Evaluation of µ-solid phase extraction for the analysis of pesticide residues in cereals

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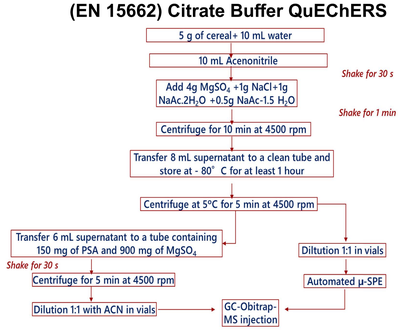
ABSTRACT

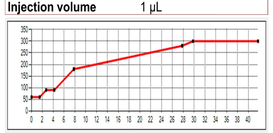
Laboratory automation in routine food control laboratories is increasing with the increased need for cost-effective, time saving, and human error reducing techniques. Novel micro-solid-phase extraction (µ-SPE) extraction devices were recently developed and adopted by some laboratories in a fully automate workflow. The system offers several workflows allowing, among others, automatic preparation of calibration standards, automatic sample dilution, and automatic clean-up of sample extracts. The system with the implemented workflows was evaluated for its applicability in the analysis of pesticide residues in cereals. The µ-SPE clean-up method was applied to acetonitrile extracts obtained from the QuEChERS sample preparation and was developed for the analysis of pesticide residues in cereals by gas chromatography-Orbitrap mass spectrometry (GC-Orbitrap-MS).

Sample Preperation and Instrumental analysis

(EN 15662) Citrate Buffer QuEChERS



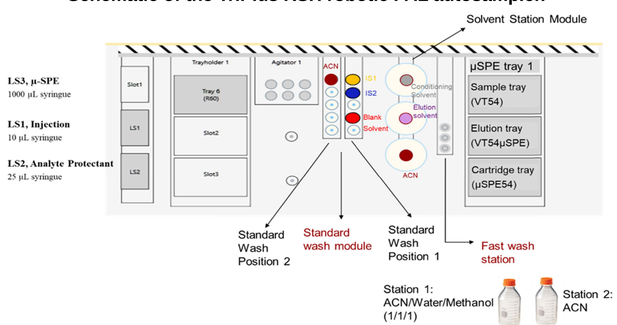
GC Parameters	
Carrier gas	He
Column	Thermo Scientific Trace GOLD TG-5SILMS 30 m length × 0.25 mm i.d. × 0.25 µm
Injection mode	PTV
Injector temperature	70°C
Carrier flow	1.2 mL/min
Injection volume	1 µL



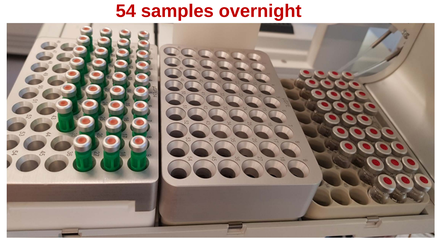
MS Parameters	
MS Transfer Line temperature	280°C
Ion source Temperature	280°C
Ionization type	EI
Acquisiton mode	Scan Mode
Scan range	50-550 m/z
Mass resolution	60 k (FWHM at m/z 200)
Lock masses (column bleed m/z)	355.06993 ; C9H27O5Si5 281.05114 ; C7H21O4Si4 207.03235 ; C5H15O3Si3 133.01356 ; C3H9O2Si2 73.04680 ; C3H9Si

Reduced labor time with the automated system

Schematic of the TriPlus RSH robotic PAL autosampler.



13 min /sample
54 samples overnight

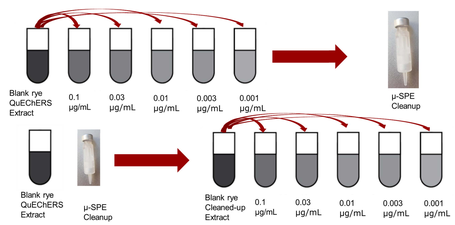


µ-SPE Cartridge tray Eluate tray Sample tray

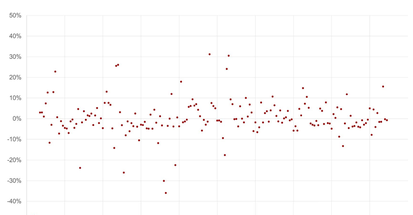
Automatic µ-SPE program steps with a total duration of 13 min

Time (mm:ss)	Steps
0:30	Required tool selected
	Syringe wash: 2 cycles at wash position 1
01:00	Load sample onto µ-SPE
	Perform 3 filling strokes
03:00	Load sample onto µ-SPE cartridge: 300 µL
01:00	Syringe wash: 2 cycles at wash position 1
01:00	Required tool selected
01:00	Syringe wash: 2 cycles at wash position 1
	Rinse
01:00	Add 15 µL internal standard
	Perform 3 filling strokes
01:00	Add internal standard: 15 µL
01:00	Required tool selected
	Syringe wash: 1 cycle at wash position 2
01:00	Rinse
00:30	Move to sample at position 1
01:00	Perform 3 filling strokes
	Aspirate 1 µL
	Inject sample

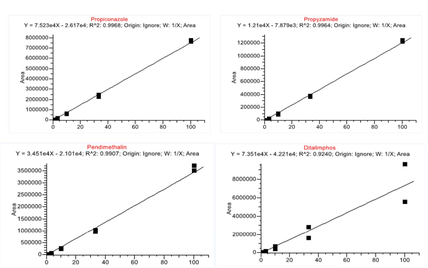
Semi-procedural standard calibration for accurate quantitative method



Comparison of the semi-procedural standard calibration to the matrix-matched calibration.

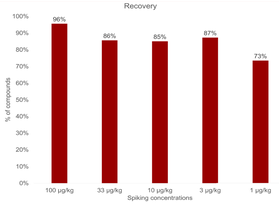


Percentage of the slopes deviation of the two calibration curves for each of the 172 compounds

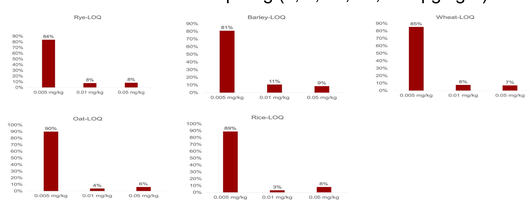


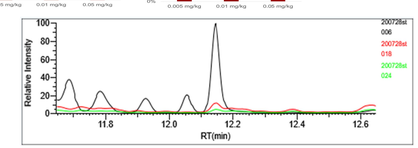
Linear curve of the matrix-matched and the semi-procedural standard calibration

Good recoveries and clean extracts



Pesticide recoveries after clean-up at five concentration levels of spiking (1, 3, 10, 33, 100 µg kg-1)





Cross-sample peak overlay of lignoceric acid methyl ester in 0.5 g mL-1 rye blank extracted with d-SPE (black; peak area: 5,667.091), µ-SPE clean-up of 0.5 g mL-1 matrix (red; peak area: 75.399), and µ-SPE clean-up of 0.25 g mL-1 matrix (green; peak area: 420.236).

CONCLUSION

The µ-SPE clean-up efficiency was demonstrated in the removal of matrix-interfering components and in the recovery of pesticides. Analysis of five types of cereals (barley, oat, rice, rye, and wheat) by GC-Orbitrap-MS showed that the method removed more than 70% of matrix components. The clean-up method was validated for 170 pesticides in rye, 159 pesticides in wheat, 142 pesticides in barley, 130 pesticides in oat, and 127 pesticides in rice. Spike recovery values were 70–120% for all pesticides and the repeatability, calculated as the relative standard deviation, was less than 20%. The limits of quantitation achieved were 0.005 mg kg−1 for almost all analytes, ensuring compliance with the maximum residue limits.