PESTICIDE RESIDUE RESEARCH GROUP

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Application of zirconium dioxide nanoparticle sorbent for the clean-up step in post-harvest pesticide residue analysis

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INTRODUCTION

The complexity of certain matrices can cause problems with the ion production efficiency and with the analytical instruments' detection systems . Consequently, there is interest in the introduction of any effective new extraction modification for matrix-dependent clean-up combinations. A possible alternative to these clean up combinations is to use yttria-stabilized zirconium dioxide nanoparticles (ZrO_2/Y_2O_3), which have a high surface area (>100 m^2/g), in the clean-up system to simultaneously obtain excellent purification effects and satisfactory results for multiple pesticides. Sorbents containing ZrO_2 can be used as the clean-up material for pesticide analysis in difficult matrices; these are better than PSA or C_{18} at removing fatty acids, esters of fatty acids, sterols and carboxylic acids.
Orange and pear blanks extracts were spiked with 18 pesticides, diluted 10 times and analyzed by UPLC-QqQ-MS/MS. a reversed-phase C8 column of 2.1 mm × 100 mm and 1.8 µm was used. Data were used to evaluate recoveries at 10 and 100 µg Kg^{-1}, linearity (r^2), LOQs, matrix effects (%), precision (RSD%), repeatability and reproducibility . To evaluate the amount of matrix compounds in the final extract with the different clean-up combinations, a LC-QTOF in full-scan mode was used. To characterize and determine the particle size of the ZrO_2 nanoparticles, a scanning electron miscroscopy (SEM) was used. An application of the method was carried out analyzing 20 real orange and pear samples

EXPERIMENTAL

Sample handling

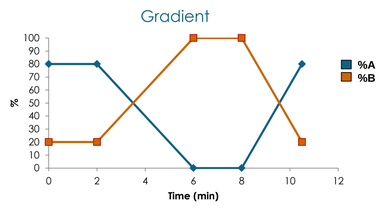
Citrate buffered QuEChERS modification
↓
Clean up: d-SPE $MgSO_4$+ ZrO_2
↓
Blank extracts
↓
Spiking at appropriate level
↓
Diluted 5 times

UPLC-MS/MS

UPLC parameters:

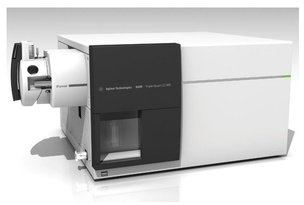
- Injection volume: 5µL
- Flow rate: 0.3 mL/min
- Column: reversed-phase C8 1.8 µm 2.1 × 100 mm
- Mobile Phases and gradient :

· A → H_2O 0.1% formic acid
· B → AcN 0.1% formic acid and 5% of water



MS parameters:

- Ion source: ESI
- Polarity: Positive and Negative
- Dynamic MRM software features



Agilent 6490 QqQ

- Full-scan mode

Agilent 6550 QTOF

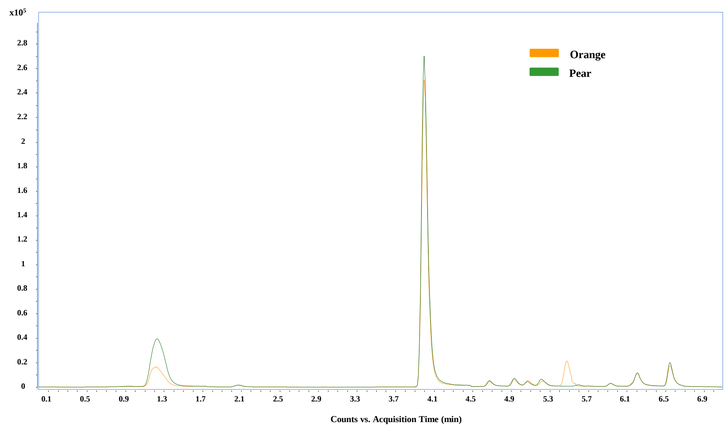
- High vacuum
- Acceleration voltage 5kV

Scanning electron microscopy HITACHI S-3500N

RESULTS

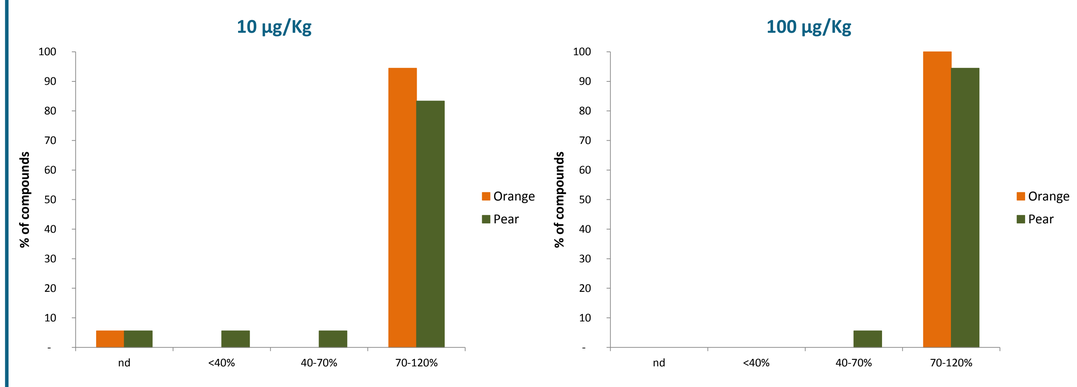
METHOD VALIDATION

Total Ion Chromatogram

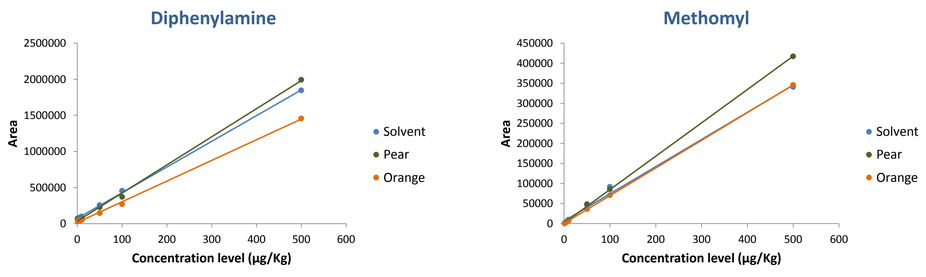


LC-QqQ-MS/MS total ion chromatograms of orange and pear extracts spiked at 10 µg Kg^{-1} and diluted 5 times.

Recoveries



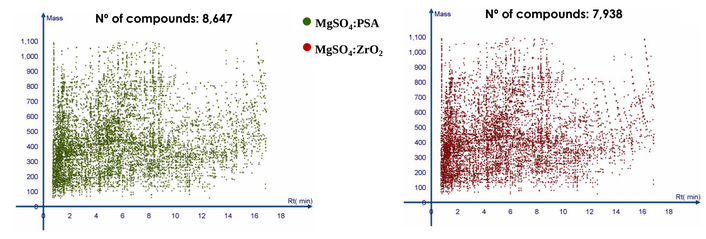
Selected linear response



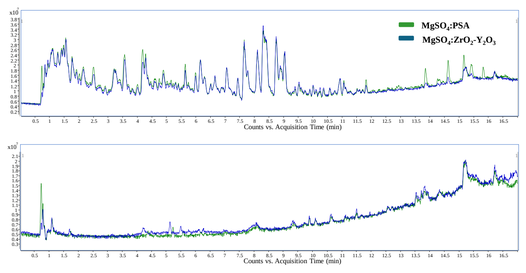
Linearity

- Linearity was evaluated at 7 calibration levels, from 1 to 500 µg/Kg (diluted 5 times).
- All the compounds had a $R^2 > 0.99$.

EVALUATION OF MATRIX COMPOUNDS

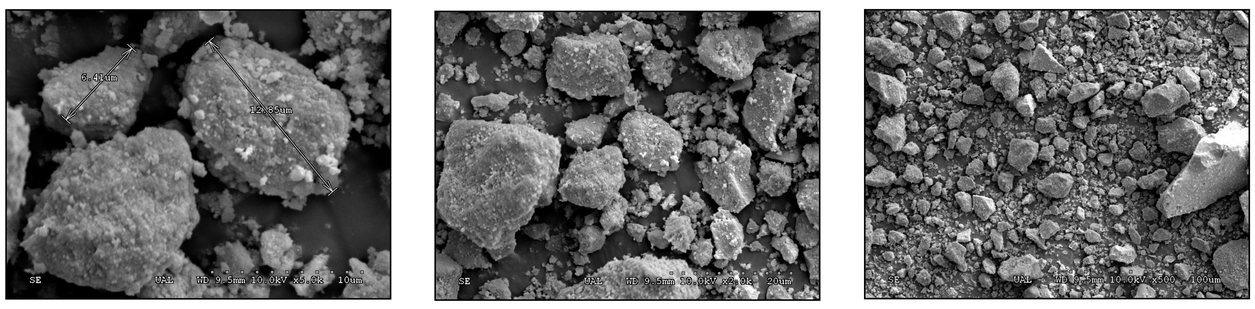


Co-eluting matrix compounds of orange extracts using LC-QTOF-MS with the different clean-up procedures. The x-axis represents the retention time and the y-axis the m/z.



LC-QToF-MS full scan chromatograms of blank orange and pear extracts diluted 5-times obtained by using QuEChERS methodology and a different clean-up.

CHARACTERIZATION BY SEM



Determination of the particle size of the ZrO_2 nanoparticles by scanning electron miscroscopy (SEM)

APPLICATION OF THE METHOD

No. of sample Orange samples	Carbendazim	Imazalil	Pyrimethanil	Thiabendazole
1	<LOQ	nd	nd	<LOQ
2	<LOQ	nd	nd	<LOQ
3	<LOQ	<LOQ	<LOQ	<LOQ
4	<LOQ	<LOQ	<LOQ	<LOQ
5	<LOQ	nd	<LOQ	<LOQ
6	<LOQ	1006.9	<LOQ	<LOQ
Pear samples				
1	<LOQ	<LOQ	<LOQ	<LOQ
2	<LOQ	755.2	892.6	<LOQ
3	63.9	1175.4	nd	<LOQ
4	<LOQ	14.5	nd	<LOQ

Concentration: µg kg^{-1}; nd: not detected. <LOQ: detected but at lower concentration (<10 µg Kg^{-1}).

CONCLUSIONS

- The method's validation parameters in terms of recovery, quantification limits (LOQs), linearity (r2), matrix effects and intra-day and inter-day precision showed that the proposed method meets the pesticide analysis requirements.
- It was applied for the determination of selected fungicides in 20 real orange and pear samples. Four different pesticide residues were detected in 10 of these commodities; 40% of the samples contained pesticide residues at a quantifiable level (equal to or above the LOQs) for at least one pesticide residue.
- It has been demonstrated that yttria-stabilized zirconium dioxide can be used as an effective d-SPE material with the QuEChERS method acting as a suitable alternative material to PSA in the extract cleanup of various matrices.

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