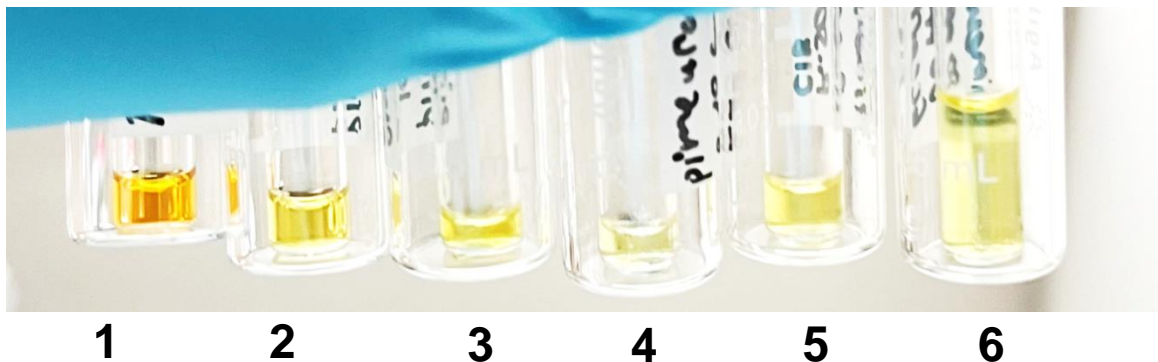


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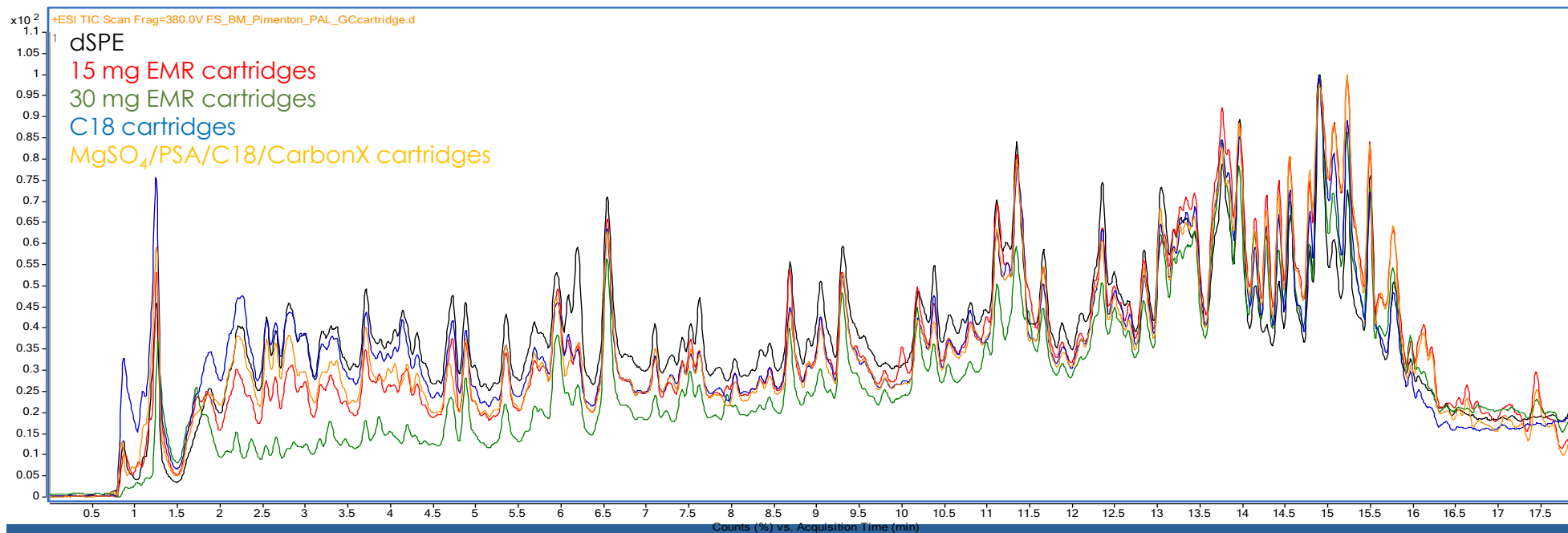


Results and discussion

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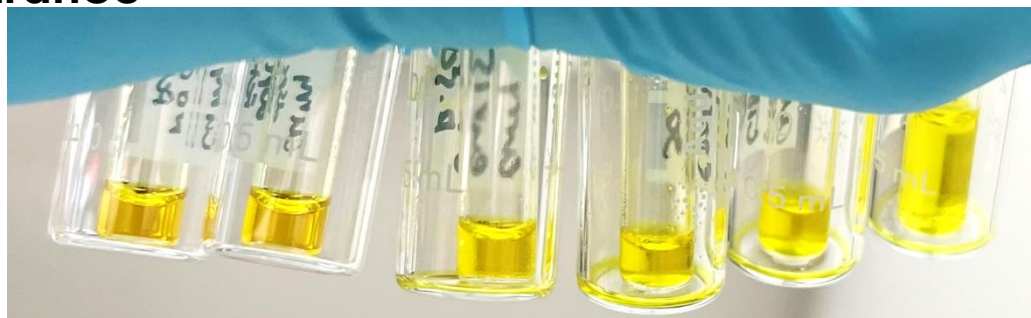


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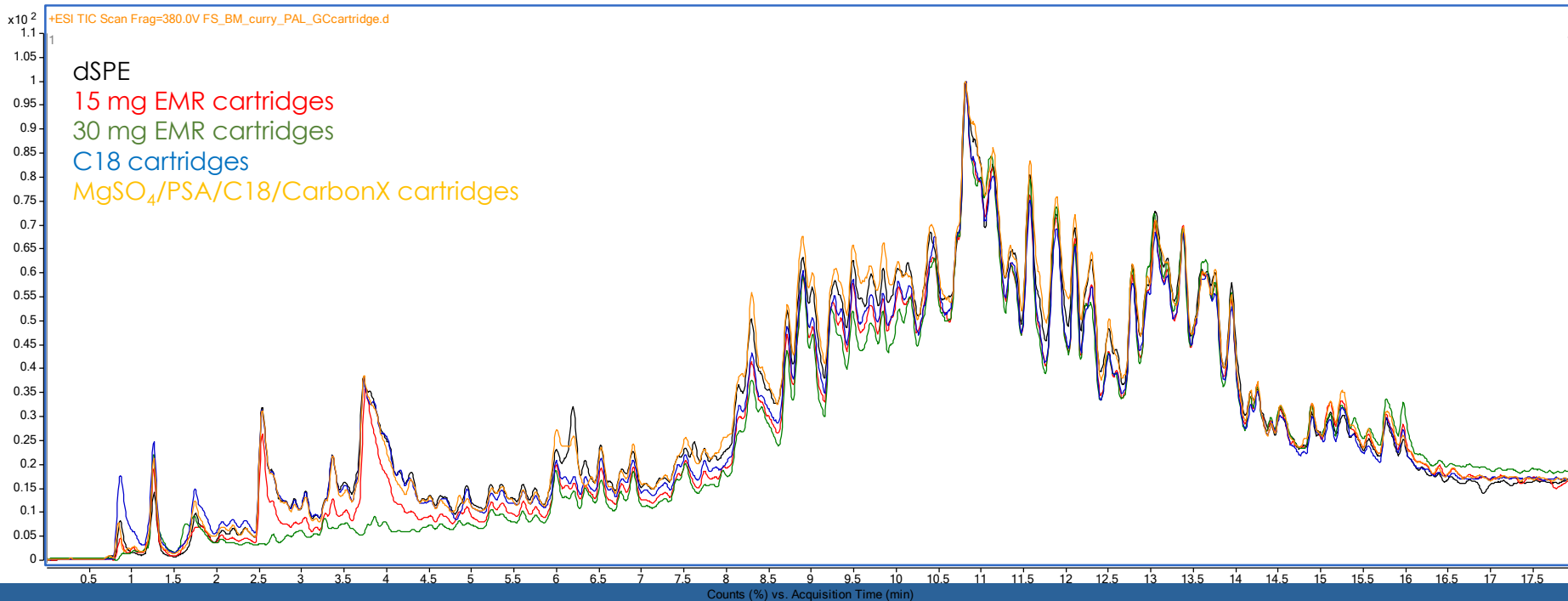
Results and discussion

- TIC's and extract appearance



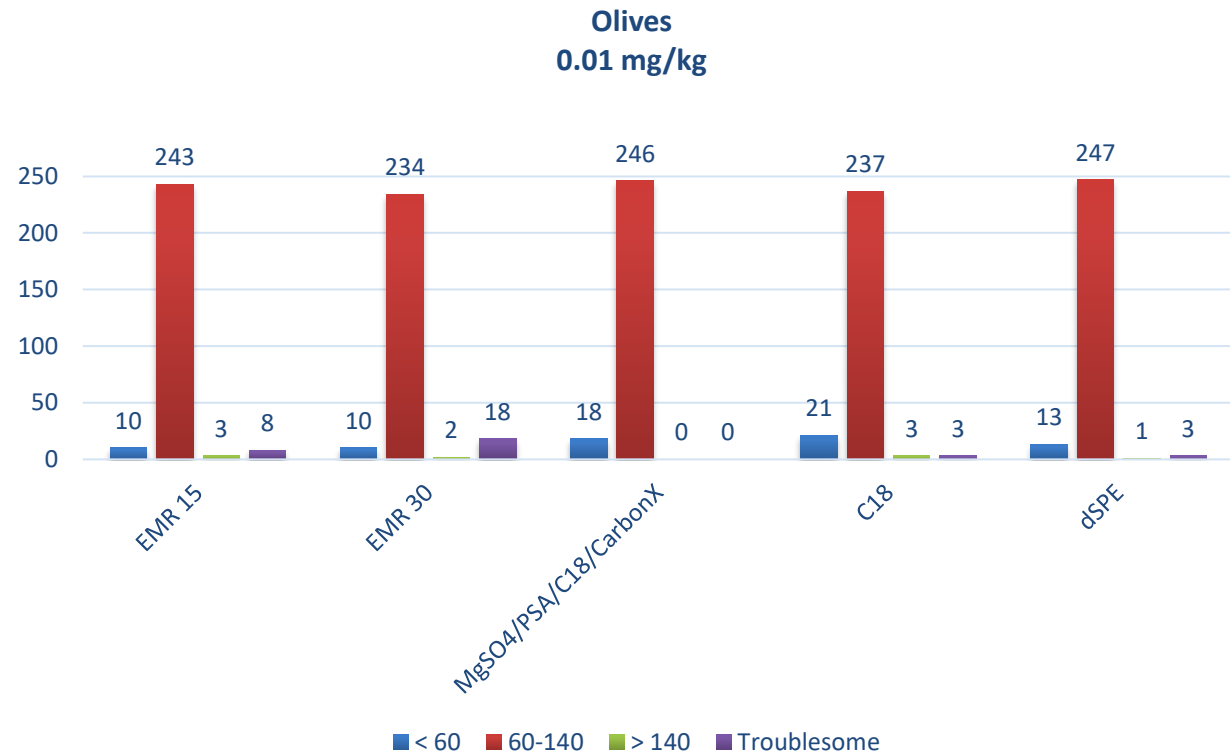
1 2 3 4 5 6

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Results and discussion

- Apparent recoveries



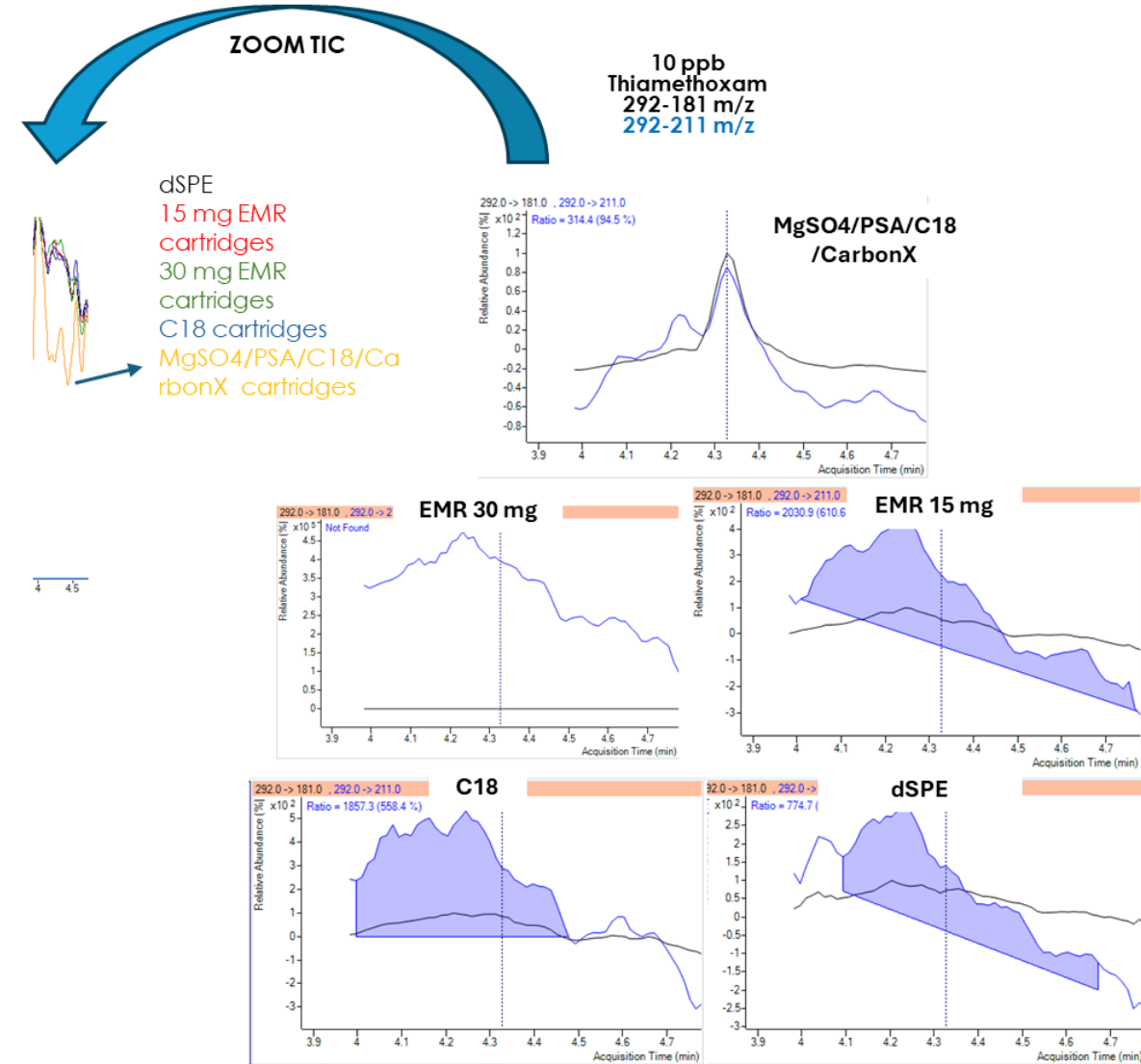
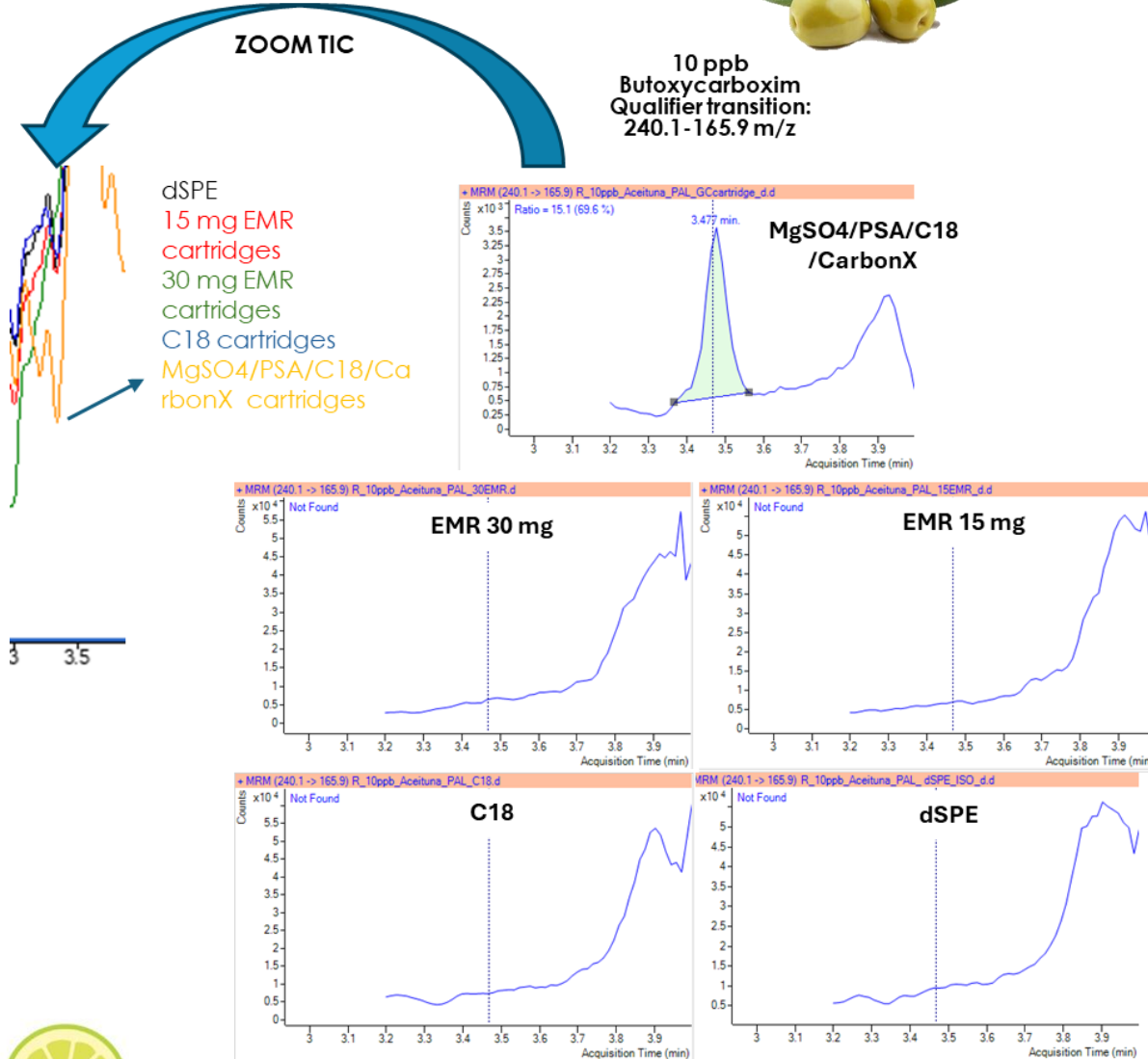
In all cases, the number of compounds between 60-140 % is similar but it is important that when we used the MgSO4/PSA/C18/CarbonX cartridges there are not compounds higher than 140% or troublesome (not detected qualifier or signal suppression).



Results and discussion

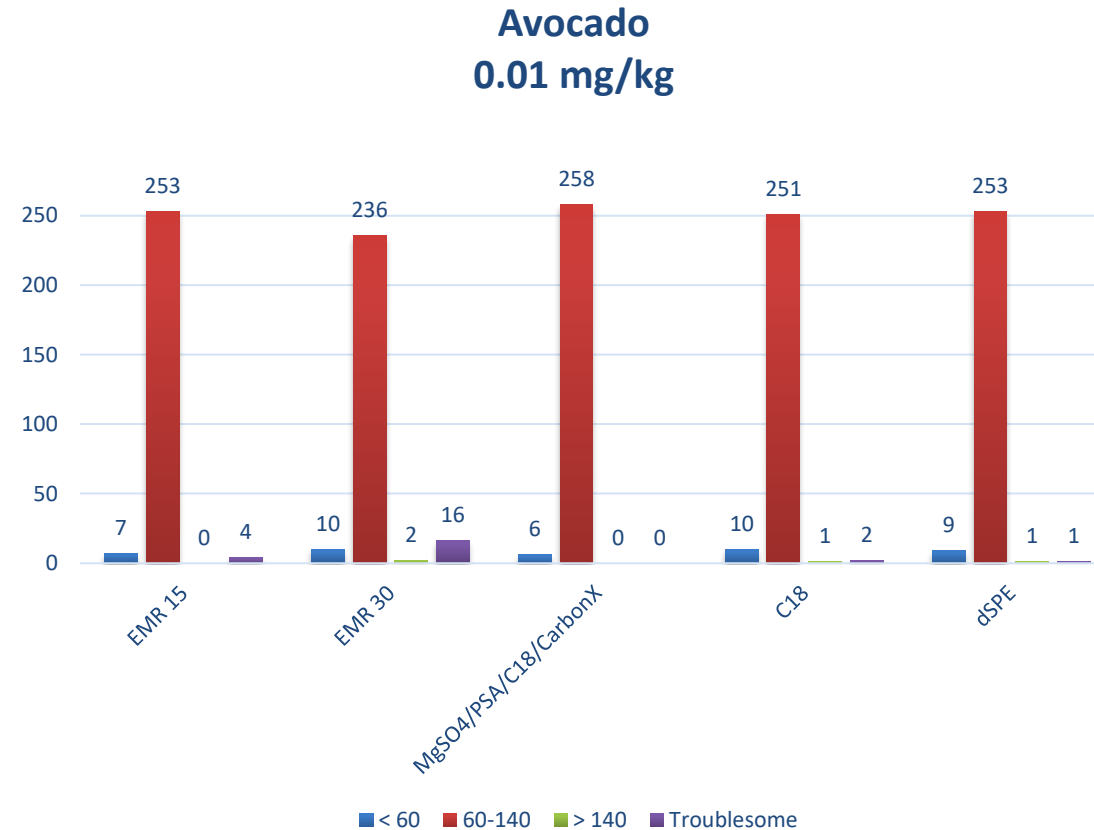


Troublesome compounds



Results and discussion

- Apparent recoveries



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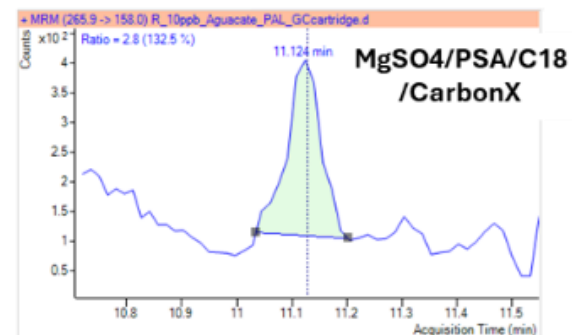
Results and discussion

Troublesome compounds

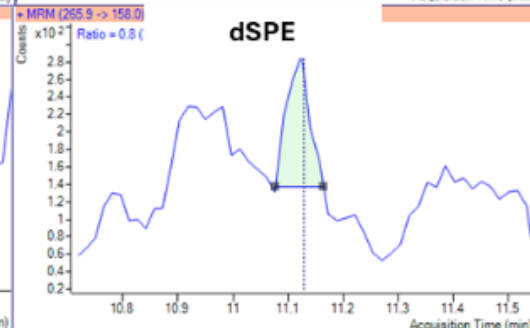
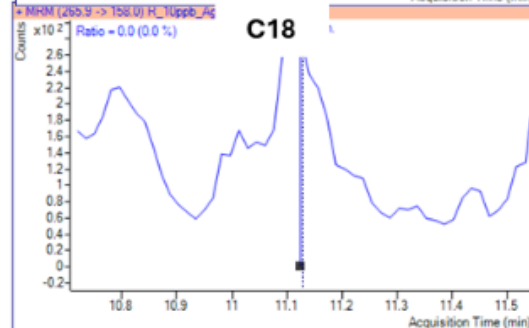
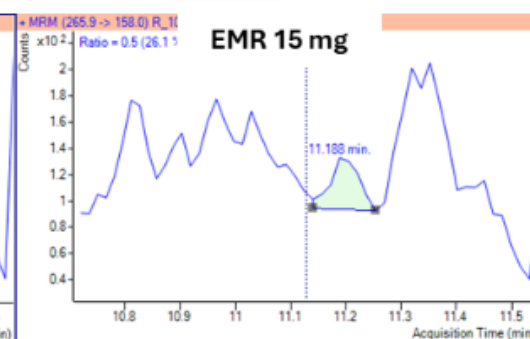
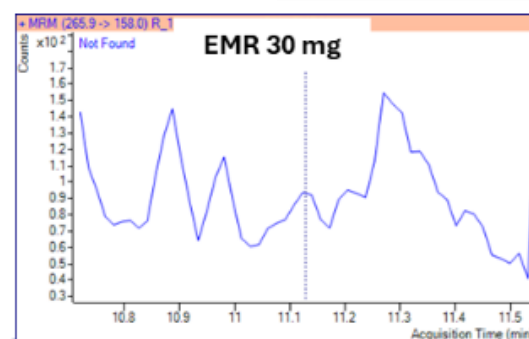


10 ppb
Fludioxonil
265.9-158 m/z

dSPE
15 mg EMR
cartridges
30 mg EMR
cartridges
C18 cartridges
MgSO4/PSA/C18/
CarbonX cartridges

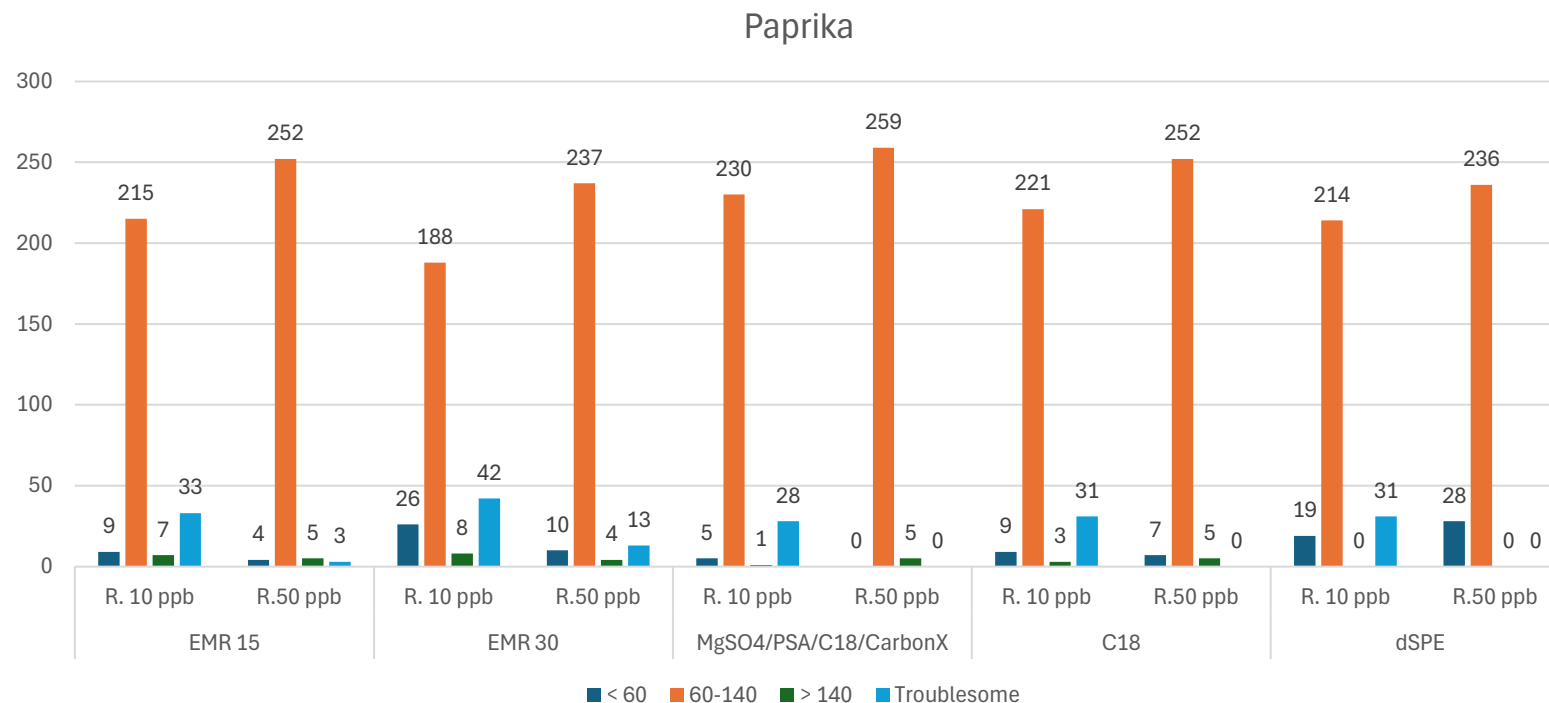


11 11.5



Results and discussion

- Apparent recoveries



The number of compounds between 60-140 % is higher when we used the MgSO₄/PSA/C18/CarbonX cartridges and there are not troublesome at 50 µg/kg (not detected qualifier or signal suppression).

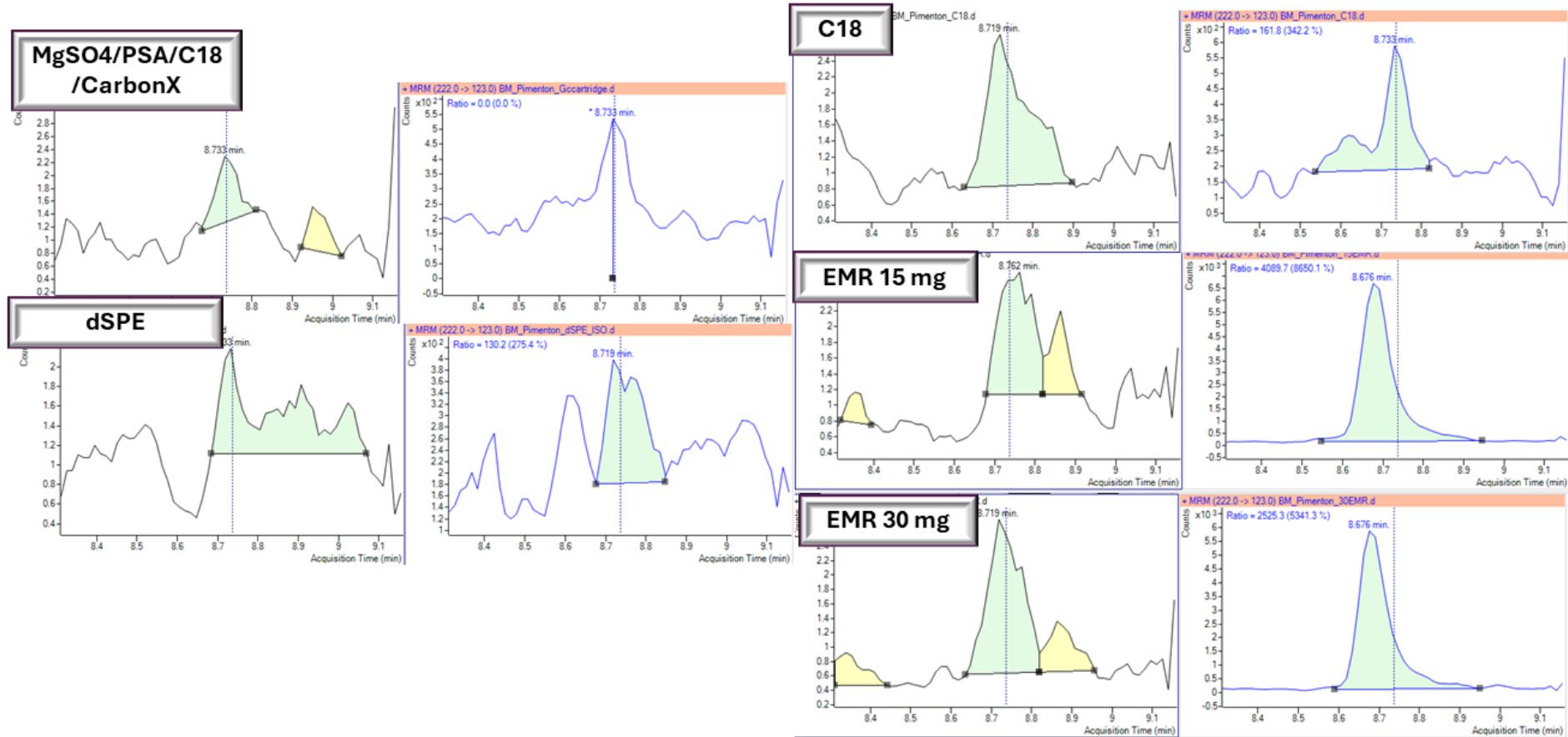


Results and discussion

Troublesome compounds

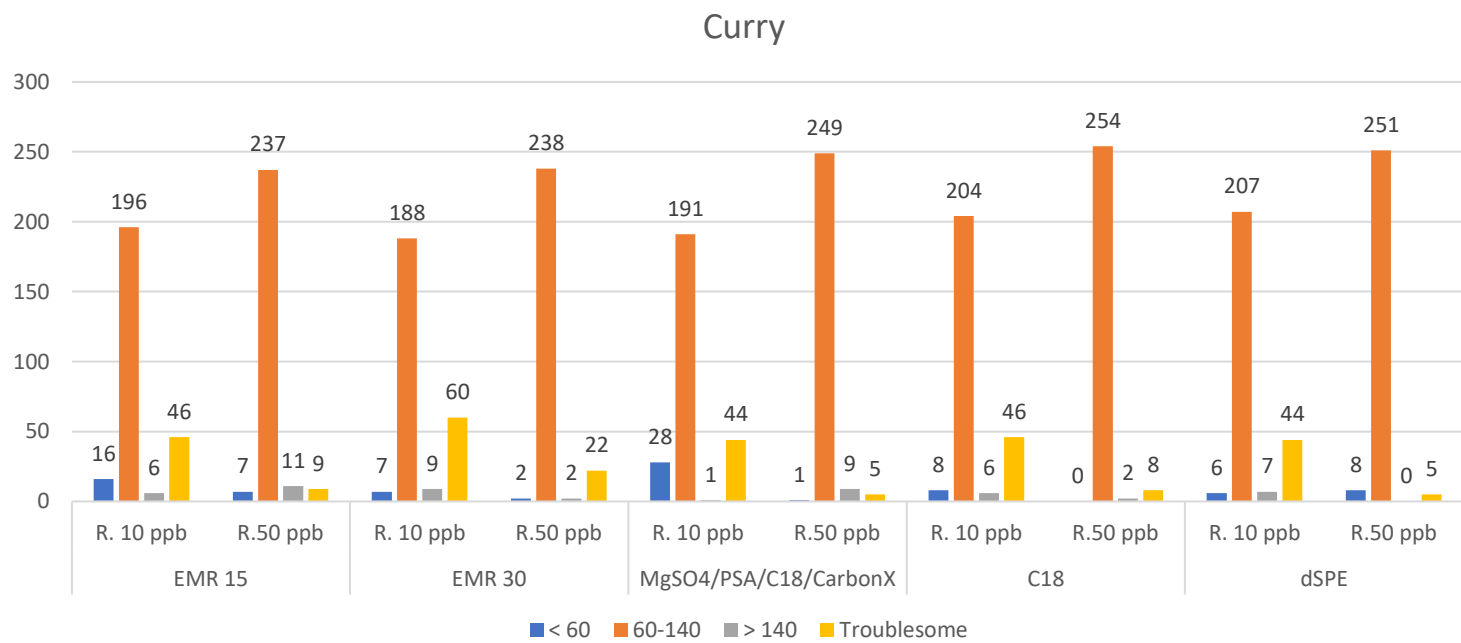


Blank of paprika
Carbofuran
222>165 m/z
222-123 m/z



Results and discussion

- Apparent recoveries



The number of compounds between 60-140 % is similar when we used the MgSO₄/PSA/C18/CarbonX or C18 cartridges or dSPE.



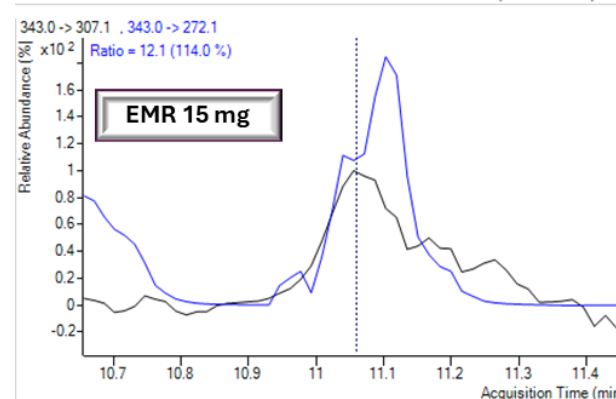
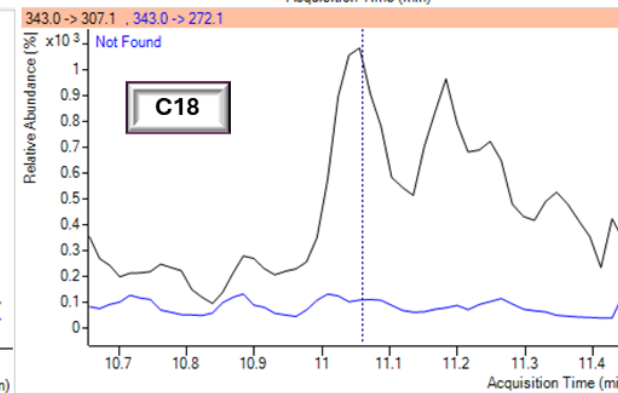
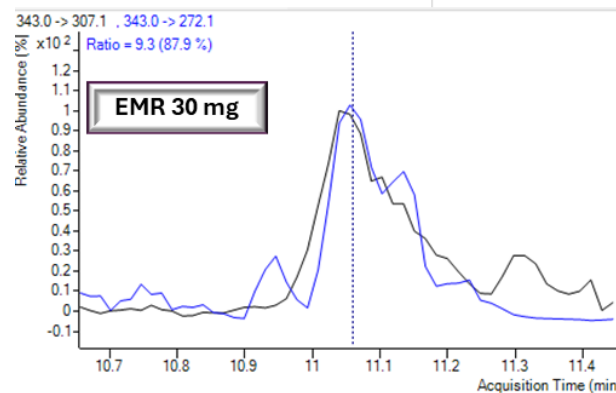
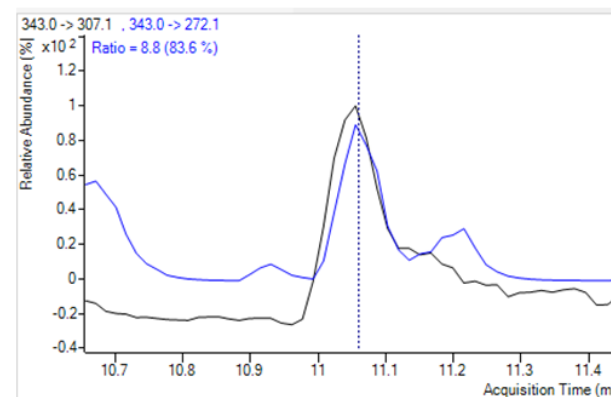
Results and discussion

Troublesome compounds



Curry spiked at 50 ppb
Boscalid
343>307 m/z
343>272.1 m/z

MgSO4/PSA/C18
/CarbonX



Conclusions



In this report, we compared various μ SPE clean-up cartridges and dSPE. Across all studied cases, approximately 90% of the compounds were recovered within a range of 60-140% in the analyzed matrices. Automation has the advantage of standardizing the clean-up process for these types of matrices. Notably, the cartridges $MgSO_4/PSA/C18/CarbonX$ and C18 achieved the highest recovery rates of compounds in the mentioned range:

Percentage of compounds in recovery range 60-140%

| Matrix | $MgSO_4/PSA/C18/CarbonX$ | C18 | EMR 15 mg | EMR 30 mg | dSPE |
|---------|--------------------------|-----|-----------|-----------|------|
| Olives | 94 | 90 | 92 | 89 | 94 |
| Avocado | 98 | 95 | 96 | 89 | 96 |
| Paprika | 98 | 95 | 95 | 90 | 89 |
| Curry | 94 | 96 | 90 | 90 | 95 |



**Thank You
for Your Attention**

