Rural Development Administration
National Institute of Agricultural Sciences

Evaluation of zirconia based sorbents for the dSPE cleanup of QuEChERS extracts within the pesticide residue analysis in low-fat food

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Introduction

Recently, zirconia-based sorbents were evaluated for the analysis of pesticide residues in high-fat food [1-3]. The aim of this study was to evaluate the performance of Z-Sep and Z-Sep plus for the cleanup step in multiresidue pesticide analysis in low-fat food using QuEChERS sample preparation. The matrices were extracted using citrate buffered QuEChERS (EN-15662) [4] and purified using PSA, Z-Sep and Z-Sep plus sorbents. The sorbents were compared by recovery experiments for 309 compounds on cucumber and grape using LC-MS/MS and GC-MS/MS, and for 137 compounds on orange and spinach using LC-MS/MS. Besides recovery rates, relative standard deviations and matrix effects were also studied.

Materials & Methods

Weigh 10 g of grinded sample

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Add 10 ml of acetonitrile and shake for 15 min

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Add 4g $MgSO_4$, 1g NaCl, 1g Na_3Citrat x $2H_2O$, 0.5g Na_2 H-Citrat-Sesquihydrate

↓

Shake for 1min. and centrifuge at 4000 rcf for 5 min

Spiking before d-SPE ⇨

↓

Transfer 6 ml of aliquot to d-SPE tube containing
1. 150 mg PSA and 0.9 g $MgSO_4$
2. 300 mg Z-Sep and 0.9 g $MgSO_4$
3. 300 mg Z-Sep⁺ and 0.9 g $MgSO_4$

⇦ Spiking after d-SPE

↓

Shake and centrifuge

↓

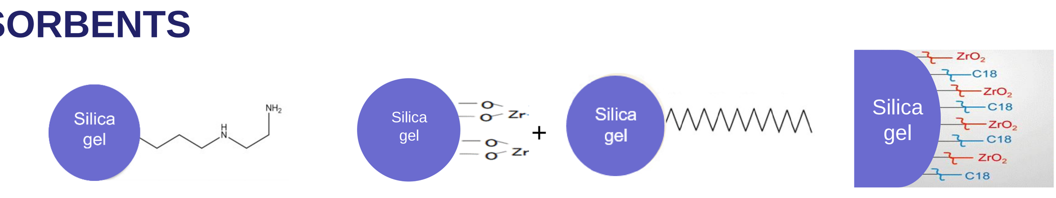
LC-MS/MS or GC-MS/MS with analyte protectants

$$Recovery = \frac{\text{Signal of spiking after d-SPE}}{\text{Signal of spiking before d-SPE}} \times 100$$

$$\%ME \text{ for LC-MS/MS} = \frac{(\text{Signal of matrix standard - Signal of solvent standard})}{\text{Signal of solvent standard}} \times 100$$

$$\%ME \text{ for GC-MS/MS} = \frac{(\text{Signal of matrix standard - Signal of cucumber standard})}{\text{Signal of cucumber standard}} \times 100$$

SORBENTS



PSA   Z-Sep (ZrO_2/C_{18} : 2/5) [5]   Z-Sep plus

INSTRUMENTATION

- Thermo Scientific Trace 1310 GC system with TSQ 8000 triple quadrupole MS/MS
- Waters UPLC with ABSciex QTrap 5500 triple quadrupole MS/MS

Results

The distribution of recovery rates achieved in the dSPE cleanup with the three sorbents is shown in Figures 1 and 2. Acidic pesticides, for which no cleanup with PSA is recommended, are also included. Overall, PSA induced the least losses but when focusing on the 70-120% range PSA and Z-Sep performed similarly well.

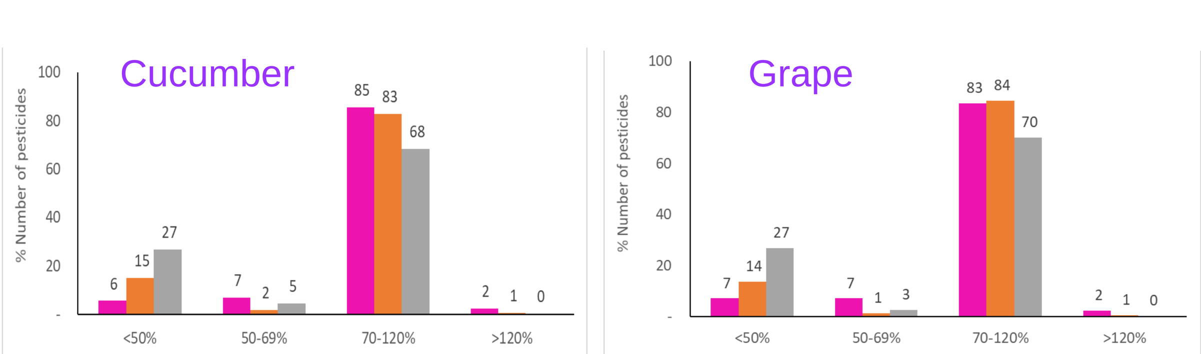


Fig. 1. Distribution of 309 pesticides within each recovery range (including acidic pesticides)

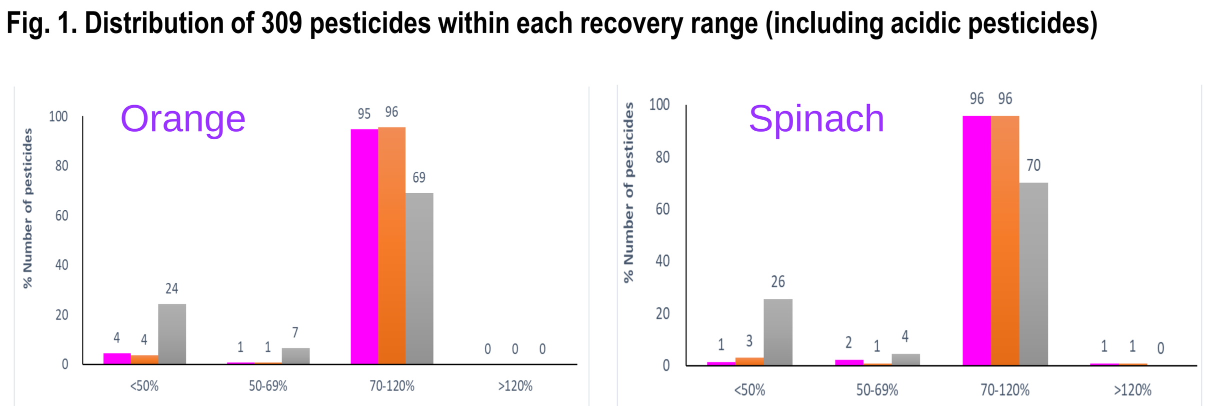


Fig. 2. Distribution of 137 pesticides within each recovery range

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Acidic pesticides, such as 2,4-D and fluazifop, were negatively affected in their recoveries by all three sorbents but the decline was only moderate with PSA, strong with Z-Sep and very strong with Z-Sep+. Z-Sep+ even removed very weakly acidic pesticides such as fenhexamid. Z-Sep+ furthermore caused a drastic decline the recoveries of **cyclohexene oxime herbicides** (e.g. cycloxydim) and **triazole fungicides** (e.g. triadimenol). **Base-sensitive pesticides**, such as dithianon, pyridate and chinomethionate, were mainly affected PSA compounds. This is mainly due to the rise of the pH in the case of PSA (see Table 1). Several compounds where recovery rates were the lowest in the case of PSA are shown in Table 2. In these cases Z-Sep is a useful alternative.

Table 1. pH values in raw and cleaned-up cucumber, grape, orange and spinach extracts

	Raw	PSA	Z-Sep	Z-Sep+
Cucumber	3.9	8.4	5.2	5.2
Grape	3.7	7.3	3.9	3.7

Table 2. Pesticides showing higher recoveries with Z-Sep or Z-Sep+ sorbent compared to PSA sorbent

Pesticide	Commodity	Recovery ± RSD		
		PSA	Z-Sep	Z-Sep+
Dithianon	Solvent	0 ± 0	92 ± 18	111 ± 9
	Cucumber	0 ± 0	68 ± 13	46 ± 10
	Grape	3 ± 15	104 ± 2	69 ± 16
	Orange	nt	nt	nt
	Spinach	nt	nt	nt
Chinomethionate	Solvent	25 ± 4	106 ± 7	95 ± 13
	Cucumber	56 ± 5	102 ± 6	89 ± 9
	Grape	45 ± 5	97 ± 3	95 ± 8
	Orange	36 ± 6	96 ± 1	99 ± 3
	Spinach	66 ± 6	106 ± 2	93±12
Probenazole	Solvent	23 ± 3	101 ± 2	101 ± 2
	Cucumber	47 ± 6	99 ± 3	102 ± 1
	Grape	59 ± 3	100 ± 1	101 ± 2
	Orange	39 ± 9	104 ± 2	106 ± 2
	Spinach	60 ± 7	106 ± 1	100 ± 1
Bensultap	Solvent	33 ± 5	65 ± 10	44 ± 22
	Cucumber	4 ± 24	70 ± 4	65 ± 8
	Grape	21 ± 30	102 ± 3	138 ± 3
	Orange	12 ± 21	94 ± 5	71 ± 6
	Spinach	1 ± 44	110 ± 6	38 ± 12
Thiosultap	Solvent	0 ± 0	90 ± 4	65 ± 6
	Cucumber	19 ± 7	88 ± 4	86 ± 10
	Grape	16 ± 13	101 ± 12	80 ± 8
	Orange	nt	nt	nt
	Spinach	nt	nt	nt
Pyridate	Solvent	41 ± 6	96 ± 1	101 ± 3
	Cucumber	75 ± 4	99 ± 3	99 ± 3
	Grape	65 ± 6	103 ± 3	100 ± 4
	Orange	12 ± 12	95 ± 6	94 ± 5
	Spinach	76 ± 11	105 ± 5	94 ± 9
Metosulam	Solvent	63 ± 2	95 ± 1	98 ± 4
	Cucumber	86 ± 2	98 ± 6	100 ± 2
	Grape	76 ± 4	104 ± 3	103 ± 3
	Orange	54 ± 5	101 ± 8	99 ± 6
	Spinach	87 ± 7	100 ± 1	109 ± 8
Rimsulfuron	Solvent	71 ± 4	94 ± 1	36 ± 9
	Cucumber	93 ± 3	99 ± 1	60 ± 2
	Grape	85 ± 2	103 ± 2	62 ± 6
	Orange	72 ± 5	96 ± 6	79 ± 5
	Spinach	88 ± 10	113 ± 4	80 ± 19

nt: not tested   <50%   50-80%   80-120%

Fig. 3. LC-MS/MS matrix effects in cucumber and grape extracts (normalized to internal standard). Pesticides with high RSD and highly biased recovery rates excluded.

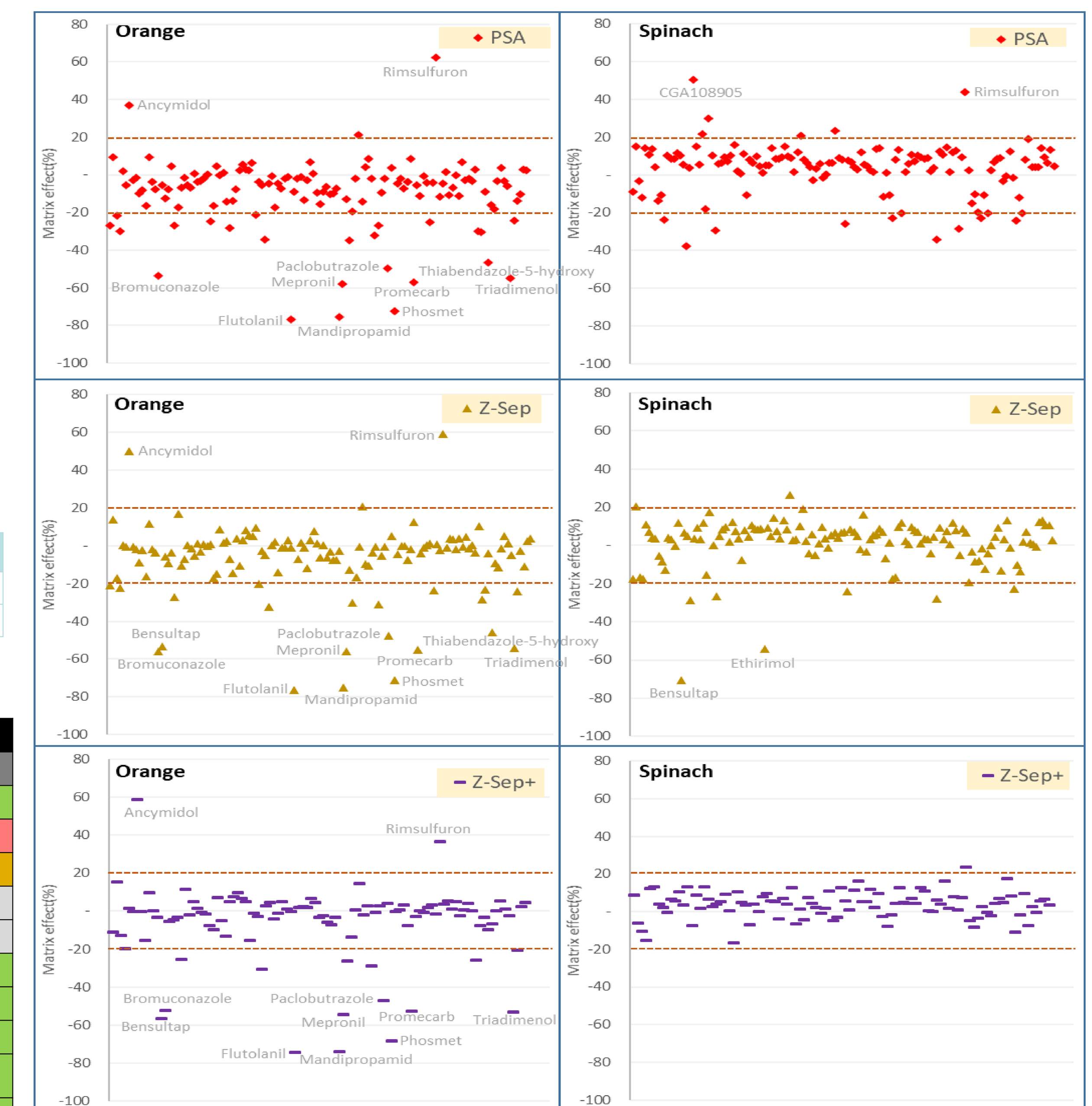

Fig. 4. LC-MS/MS matrix effects in orange and spinach extracts (normalized to internal standard). Pesticides with high RSD and highly biased recovery rates excluded.

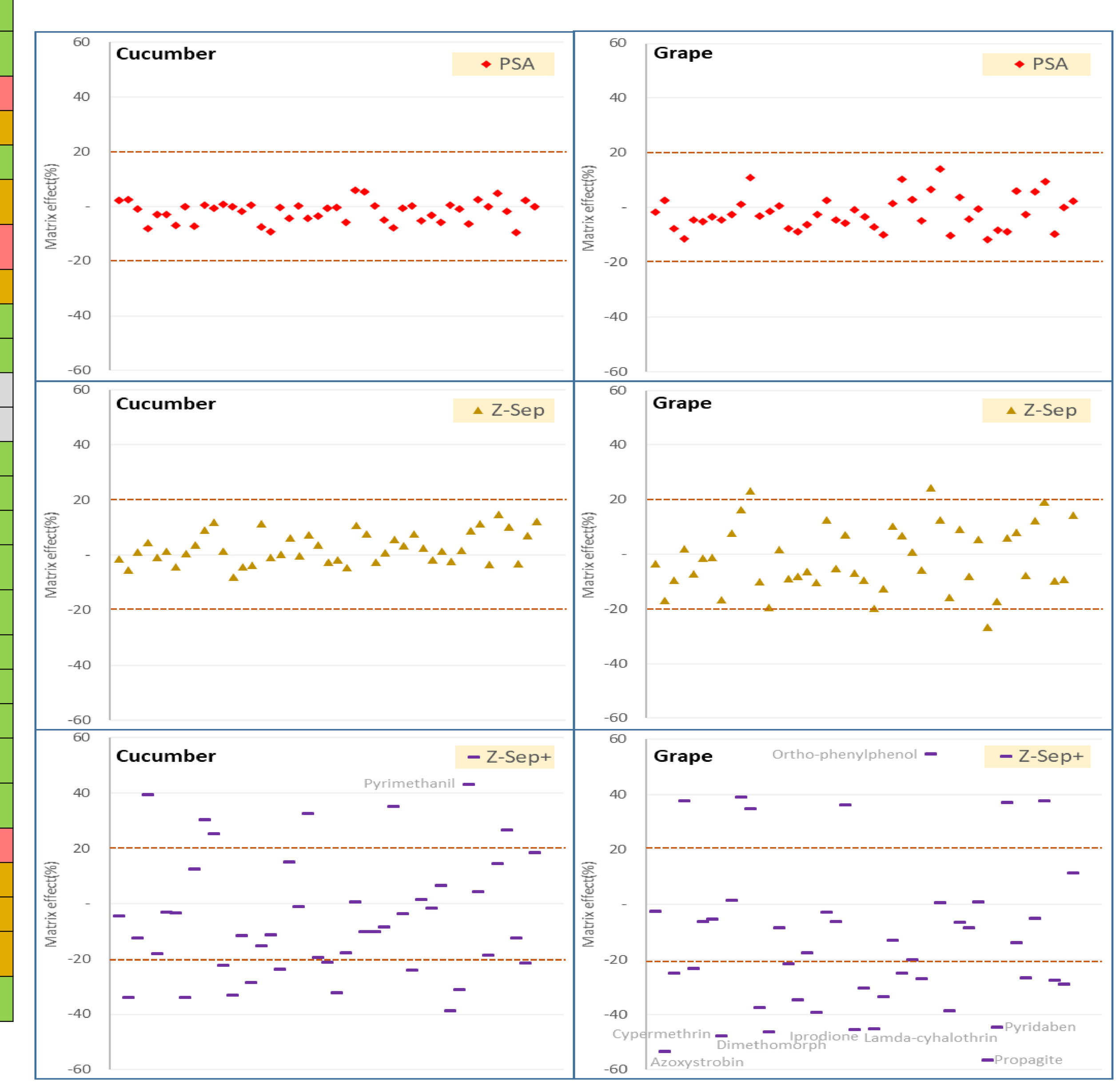

Fig. 5. GC-MS/MS matrix effects in cucumber and grape extracts (normalized to internal standard). Calculated against signals in cucumber raw extract.

Conclusions

- From cucumber and grape extracts satisfactory recoveries within the 70-120% range were obtained for 83-85% of the compounds using PSA, 82-84% of the compounds using Z-Sep and 68-70% of the compounds using Z-Sep+.
- In orange and spinach satisfactory recoveries were obtained for 95-96% of compounds using PSA, 96% of the compounds using Z-Sep and 69-70% of the compounds using Z-Sep+.
- Zirconia-based sorbents proved to provide higher recoveries for base-sensitive compounds compared to PSA.
- Following d-SPE cleanup with zirconia-based sorbents the pH of the extracts remained acidic (3.7~5.2), which is beneficial for base-sensitive pesticides. Following cleanup with PSA the pH of the extract increased to 7.3-8.4.
- The best results in terms of matrix effects in LC-MS/MS were obtained using Z-Sep+, while matrix effects for PSA and Z-Sep were similar. In GC-MS/MS, PSA and Z-Sep gave similar matrix effects.
- The study suggests that Z-Sep sorbent can be used as an alternative to PSA in the dSPE cleanup of QuEChERS extracts of low-fat food.

References

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