ADVANTAGES IN USING AN AUTOMATED CLEAN-UP STEP IN PESTICIDE MULTIRESIDUE METHODS BY LC-MS/MS

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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-extractives 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 µSPE clean-up workflow, in both cases based on QuEChERS extraction. The latter procedure employed clean-up cartridges containing a mixture of sorbent materials (anhydrous MgSO4/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 µSPE recoveries were only between 70-120%. Furthermore, closer calibration line slopes were provided when µSPE 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 µSPE 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 µSPE
    - Tomato/Orange: anhydrous MgSO4 + PSA
    - Avocado: Z-Sep
    - Tea: CaCl2 + PSA
  - Automated µSPE

- **Analysis by LC-QqQ-MS/MS**
  - Triple Quadrupole TQ-Auto™
    - Ion spray voltage (+): 3500 V
    - Ion spray voltage (+): 2500 V
    - Spray gas: 1 (arbitrary units)
    - Ion transfer tube: 325 °C
    - Ion spray temp.: 350 °C
    - Working mode: SIM

- **Results**
  - **TIC’s and extract appearance**
    - Sample: Avocado
  - **Linearity**
    - Manual µSPE
    - Automated µSPE
  - **Acidic compounds**
    - 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)

- **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. 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 µSPE 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 µSPE cartridges, such as acidic compounds (fluazinap, halofop and chlazinap), 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 µSPE avoids the qualitative and quantitative errors that are produced when βSPE is applied.