EVALUATION OF DIFFERENT CLEAN-UP PROCEDURES OF MULTIRESIDUE METHODS IN SPICES BY LC-MS/MS

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Overview

Clean-up step is essential during the multiresidue sample preparation process to remove undesired matrix components that may cause analytical interferences or suppression effect. However, its application generally by specific sorbents entails time-consuming work producing low recoveries for some compounds. Moreover, it usually needs to be adapted to the different co-extractives from the matrix present in the samples by using different chemical sorbents increasing the number of validation procedures. Therefore, the development of a more efficient and automated and unified clean-up procedure means a significant time reduction and laboratory work with improved performance.

In this study, extracts from different spices (paprika, curry, turmeric and cayenne pepper) were purified by manual dispersive clean-up in parallel with an automated µSPE clean-up workflow, in both cases based on QuEChERS extraction for a target list of 200 pesticides. The latter procedure evaluated different clean-up cartridges containing a mixture of sorbent materials (anhydrous MgSO4/PSA/C18/CarbonX) or with EMR as sorbent material. All the samples were analysed by liquid chromatography mass spectrometry and the results obtained from both procedures have been compared in terms of the extract cleanness, performance, interferences, and sample workflow.

Methods

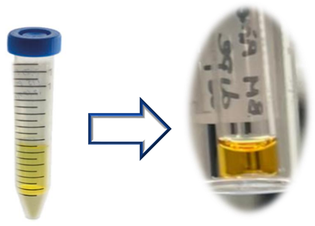
❑ Extraction step

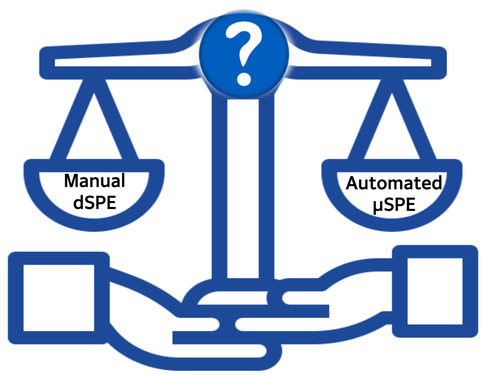
Citrate QuEChERS

❑ Clean up step

Manual dSPE

- EMR-Lipid Bond Elut and Polish tube $NaCl/MgSO_4$

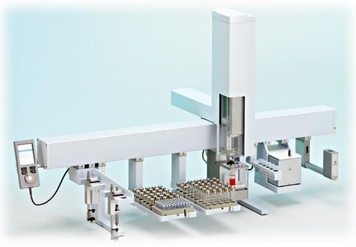




Automated µSPE

❑ EMR

❑ Anhydrous MgSO4+PSA+C18+CarbonX



❑ Analysis by LC-QqQ-MS/MS

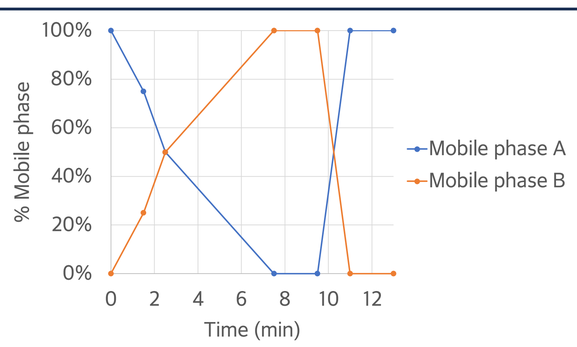
Column: Shim-pack UC-X 2.1x150 mm and 3 µm particle size

Column temperature: 40˚C

Flow rate: 0.350 ml/min

Injection volume: 5 µL

Autosampler temperature: 15˚C



Triple Quadrupole LCMS-8060

Ionisation mode: Positive and negative

Capillary (positive and negative): 4 kV

Switching polarity: 5 ms

Intereface temperature: 300

Desolvation line temperature: 526 ºC

Heat block temperature: 400ºC

Nebulizer gas flow: 3 L/min

Heating gas flow: 10 L/min

Drying gas flow: 10 L/min

- 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)

Steps:

1. Condition µSPE cartridge (100 µL ACN 20% H_2O)
2. Elution cartridge step with sample (150 µL)

Steps:

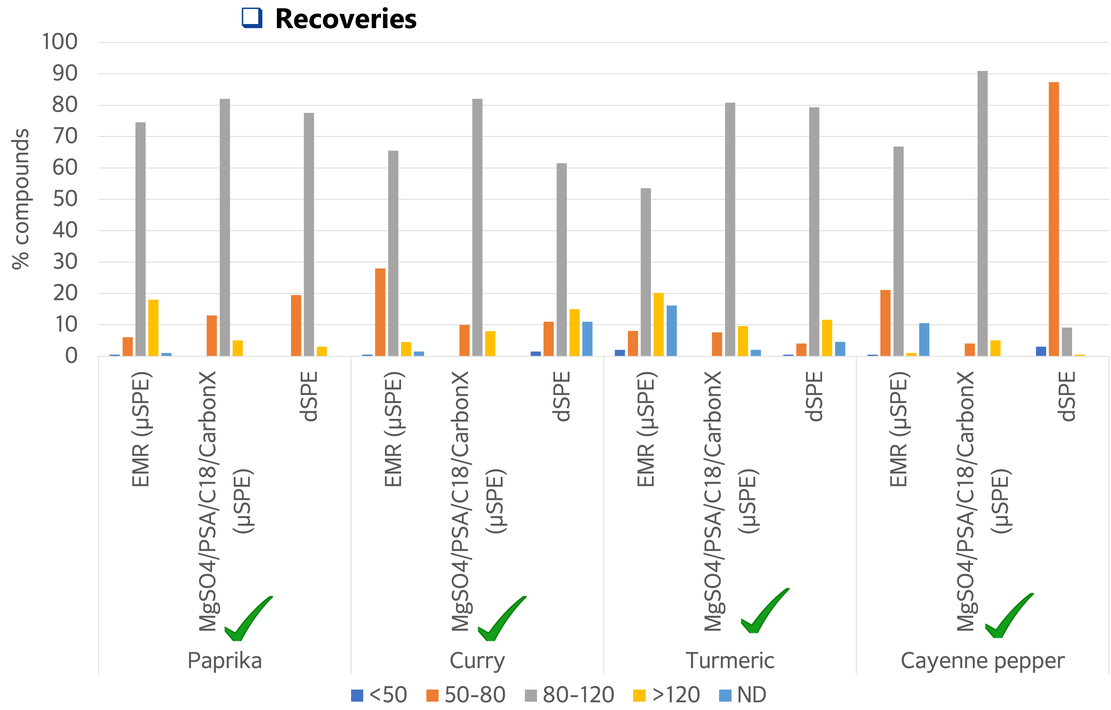
1. Condition µSPE cartridge (100 µL ACN)
2. Elution cartridge step with sample (200 µL)
3. Elution cartridge with AcN (5% formic acid) (100 µL)

Results

❑ TICs, extract appearance and interferences

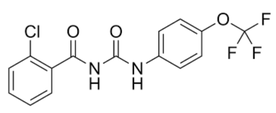
Blank sample: Turmeric

❑ Recoveries



Curry

Triflumuron



Transitions
359.0>139.0
359.0>156.0

Matrix interference

dSPE

Blank sample: curry

Curry spiked at 10µg/kg Triflumuron

Triflumuron

µSPE (MgSO4/PSA/C18/CarbonX)

Blank sample: curry

Curry spiked at 10µg/kg Triflumuron

Conclusions

The use of an automated µSPE clean-up reduces the laboratory workflow and allows increased sample throughput in routine analysis by eliminating tedious manual steps. 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 recovery terms, more than 80 % of the evaluated compounds gave rise to good recoveries with values between 80-120 % in all matrices with automated µSPE clean-up with the mixture-cartridges (anhydrous MgSO4/PSA/C18/CarbonX). The largest difference, in general terms, was observed in cayenne where 11 % of the compounds were not detected with EMR cartridges and in dSPE the highest number of compounds recovered (91%) was in the range of 50-80% recoveries. Finally, when comparing the mixture-cartridges and EMR-cartridges, the former was selected because although the baseline of TIC was higher than EMR, it was still cleaner than the manual dispersive clean-up. It also provides good repeatability - an RSD (%) < 10% avoiding excessive retention of the compounds. Consequently, this technique is a very useful option for routine analyses of spices, greatly simplifying the work of muti-residue methods.

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