Development of a novel and concise multi-plug filtration method for cleaning up pesticide residue samples in seconds

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Outline

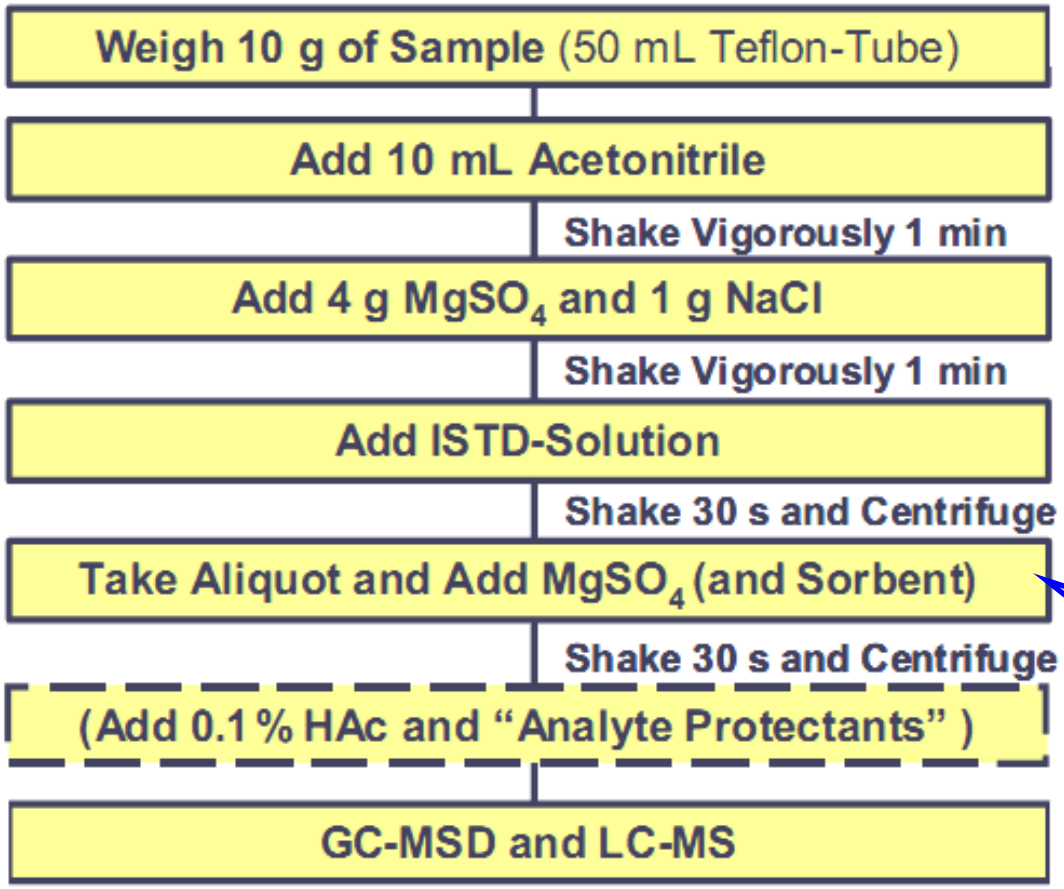
- Introduction of cleanup methods in residue analysis
- MWCNTs as alternative r-DSPE materials
- M-PFC for analysis of pesticide residues
- Discussion and Conclusion

Introduction of QuEChERS method

- Quick
- Easy
- Cheap
- Effective
- Rugged
- Safe

M. Anastassiades, S.J. Lehotay, D. Stajnbaher, F.J. Schenck, J. AOAC Int. 86 (2003) 412.

QuEChERS method



reversed-dispersive solid phase extraction (r-DSPE)

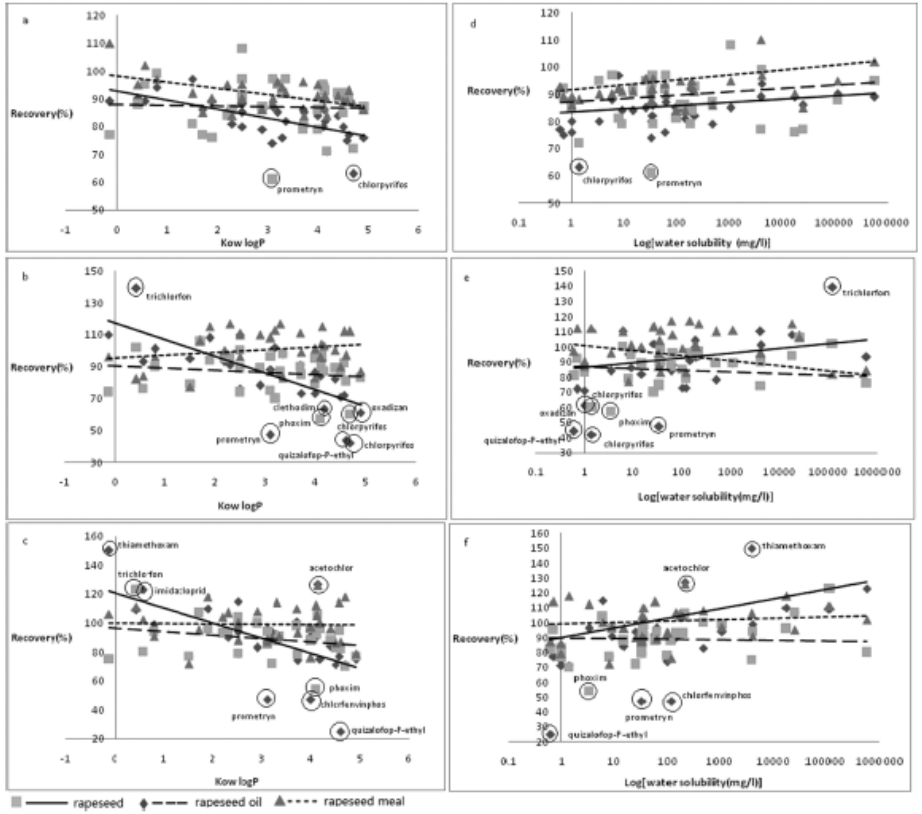


Figure 2. Influence of pesticides' *n*-octanol–water partition coefficients (kowlogP) and water solubility on their recovery.

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Determination of Multiresidues in Rapeseed, Rapeseed Oil, and Rapeseed Meal by Acetonitrile Extraction, Low-Temperature Cleanup, and Detection by Liquid Chromatography with Tandem Mass Spectrometry

Yaping Jiang,[†] Yanjie Li,[†] Yuting Jiang,[†] Jianguo Li,[§] and Canping Pan*[,†]

QuEChERS method

- High recoveries
- High sample throughput
- Non-sophisticated equipment
- Smaller volume of organic solvent
- Low cost per sample

QuEChERS method

- r-DSPE sorbents

PSA: remove various polar organic acids, polar pigments, some sugars and fatty acids.

GCB: remove sterols and pigments

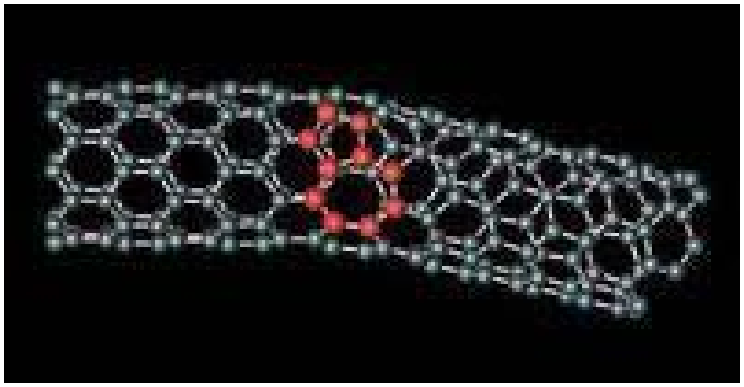
C18: remove non-polar interfering substances

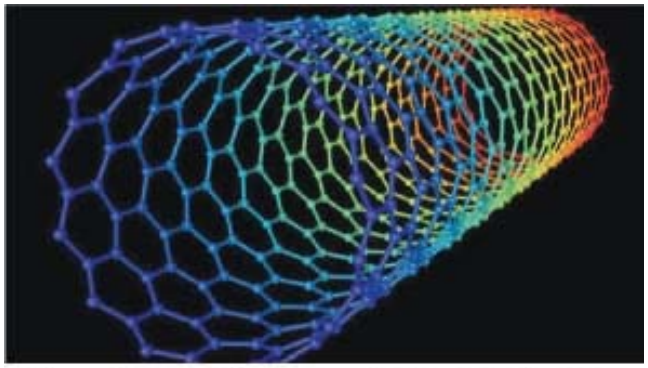
- Not good enough to remove interferences
- SPE is necessary.

MWCNTs as alternative r-DSPE materials

Modified Multiple Walled Carbon Nanotubes :

- Special physical and chemical characteristics
- Large surface area
- Excellent adsorption ability





MWCNTs as alternative r-DSPE materials

Representative matrices:

Cabbage, spinach, grape, orange

Complex matrices:

Leek, ginger, onion, garlic

Weigh 10 g of Sample (50 mL Teflon-Tube)

Add 10 mL Acetonitrile

Shake vigorously 1 min

Add 4 g $MgSO_4$ and 1g NaCl

Shake 1 min and Centrifuge

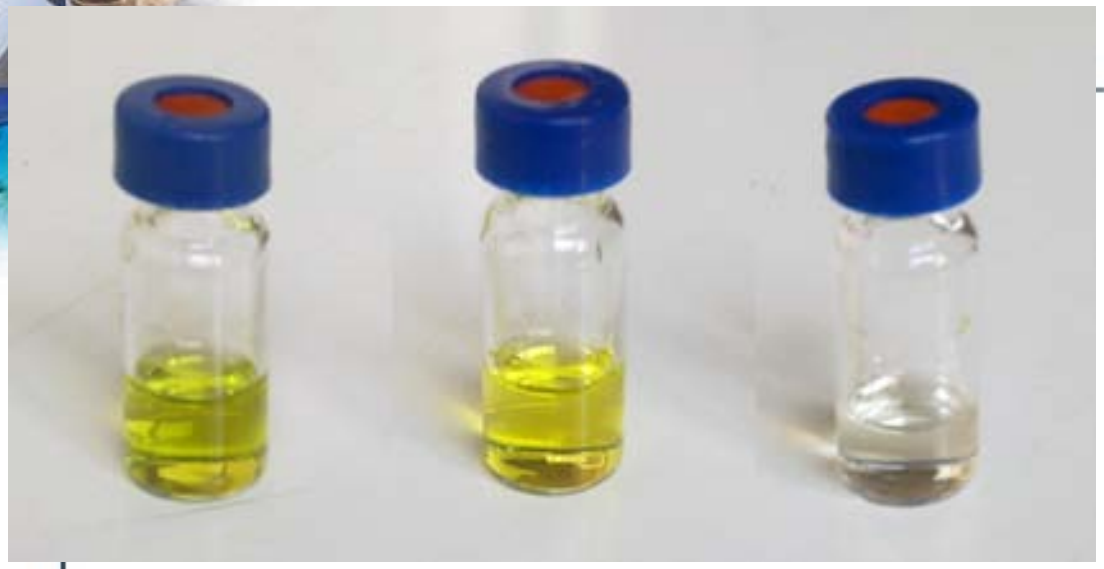
Take 1 mL of Aliquot and Add 150 mg $MgSO_4$ and 10 mg MWCNTs

Shake 30 s and Centrifuge

GC-MS

J. Chromatogr. A 1225 (2012) 17– 25

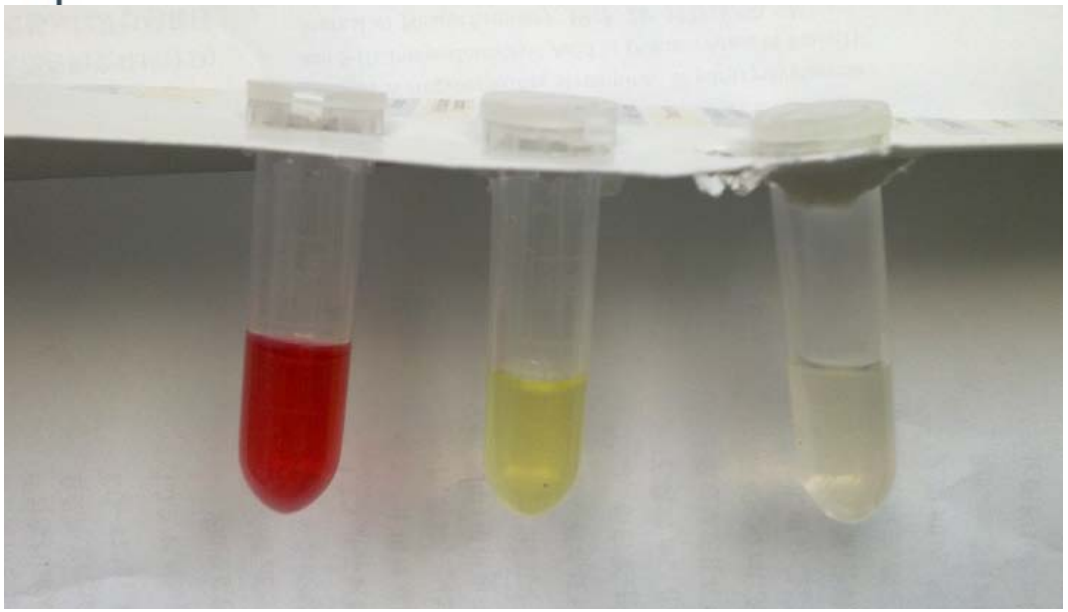
J. Sep. Sci. 2012, 35, 153–158



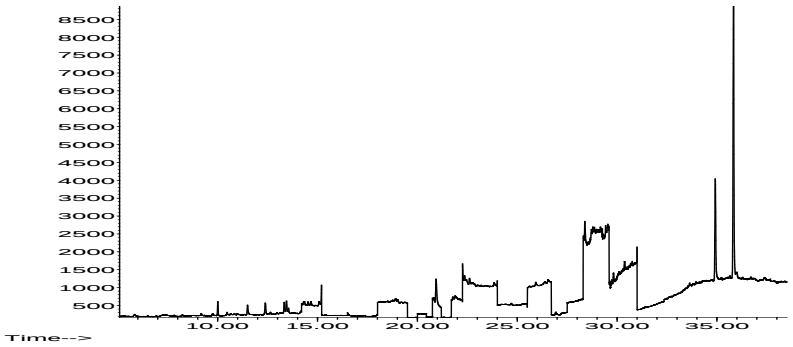
Without r-DSPE

r-DSPE (PSA)

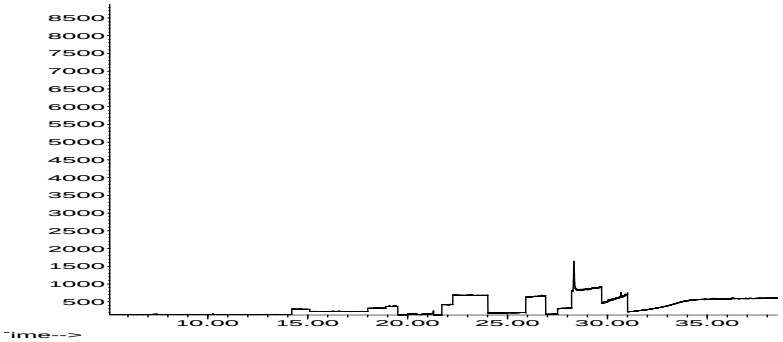
r-DSPE (MWCNTs)



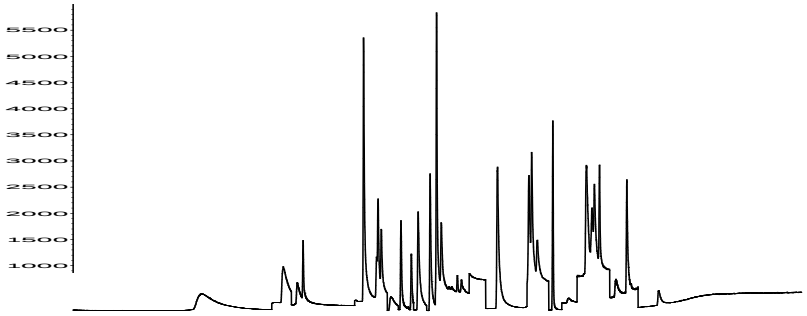
a）Chromatogram for a typical blank sample with PSA cleanup



b）Chromatogram for a typical blank sample with MWCNTs cleanup



c）Chromatogram for a spiked sample with MWCNTs cleanup.



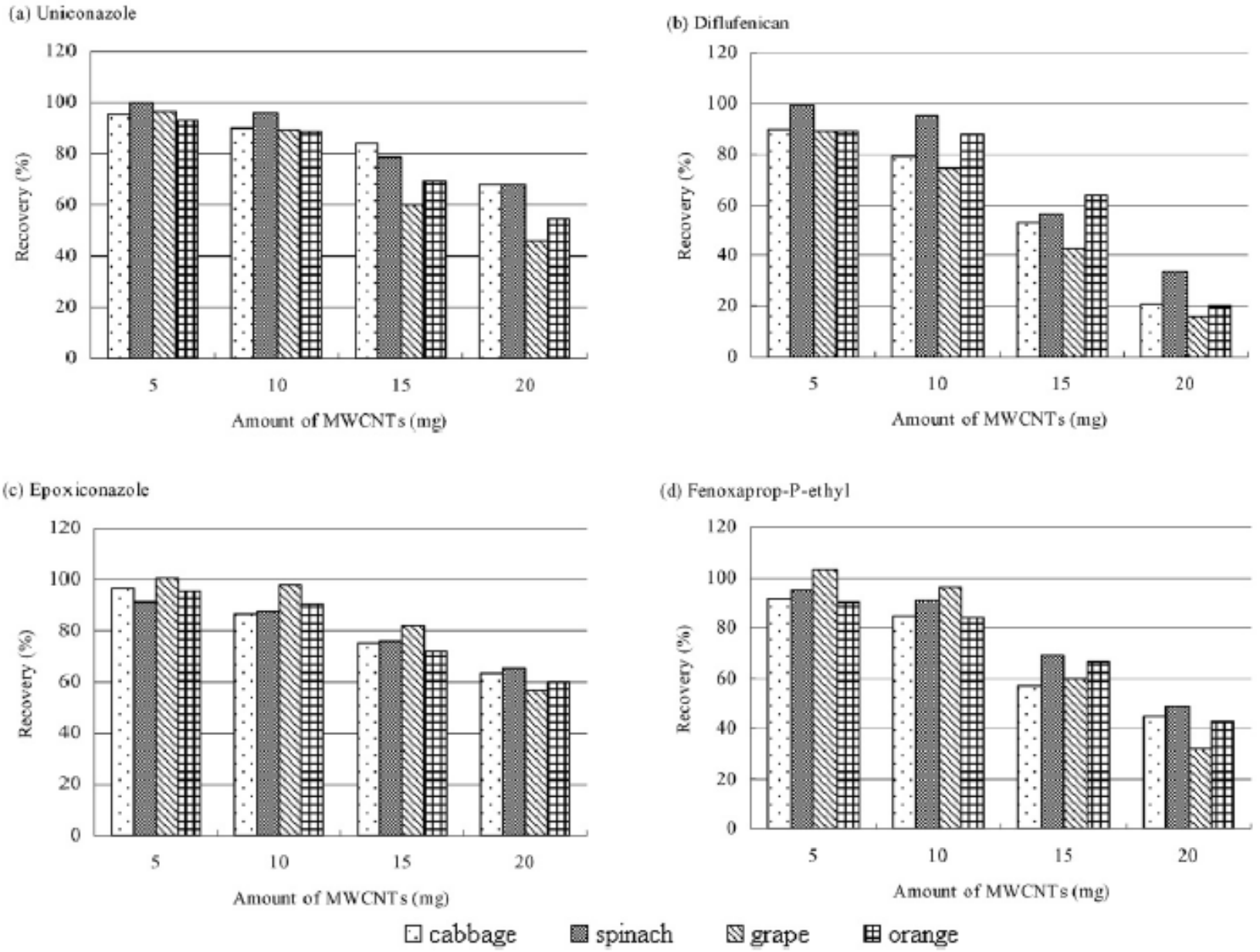


Fig. 1. Effects of amount of MWCNTs on method recoveries.

MWCNTs as alternative r-DSPE materials

Thirty pesticides with different LogP and different chemical structural catalogues

- Recoveries: 71 %-110 %
- RSD: lower than 15 %
- LOQ：0.003-0.05 mg/kg
- LOD：0.001-0.02 mg/kg

MWCNTs as alternative r-DSPE materials

Tea samples:

Green tea

Oolong tea

Puer tea

Weigh 5 g of Sample (50 mL Teflon-Tube)

Add 10 m L water and 10 mL Acetonitrile

Shake vigorously 1 min

Add 4 g $MgSO_4$ and 1g NaCl

Shake 1 min and Centrifuge

Take 1 mL of Aliquot and Add 150 mg $MgSO_4$, *5mg GCB, 25 mg PSA and 15 mg MWCNTs*

Shake 30 s and Centrifuge

LC-MS/MS

J. Agric. Food Chem. 2012, 60, 4026− 4033

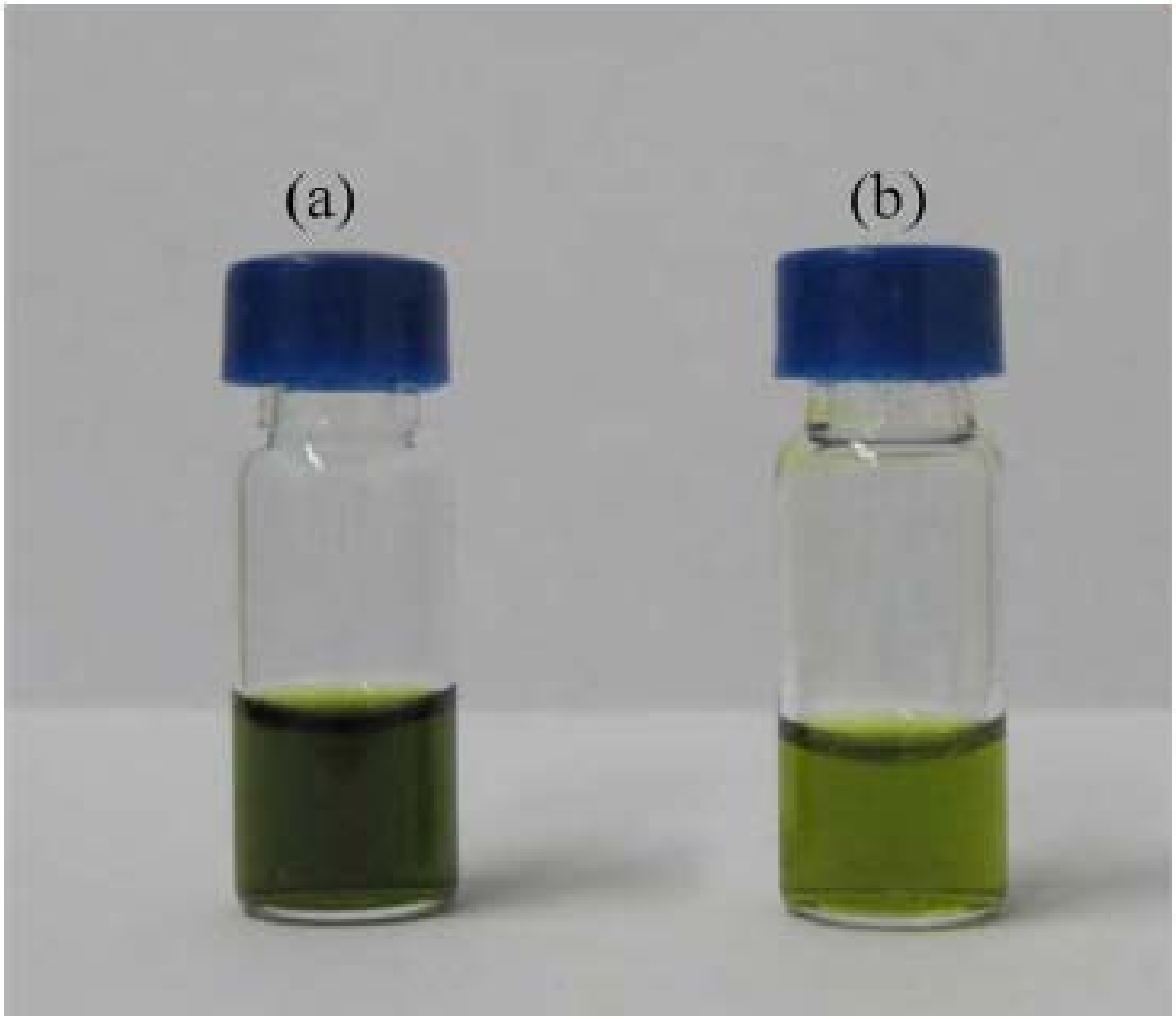
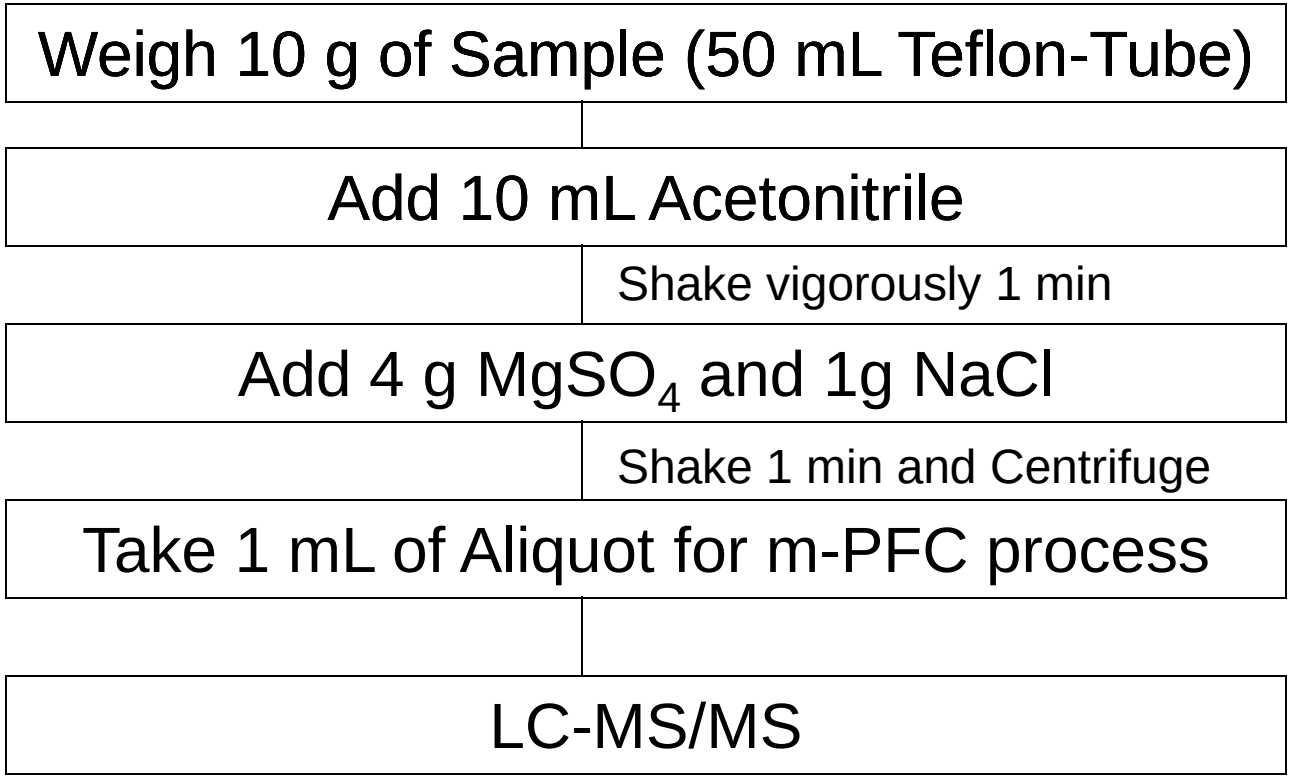


Figure 3. Photography of cleanup performance by different r-DSPE sorbents: (a) extract for green tea with PSA and GCB cleanup; (b) extract for green tea with MWCNT, PSA, and GCB cleanup.

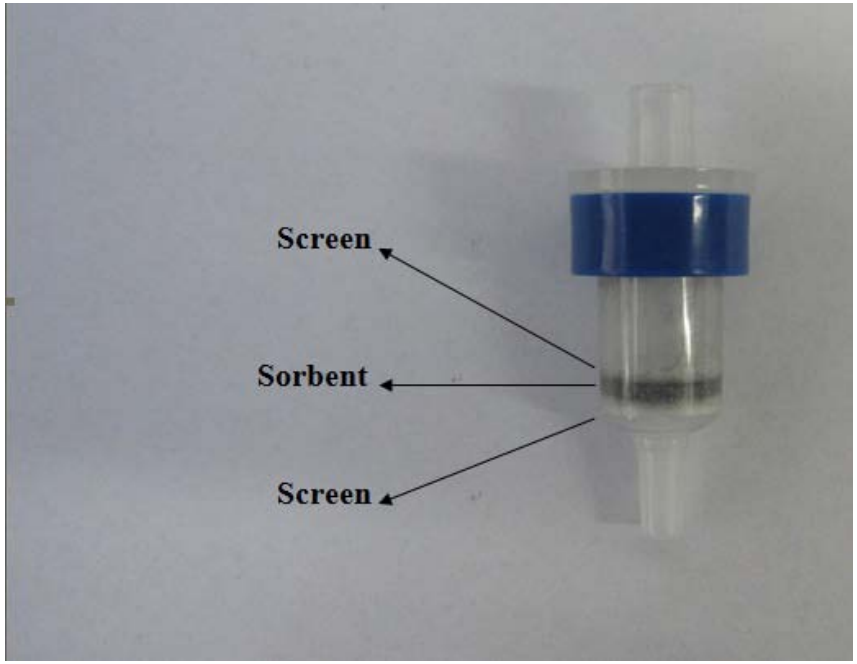
Multi-plug filtration cleanup (m-PFC) for analysis of pesticide residues

Representative matrices:
Apple
Cabbage
Potato



Multi-plug filtration cleanup (m-PFC) for analysis of pesticide residues

Sorbent: 10 mg MWCNTs mixed with 150 mg $MgSO_4$



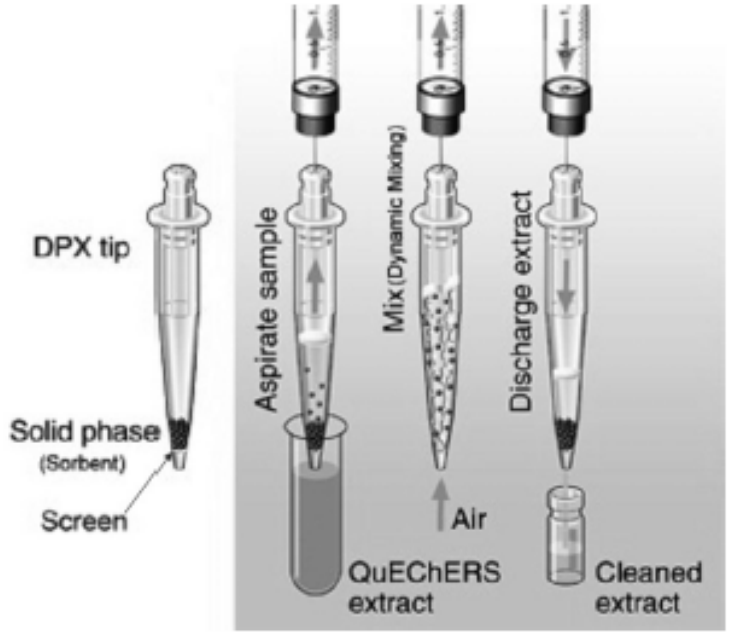


Figure 2. Schematic diagram of a DPX cleanup. Modified schematic diagram adapted from the online publication of GERSTEL, http://www.gerstel.de/pdf/p-gc-an-2009-01.pdf (Guan, H.; Brewer, W. E.; Morgan, S. L.; Stuff, J. R.; Whitecavage, J. A.; Foster, F. D. Automated Multi-Residue Pesticide Analysis in Fruits and Vegetables by Disposable Pipette Extraction (DPX) and Gas Chromatography/Mass Spectrometry. **2009**, AN/2009, 1–7).

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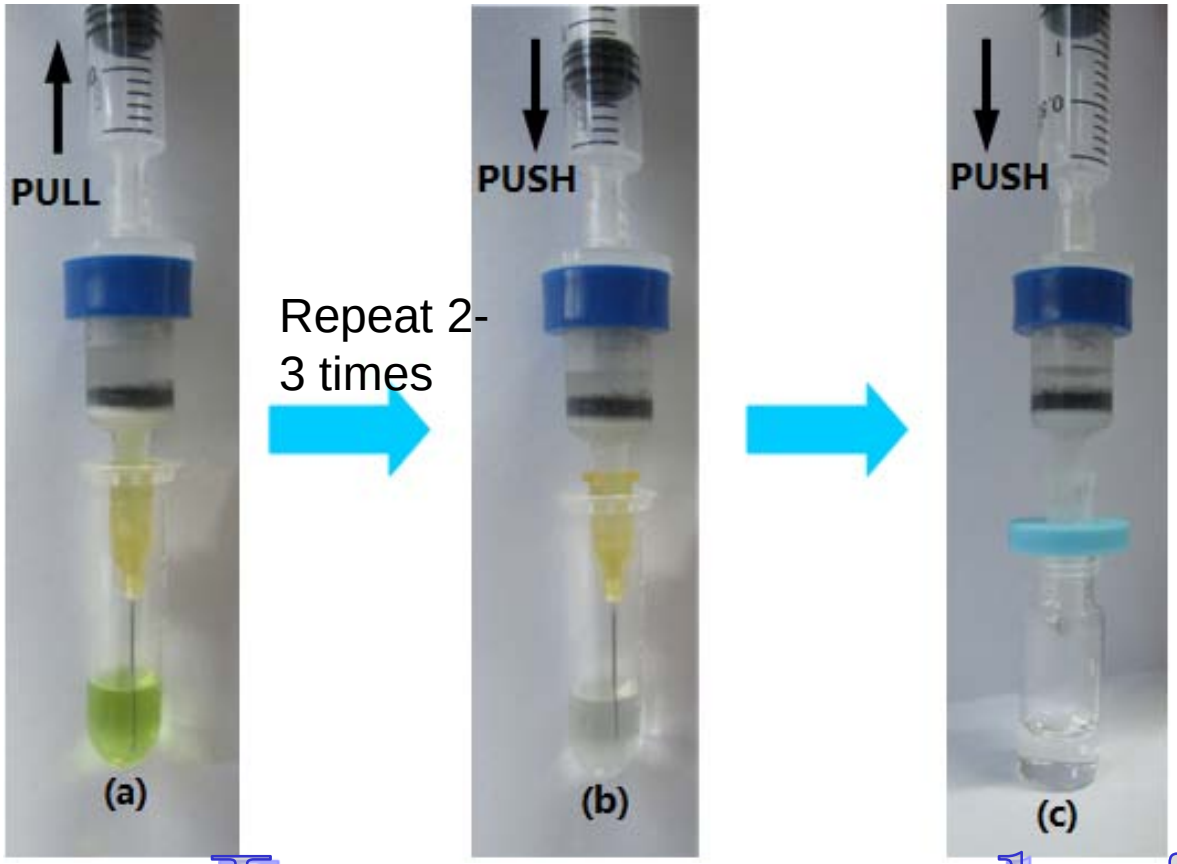
Multiresidue Analysis of 58 Pesticides in Bean Products by Disposable Pipet Extraction (DPX) Cleanup and Gas Chromatography–Mass Spectrometry Determination

Ziang Li,[†,‡] Yanjie Li,[‡] Xiaochen Liu,[‡,§] Xuesheng Li,[‡,∥] Li Zhou,[‡] and Canping Pan*[,‡]

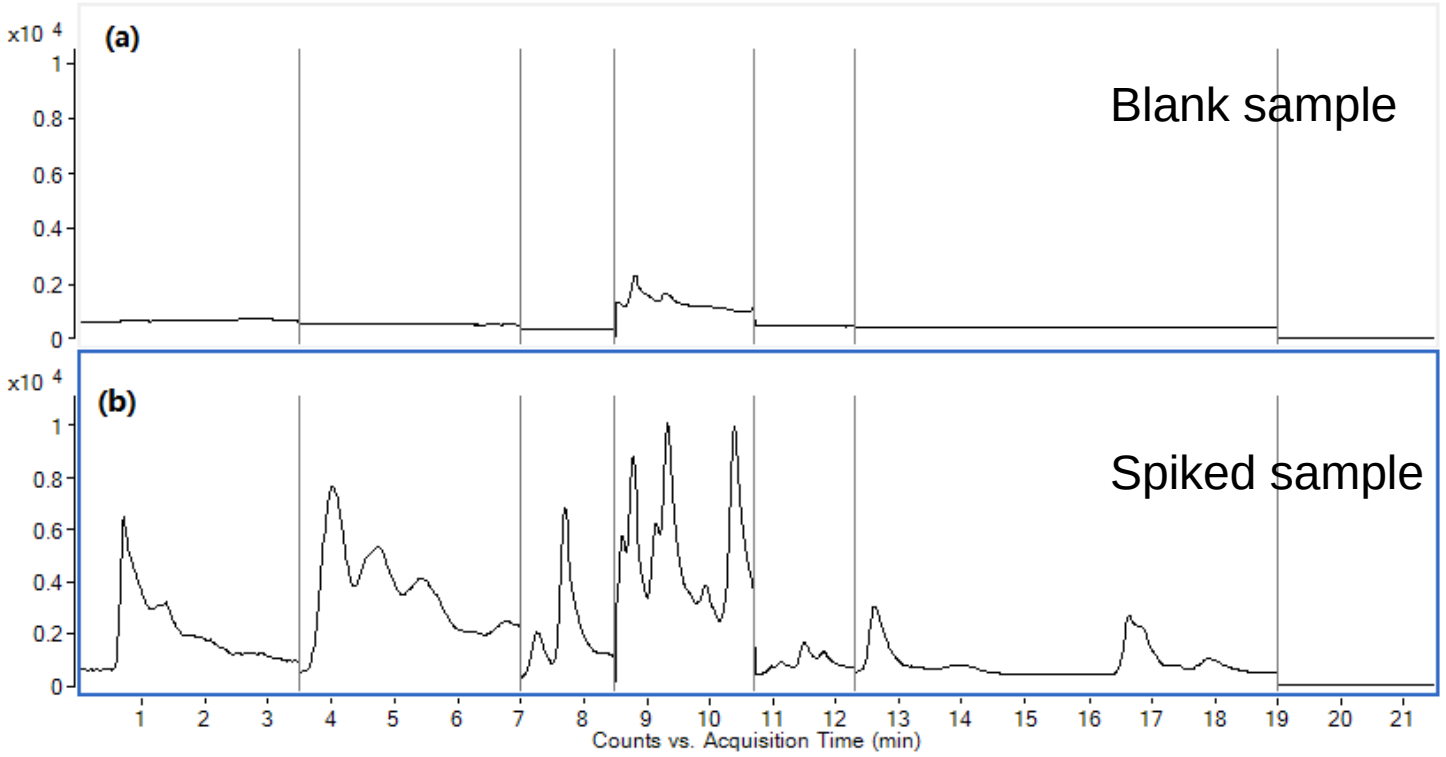
Multi-plug filtration cleanup (m-PFC) for analysis of pesticide residues

M-PFC process



In seconds!

Multi-plug filtration cleanup (m-PFC) for analysis of pesticide residues



J. Chromatogr. A under review

•Table MRM transitions and other LC-MS/MS parameters

Pesticide	RT (min)	Confirmation transition [a]	Quantification transition [a]	Fragmentor (V)
acetamiprid	1.59	223→90 (20)	223→126 (15)	80
acetochor	9.59	270→148 (10)	270→224 (10)	120
anilofos	11.60	368→125 (10)	368→199 (5)	100
atrazine	5.43	216→132 (20)	216→174 (15)	120
azoxystrobin	9.00	404→344 (15)	404→372 (10)	85
butachlor	13.01	312→162 (20)	312→238 (10)	80
carbendazim	0.75	192→132 (25)	192→160 (20)	90
carboxin	6.19	236→87 (20)	236→143 (20)	120
chlorfenvinphos	10.01	359→155 (10)	359→99 (25)	120
chlorpyrifos	13.12	350→97 (15)	350→198 (20)	100
clethodim	12.22	360→268 (10)	360→164 (20)	120
clomazone	7.92	240→89 (30)	240→125 (20)	120
diazinon	10.76	305→97 (25)	305→153 (20)	160
dichlorvos	3.28	221→109 (15)	221→109 (15)	120
difenoconazole	10.24	406→337 (15)	406→251 (20)	160
diniconazole	9.61	326→159 (30)	326→70 (25)	120

Pesticide	Average recovery, % (RSD, %) (n=5)					
	Apple		Cabbage		Potato	
	10μg kg^{-1}	100μg kg^{-1}	10μg kg^{-1}	100μg kg^{-1}	10μg kg^{-1}	100μg kg^{-1}
acetamiprid	99(2)	101(3)	103(5)	91(3)	97(5)	104(4)
acetochor	102(10)	110(6)	95(7)	95(3)	<LOQ	117(12)
anilofos	106(5)	89(11)	99(4)	100(4)	94(5)	99(4)
atrazine	104(6)	101(3)	97(2)	90(2)	97 (4)	103(7)
azoxystrobin	107(16)	103(12)	108(11)	100(5)	106(10)	102(6)
butachlor	<LOQ	98(6)	<LOQ	94(3)	92 (5)	104(6)
carbendazim	38(9)	34(6)	24(21)	29(16)	40(17)	22(19)
carboxin	82(9)	82(4)	75(8)	71(5)	77 (6)	88(6)
chlorfenvinphos	99(15)	95(13)	90(2)	96(3)	114(12)	107(4)
chlorpyrifos	115(12)	85(8)	96(11)	91(7)	<LOQ	101(9)
clethodim	84(15)	88(7)	75(7)	74(9)	84(12)	95(6)
clomazone	111(13)	96(6)	96(4)	98(4)	104(7)	109(4)

Table 3. Determination coefficients (R^2) of calibration curve, method LOD and LOQ for the studied pesticide using m-PFC met

Pesticide	R^2			LOD(μg kg^{-1})			LOQ(μg kg^{-1})		
	Apple	Cabbage	Potato	Apple	Cabbage	Potato	Apple	Cabbage	Potato
acetamiprid	0.998	1.000	1.000	1	1	1	2	3	3
acetochor	0.999	0.995	0.993	3	1	3	10	5	10
anilofos	0.992	0.996	0.997	1	1	1	3	2	3
atrazine	1.000	1.000	0.998	1	1	1	3	3	3
azoxystrobin	1.000	0.997	1.000	2	1	1	6	3	3
butachlor	1.000	0.999	1.000	5	5	3	15	15	10
carbendazim	0.997	0.993	1.000	1	2	2	3	6	6
carboxin	1.000	0.999	0.999	1	1	1	3	3	3
chlorfenvinphos	0.994	0.996	0.993	1	1	2	2	4	5
chlorpyrifos	1.000	0.999	0.993	1	1	1	3	3	2
clethodim	0.992	0.995	0.990	1	1	1	3	3	3
clomazone	1.000	1.000	1.000	2	2	2	6	5	6
diazinon	0.996	0.994	0.998	1	1	1	3	3	3
dichlorvos	1.000	0.998	0.910	3	5	5	10	15	15
difenoconazole	0.993	1.000	0.998	1	1	1	3	3	3
diniconazole	0.999	0.999	1.000	1	1	2	2	2	5
fenoxaprop-P-ethyl	0.992	0.999	0.999	1	1	1	2	5	3
fluazifop-P-butyl	1.000	1.000	1.000	1	1	2	3	3	5
flurochloridone	0.997	0.995	0.998	3	3	5	10	10	10
flutriafol	0.996	0.999	0.999	1	1	1	2	5	5
haloxyfop-P-methyl	1.000	1.000	0.998	1	2	3	3	6	10
imidacloprid	0.997	0.997	1.000	1	1	3	3	2	10
metalaxyl-m	1.000	0.999	0.998	1	1	2	2	3	6

Conclusion

- A modified QuEChERS method
- MWCNTs using as r-DSPE materials in place of PSA.
- m-PFC technology based on MWCNTs

- Future Work:

- different modified MWCNTs materials fit for different purposes in cleanup
- Stable and automatic device
- In pharmaceutical and bimolecular, etc samples