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Overview

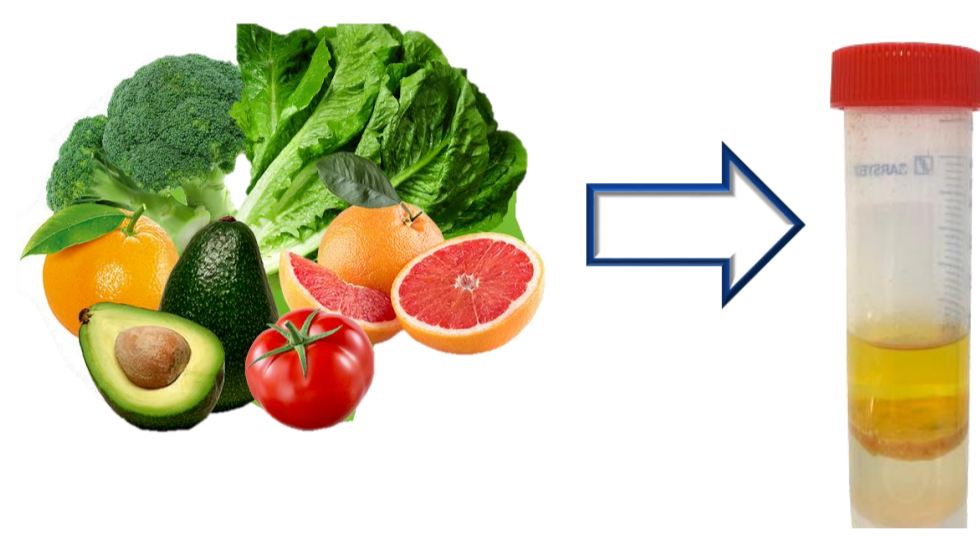
A clean-up step is often essential during the extraction process to remove undesired matrix components that may cause analytical interferences. However, this additional procedure entails time-consuming work. Moreover, it usually needs to be adapted to the different co-extracts from the matrix present in the samples. Therefore, the development of an automated and unified clean-up procedure means a significant reduction in the time and laboratory work needed for pesticide residue analysis.

In this study, different matrices (tomato, orange, rice, avocado and black tea) were extracted by manual dispersive clean-up (different procedures according to the matrix group) in parallel with an automated μ SPE clean-up workflow, in both cases based on QuEChERS extraction. The latter procedure employed clean-up cartridges containing a mixture of sorbent materials (anhydrous $MgSO_4$ /PSA/C18/CarbonX) suitable for multiple matrices. All the samples were analysed by liquid chromatography and the results obtained from both procedures have been compared in terms of the extract cleanliness, recoveries, interferences, and sample workflow. At the levels studied, similar recoveries were achieved by both techniques (manual and automated) except for reactive compounds when PSA was used as the sorbent material, for which the μ SPE recoveries were only between 70-120%. Furthermore, closer calibration line slopes were provided when μ SPE was applied to the different matrices studied. It is important to note that up to 30 % more samples per day can be analysed using an automated μ SPE compared to the manual method (which requires shaking, centrifuging, then taking the supernatant and adding formic acid in ACN); it also provides good repeatability - an RSD (%) < 10%. Consequently, this technique is a very useful option for routine analyses, greatly simplifying the work of analytical laboratories.

Methods

Extraction step

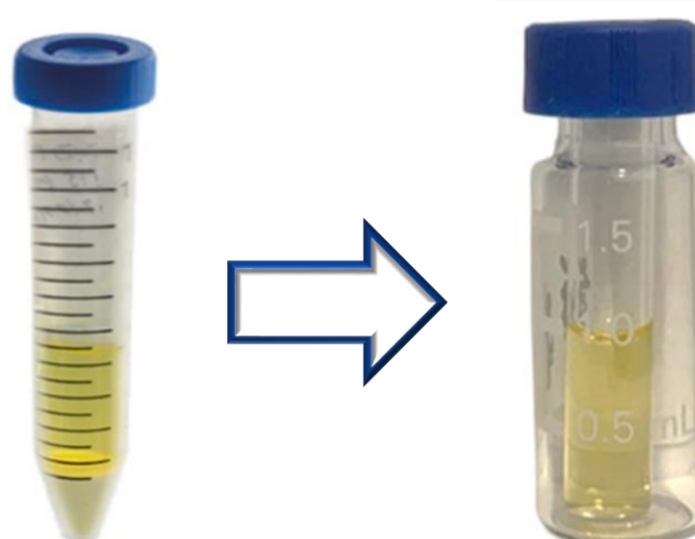
Citrate QuEChERS



Clean up step

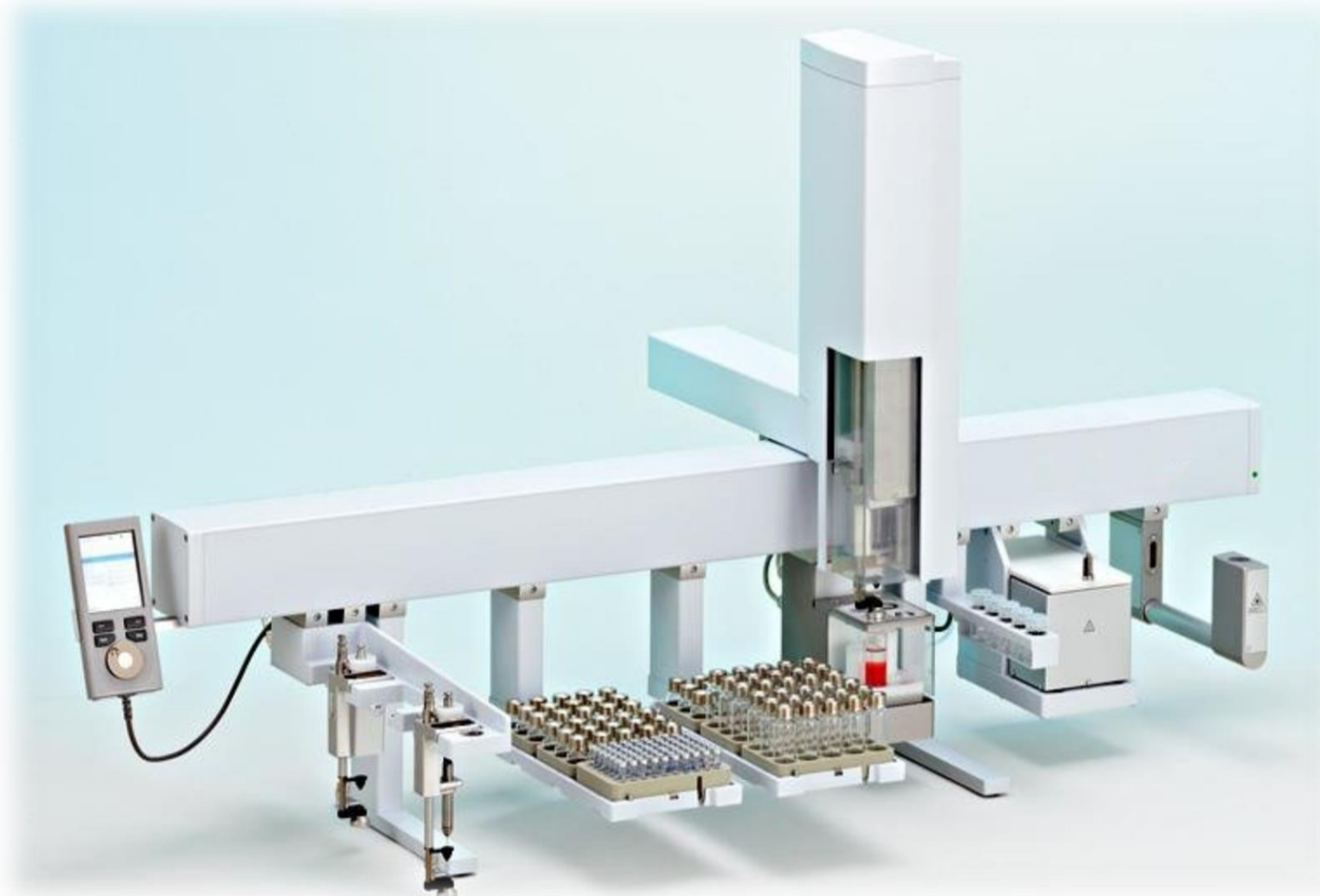
Manual dSPE

- Tomato/Orange: anhydrous $MgSO_4$ + PSA
- Avocado: Z-sep
- Tea: $CaCl_2$ + PSA



Automated μ SPE

μ SPE Cartridge:
Anhydrous $MgSO_4$ +PSA+ C18+CarbonX



Steps:

- Condition μ SPE cartridge (100 μ L ACN)
- Elution cartridge step with sample (200 μ L)
- Elution cartridge with AcN (5% formic acid) (100 μ L)

Analysis by LC-QqQ-MS/MS

Column: Accucore C₁₈
2.1 x 100 mm,
particle size 2.6 μ m

Column temperature: 30°C

Flow rate: 0.350 ml/min

Injection volume: 2.5 μ L

Autosampler temperature: 10°C



Triple Quadrupole TSQ Altis™

Ion spray voltage (+): 3500 V

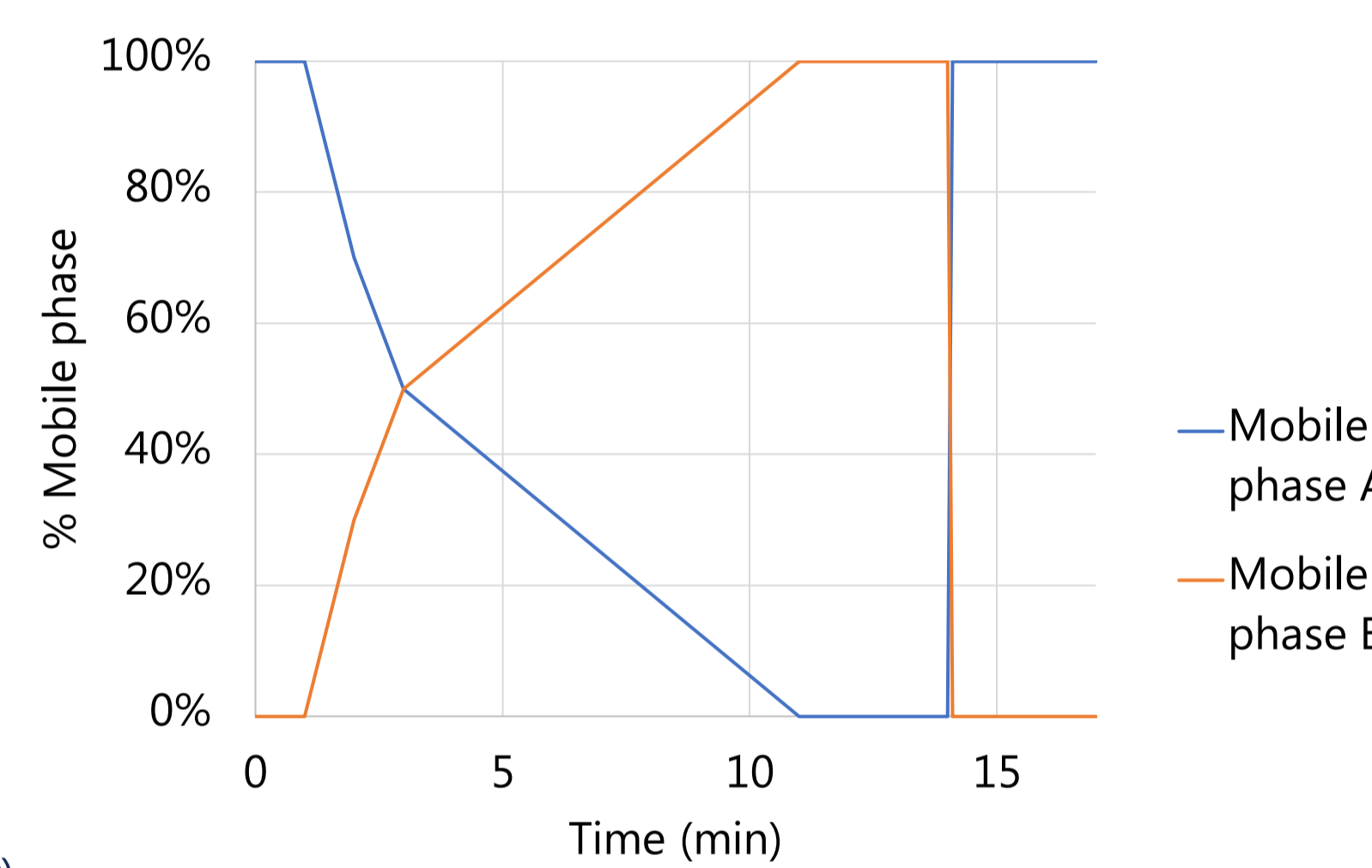
Ion spray voltage (-): 2500 V

Sweep gas: 1 (arbitrary units)

Ion transfer tube: 325 °C

Vaporiser temp.: 350 °C

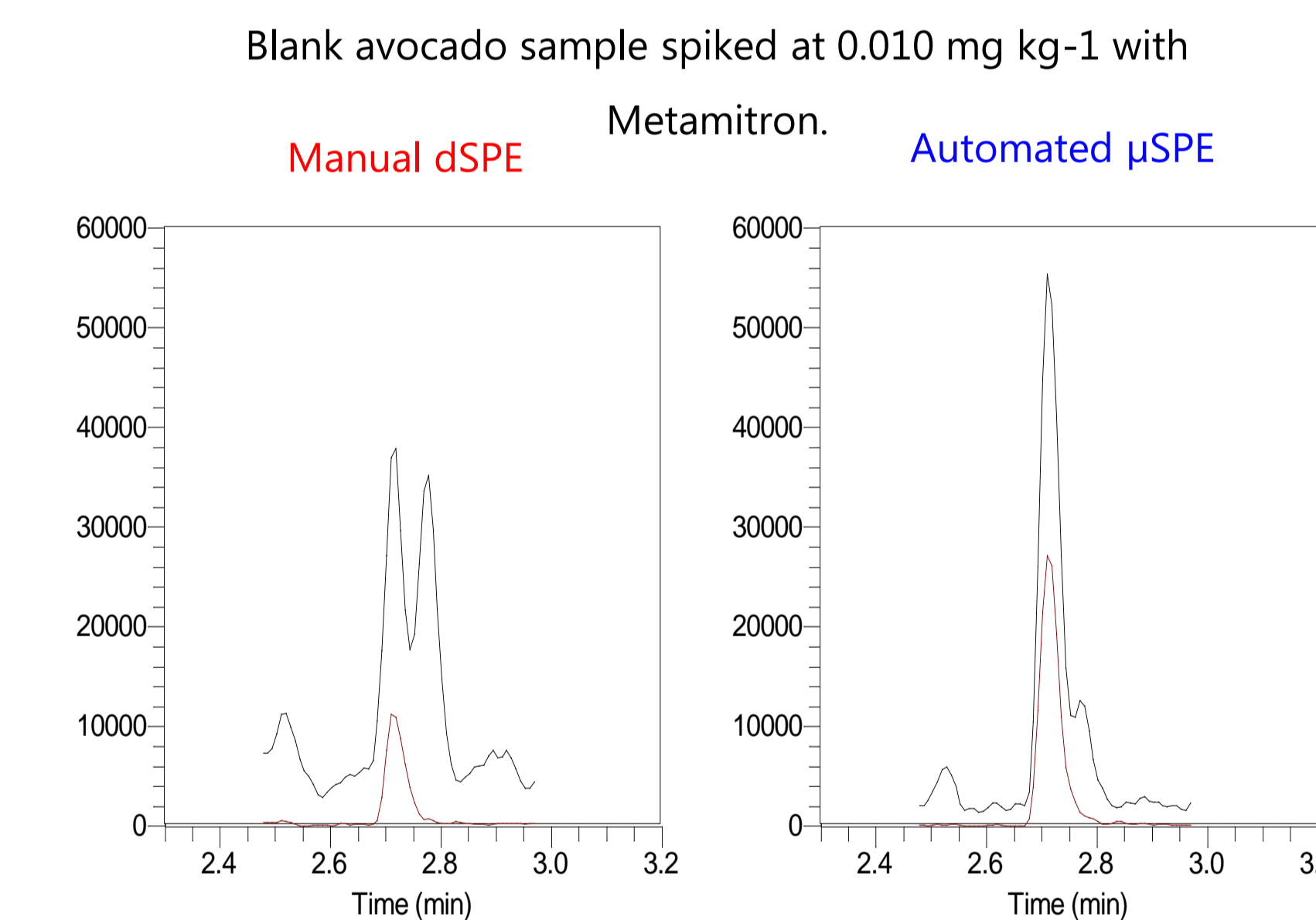
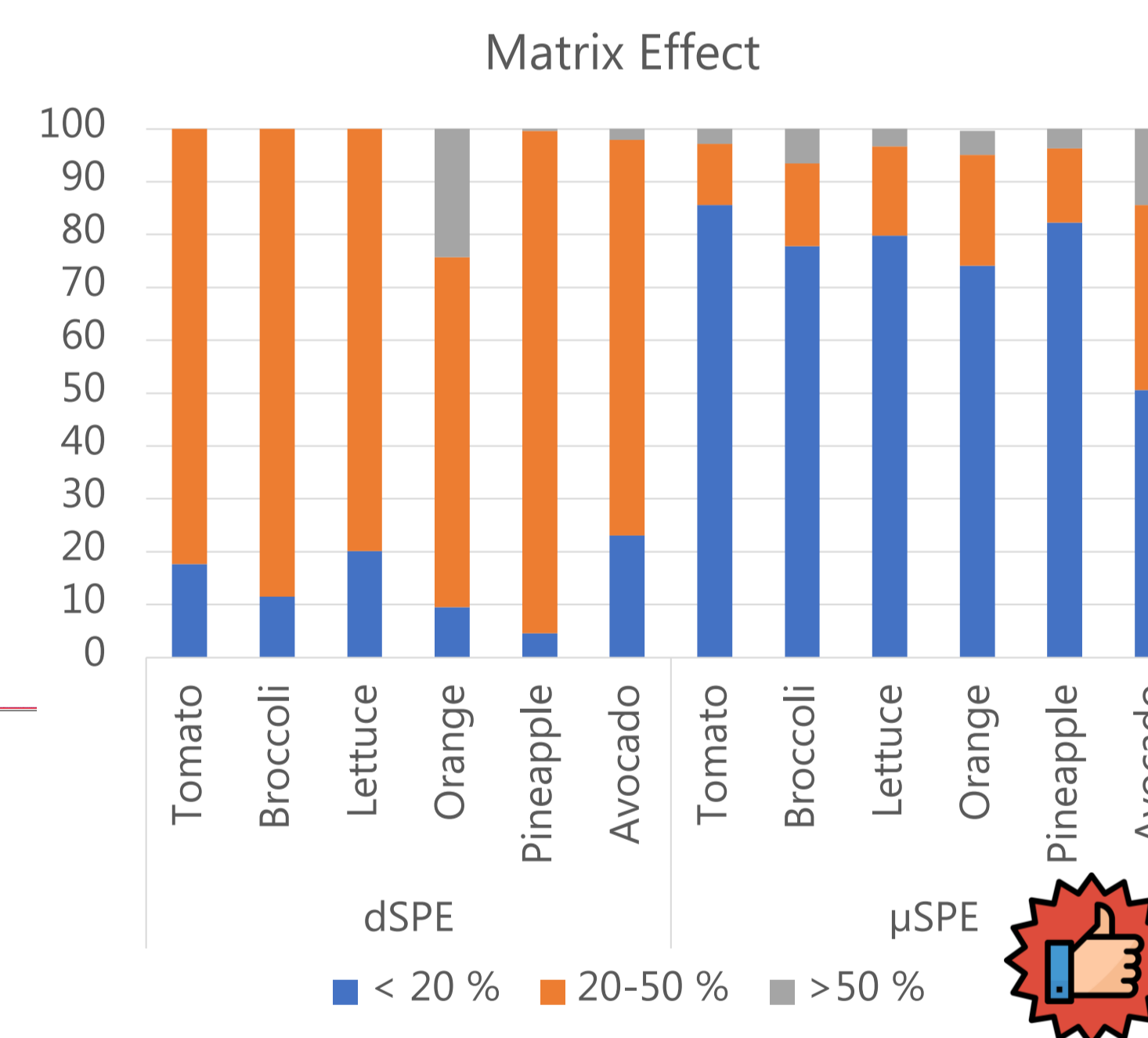
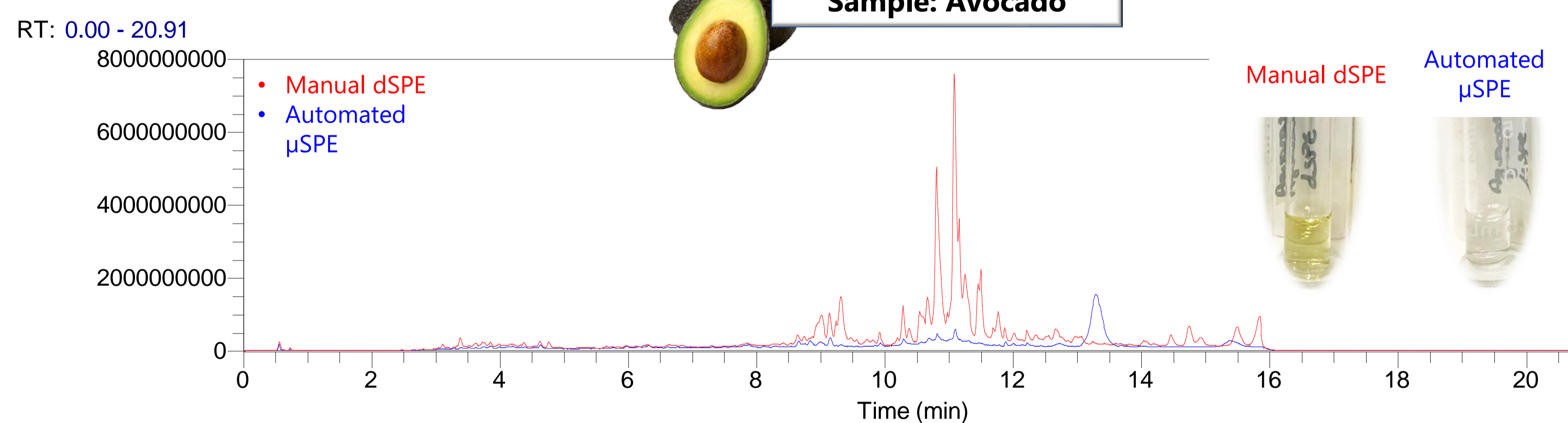
Working mode: SRM



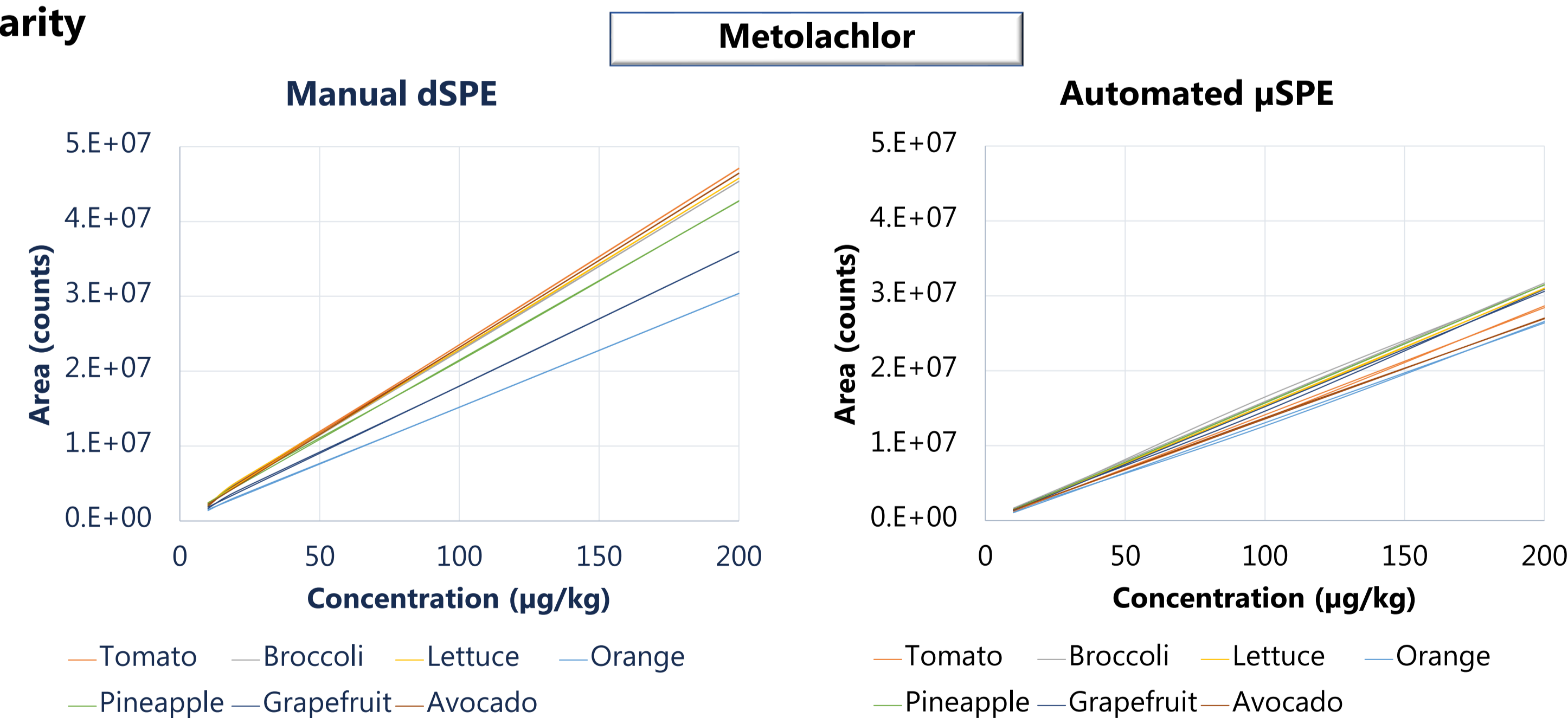
- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)
- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)

Results

TICs and extract appearance



Linearity



For all the cases studied, the calibration curves had very close slopes offering good quantitative results for the different commodities; when μ SPE was employed for the clean-up, a single calibration curve was used. The total amount of injected sample for the dSPE method was 0.5 mg whereas for the μ SPE method, it was 0.33 mg. Injecting less matrix should result in less equipment maintenance and a lower signal suppression effect.

Conclusions

The use of an automated μ SPE clean-up reduces the laboratory workflow and allows increased sample throughput in routine analysis by eliminating tedious manual steps. Moreover, as only a single clean-up is employed equally for all commodities, greater homogeneity is typically obtained in the calibration curves. Instrument maintenance is also positively affected because, generally, cleaner extracts are obtained and so the lifespan of certain instrument parts (such as the ion source and columns) increase.

In general, the μ SPE method provides recoveries that are very similar to those obtained with manual clean-up because the extraction step is the same for both approaches. However, some compounds are positively affected when using μ SPE cartridges, such as acidic compounds (fluazifop, haloxyfop and quizalofop), where, in general, recoveries < 50% are obtained when manual dispersive clean-up is used (they are retained by the PSA sorbent). The automated clean-up step can attain recoveries from 70 % -120 % because a final elution step of the cartridge (with acidified acetonitrile) was included. In conclusion, automatic μ SPE avoids the qualitative and quantitative errors that are produced when dSPE is applied.

Acidic compounds

Steps:

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- Elution cartridge step with sample (200 μ L)

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- Elution cartridge step with sample (200 μ L)
- Elution cartridge with AcN (5% formic acid) (100 μ L)

