Validation Studies of Disposable Pipette Extraction of Pesticides in Fruit and Vegetables

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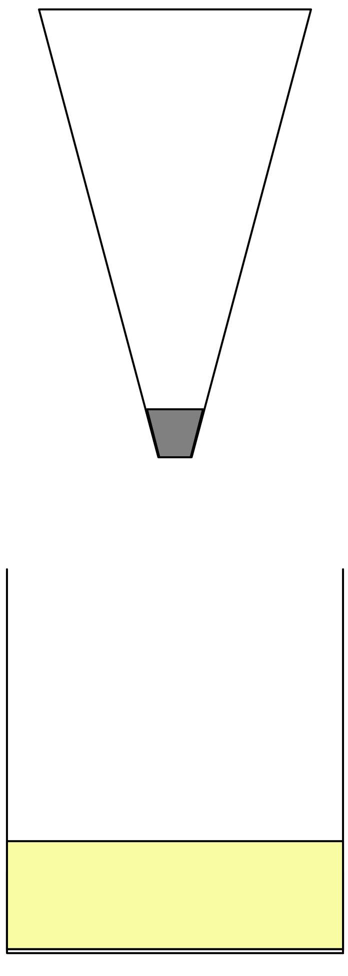
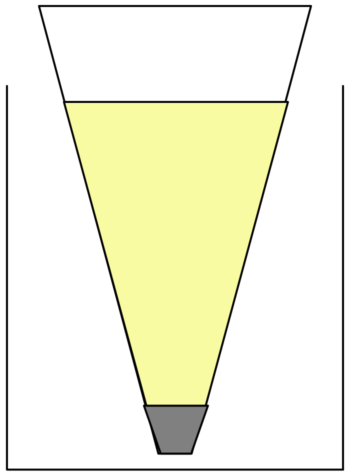
DPX in action

1) Place DPX tip into sample



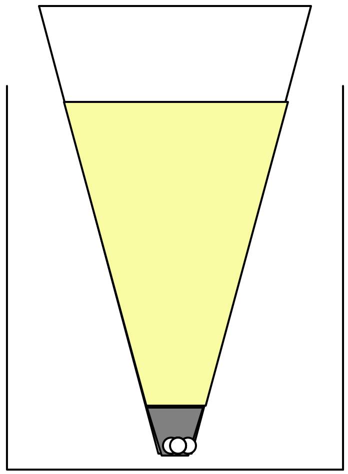
DPX in action

2) Draw in sample solution
- no conditioning required



DPX in action

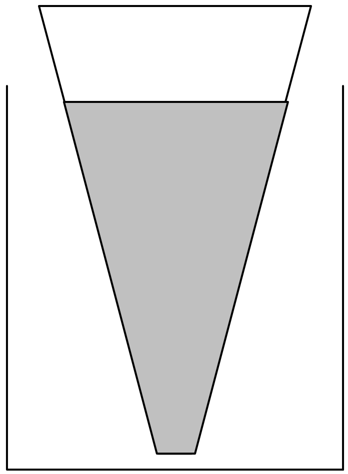
3) Draw in air to mix solution—air bubbles cause perturbation of solution and thereby causes mixing of the solution with the sorbent.



DPX in action

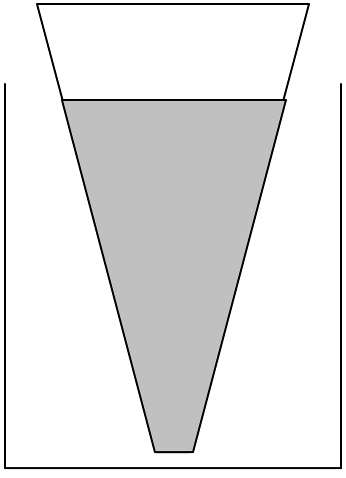
4) The sample solution becomes a pseudo-homogenous solution with sorbent.

- Extractions are very reproducible
- Efficiency is based on equilibration time, which is easily controlled
- Flow rates which are not easily controlled are NOT relevant to efficiency



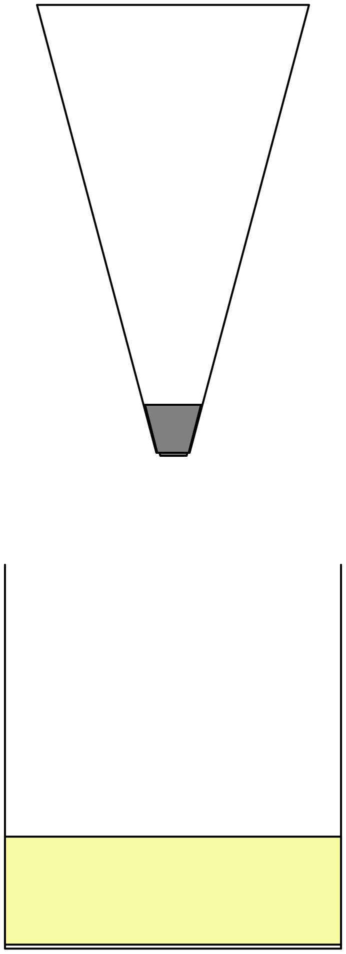
DPX in action

5) Remove from sample and let equilibrate (app. 20 seconds).



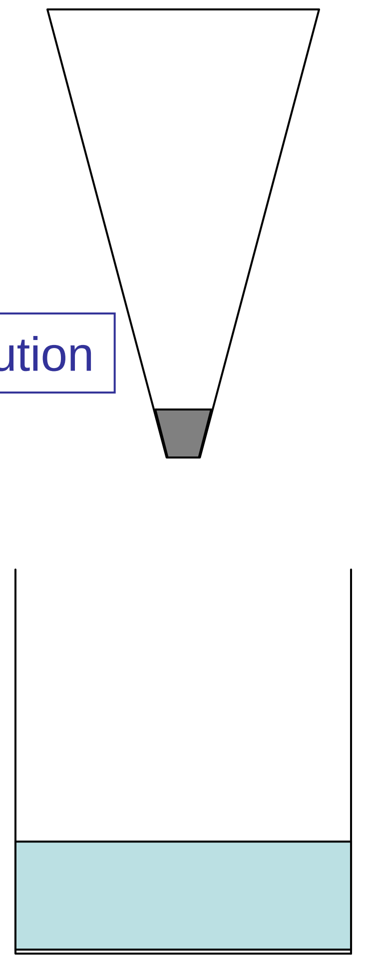
DPX in action

6) Dispense sample solution



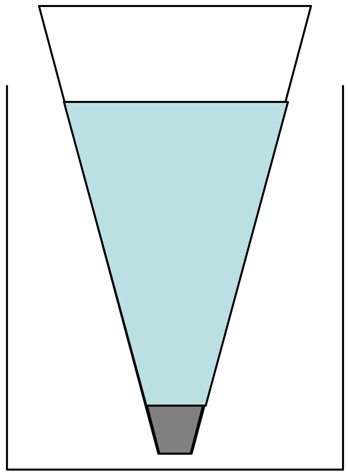
DPX in action

7) Place DPX tip into wash solution



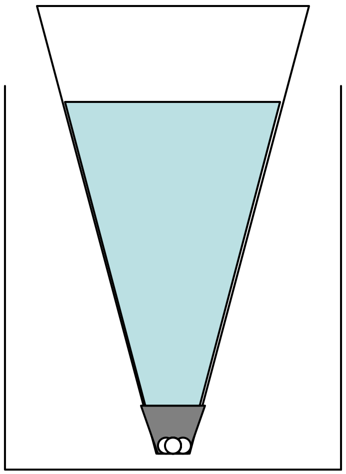
DPX in action

8) Draw in wash solution



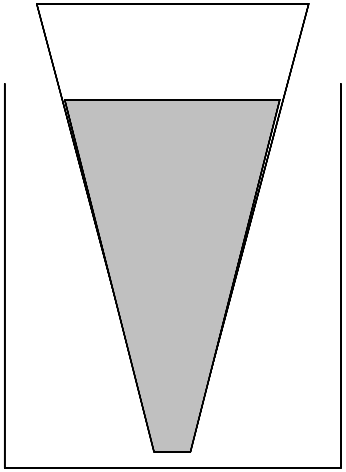
DPX in action

9) Draw in air to mix solution—air bubbles provides thorough “mixing”.



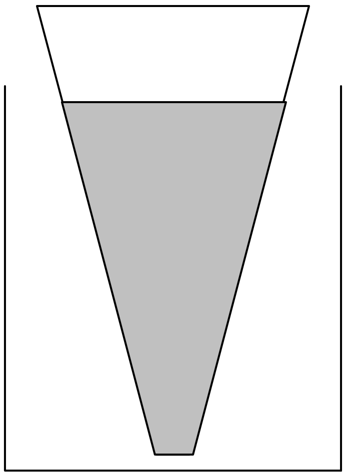
DPX in action

10) The sample solution becomes a pseudo-homogenous solution



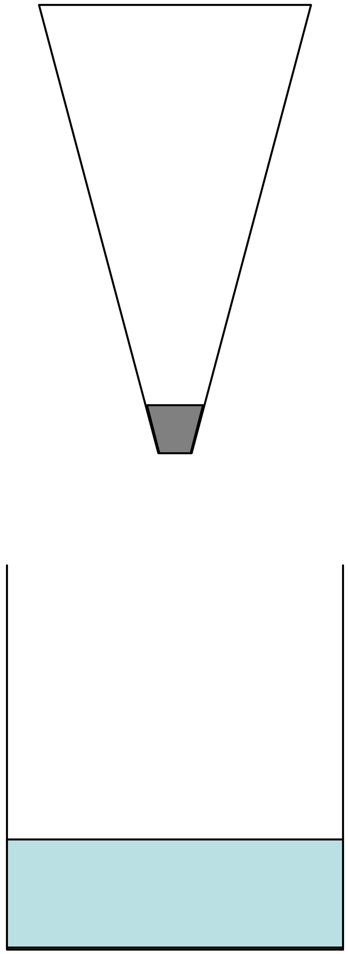
DPX in action

11) Allow to equilibrate for short time (app. 10 seconds)



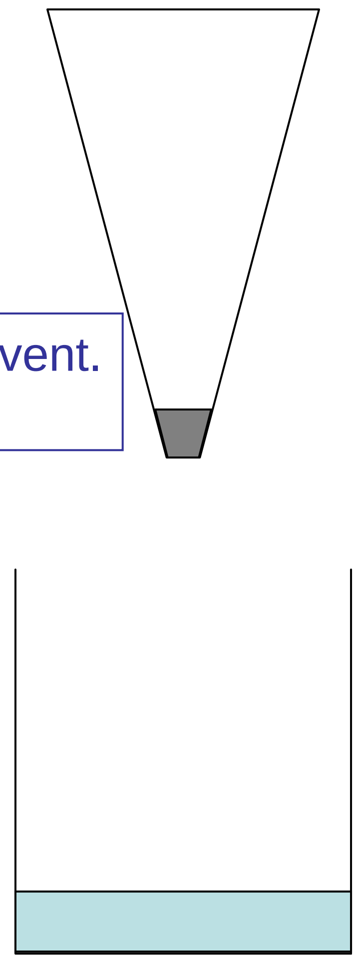
DPX in action

12) Dispense wash solution



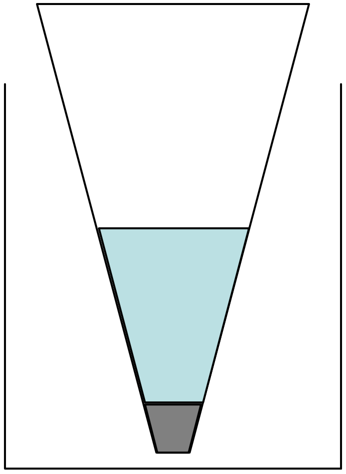
DPX in action

13) Place DPX tip into elution solvent.
- Low volume of solvent



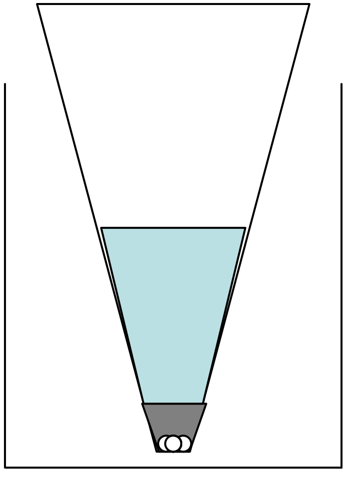
DPX in action

14) Draw in elution solvent.



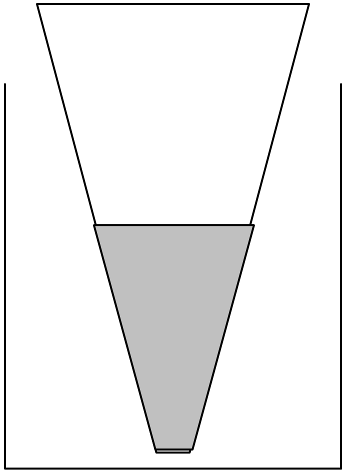
DPX in action

15) Draw in air to mix solution—air bubbles provides thorough "mixing".

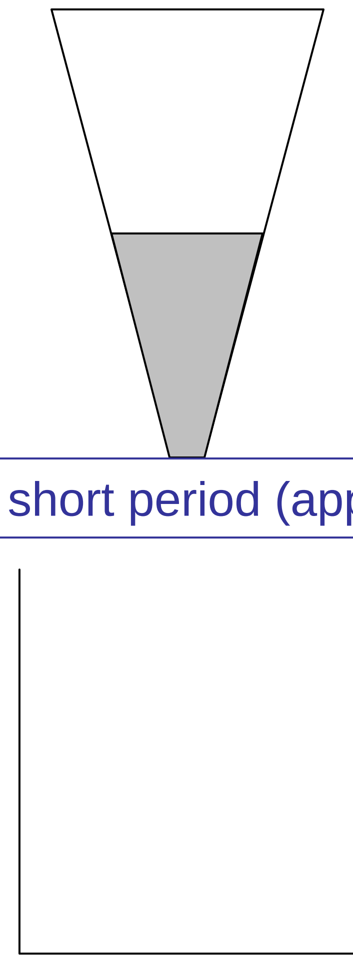


DPX in action

16) The sample solution becomes a pseudo-homogenous solution

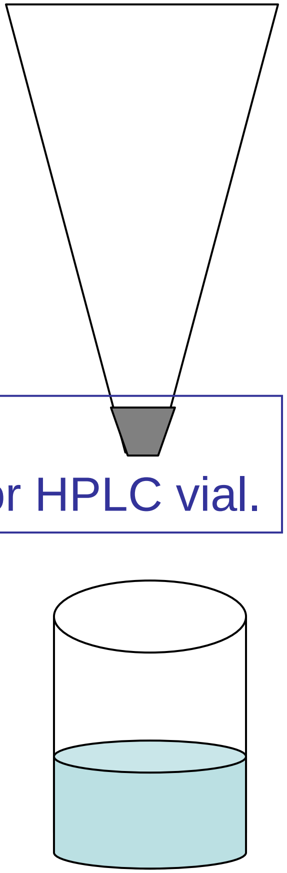


DPX in action



17) Allow to equilibrate for a short period (app. 10 seconds)

DPX in action



18) Dispense elution solvent.

➢May dispense directly into GC or HPLC vial.

DPX in QuEChERS Study

Extract in acetonitrile following QuEChERS procedure

- 15 g sample plus 15 mL ACN
- Add salt ($MgSO_4$ and NaCl)
- Shake, centrifuge

DPX in QuEChERS Study

DPX-RP (nonpolar compounds):

Take 1mL and add 2.4 mL H2O plus 0.8 mL sat'd NaCl
Perform DPX extraction (app. 3-4 minutes)
Inject into **GC-ECD** (*no solvent evaporation*)

DPX in QuEChERS Study

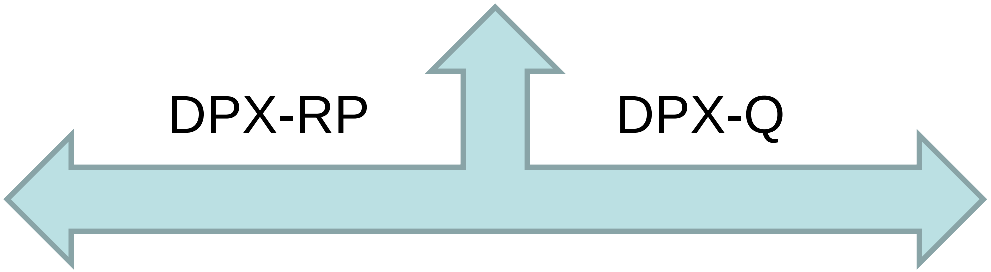
DPX-Q (polar compounds):

Take 1mL ACN solution
Extract in and out of “DPX-Q”
Rapidly remove water and salts (app. 1 minute)
Inject into **HPLC/MS/MS or GC/MS**
OR solvent exchange and inject into GC-NPD

Takes several minutes (app. 20 min) to solvent exchange

DPX scheme

ACN solution



Nonpolar
- OC's
- Some OP's
- pyrethroids

Polar
- Some OP's
- carbamates

GC-ECD
GC/MS
(GC-NPD/FPD)

GC-NPD (FPD)
GC-MS
HPLC/MS/MS

DPX Results

DPX-RP

Carrots (GC-ECD)	type	ECD	%RSD
HCB	OC	91.7	4.5
chlorothalonil	OC	111.9	4.9
chlopyriphos	OC/OP	103.2	3.5
endosulfan-I	OC	99.2	4.4
p,p'-DDE	OC	89	1
endofulfan-II	OC	99.9	2.9
ethion	OP	98.7	3.6
endofulfan-SO4	OC	103.8	1.7
phosmet	OP	108	0.2
azinphos-methyl	OP	107.1	1.5
trans-permethrin	OC	81	8.3

DPX-Polyamino (cleanup)

Carrots (GC-NPD)	**type**	NPD	%RSD
methamidophos	OP	58.9	7.3
acephate	OP	58.3	16.9
chlopyriphos	OC/OP	77.4	3.9
TPP (int std)	OP	78.8	3.7

DPX Results

DPX-RP

Orange (GC-ECD)	type	ECD	%RSD
HCB	OC	49.9	3.2
chlorothalonil	OC	63.9	6.8
chlopyriphos	OC/OP	58.6	5.2
endosulfan-I	OC	62.1	6.9
p,p'-DDE	OC	52.4	6.0
ethion	OP	64.2	4.4
endofulfan-II	OC	63.0	6.7
endofulfan-SO4	OC	67.9	7.9
phosmet	OP	66.4	6.4
azinphos-methyl	OP	111.2	8.4
trans-permethrin	OC	105.9	12.6

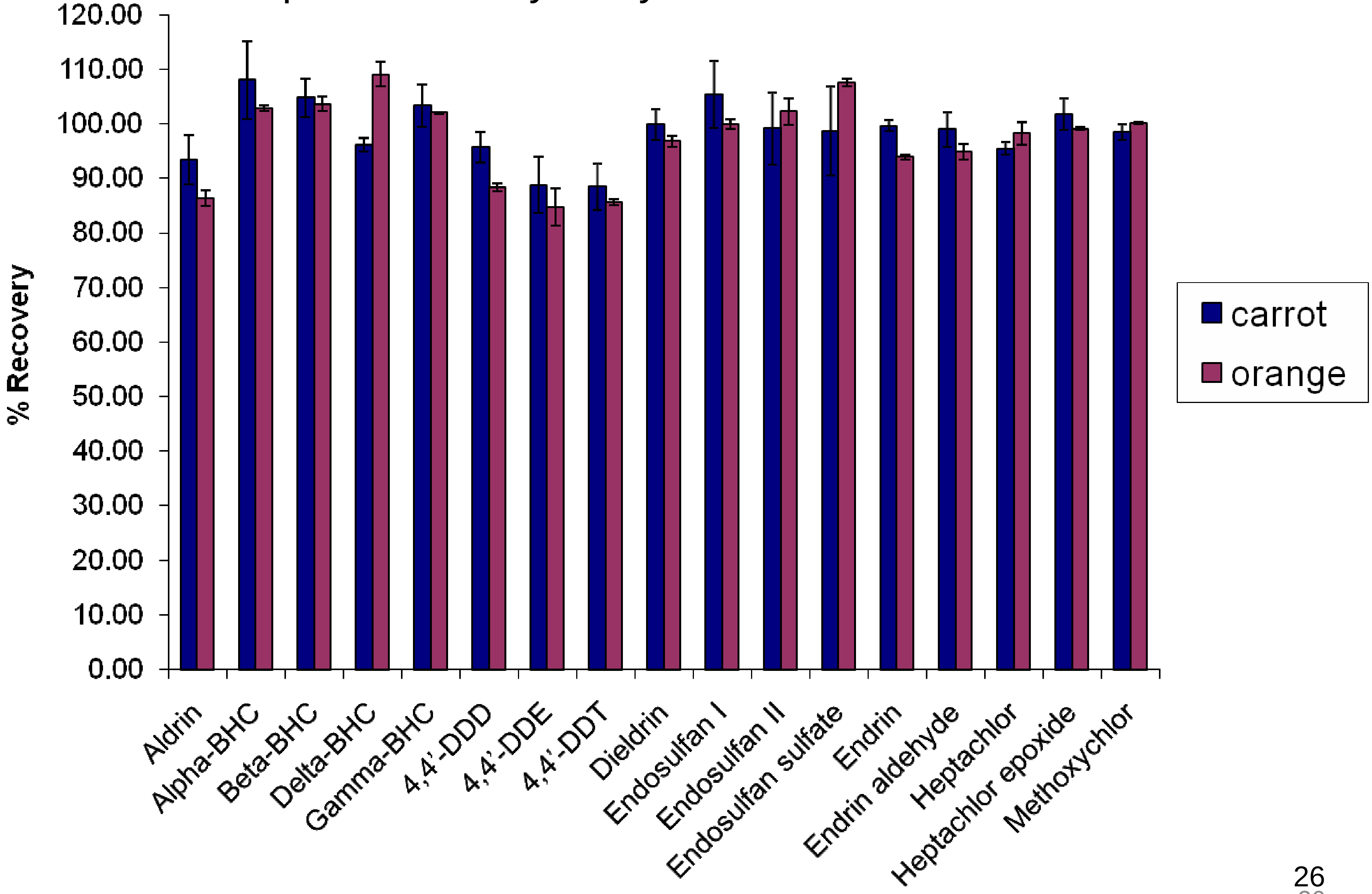
DPX-Polyamino (cleanup)

Orange (GC-NPD)	**type**	NPD	RSD
methamidophos	OP	69.7	8.2
Acephate	OP	80.3	12.8
Chlopyriphos	OC/OP	88.7	6.1
TPP (int std)	OP	89.6	7.1

lower recoveries with elutions from the “bottom**” (similar results with spinach)**

Results and discussion

Spiked recovery study results for fortified OCs



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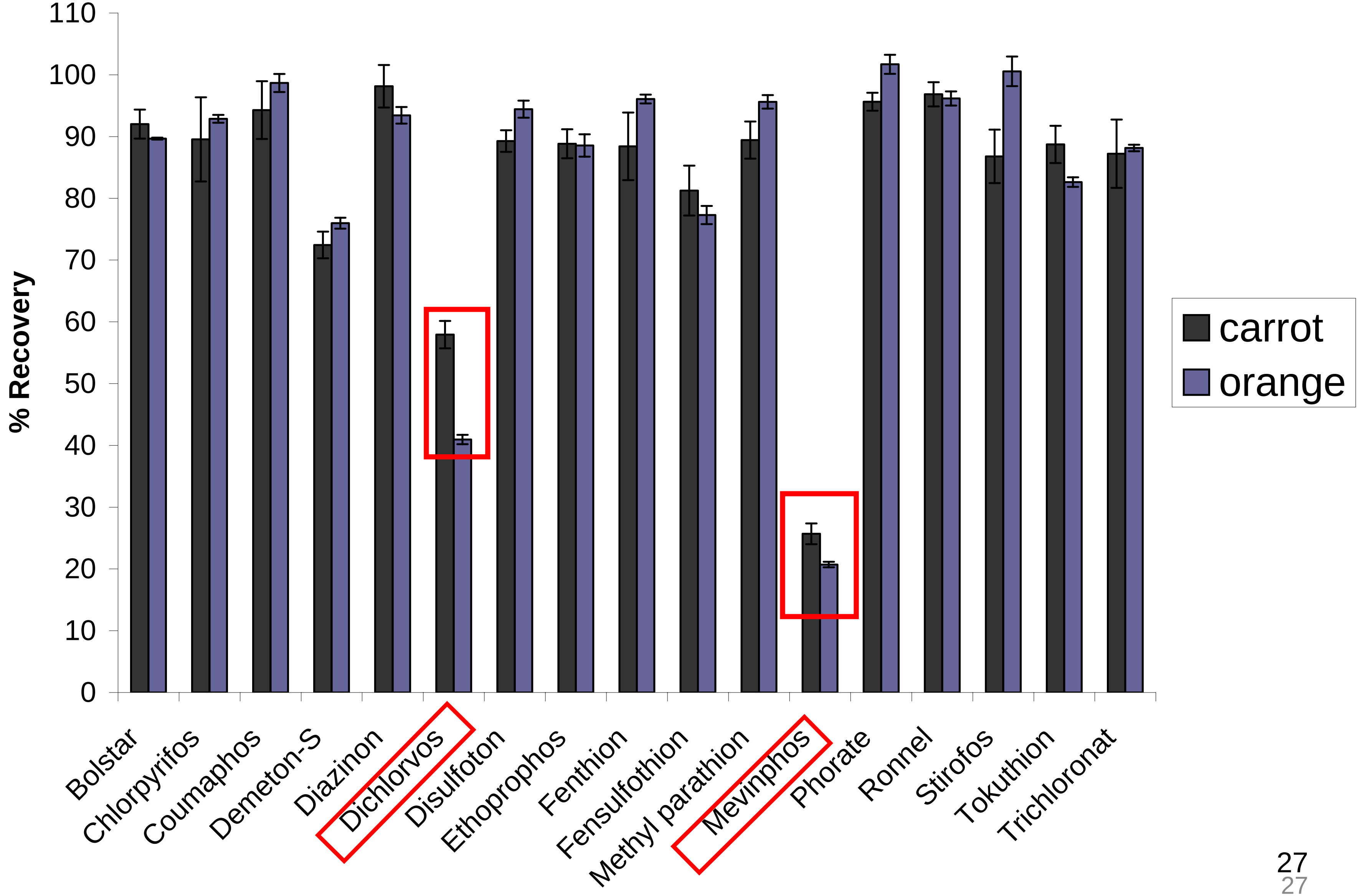
Results and discussion

Spiked recovery study results for fortified OPs



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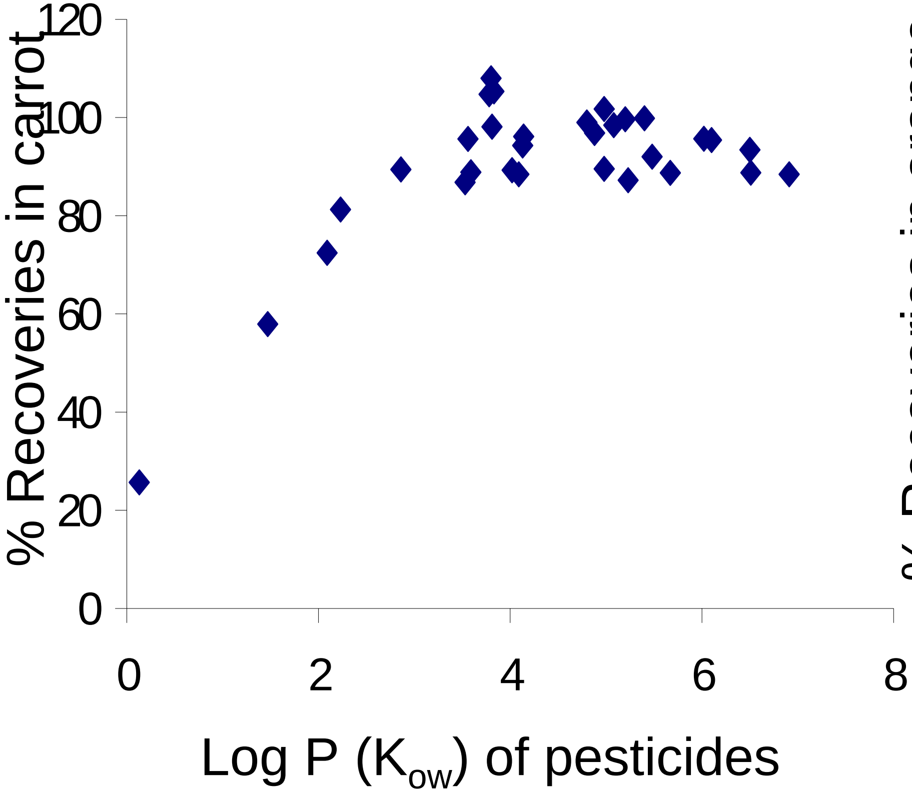
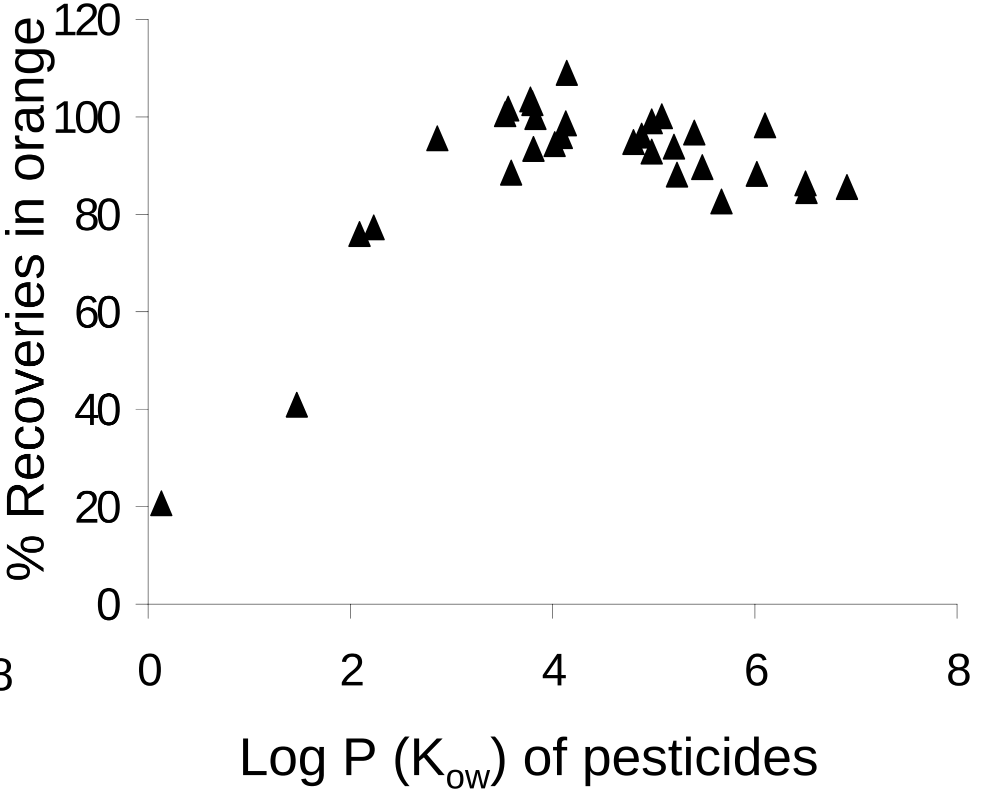
Results and discussion

Hydrophobicity and recovery





It is possible to estimate the recovery using the log P (K_{ow}) value of the pesticide.

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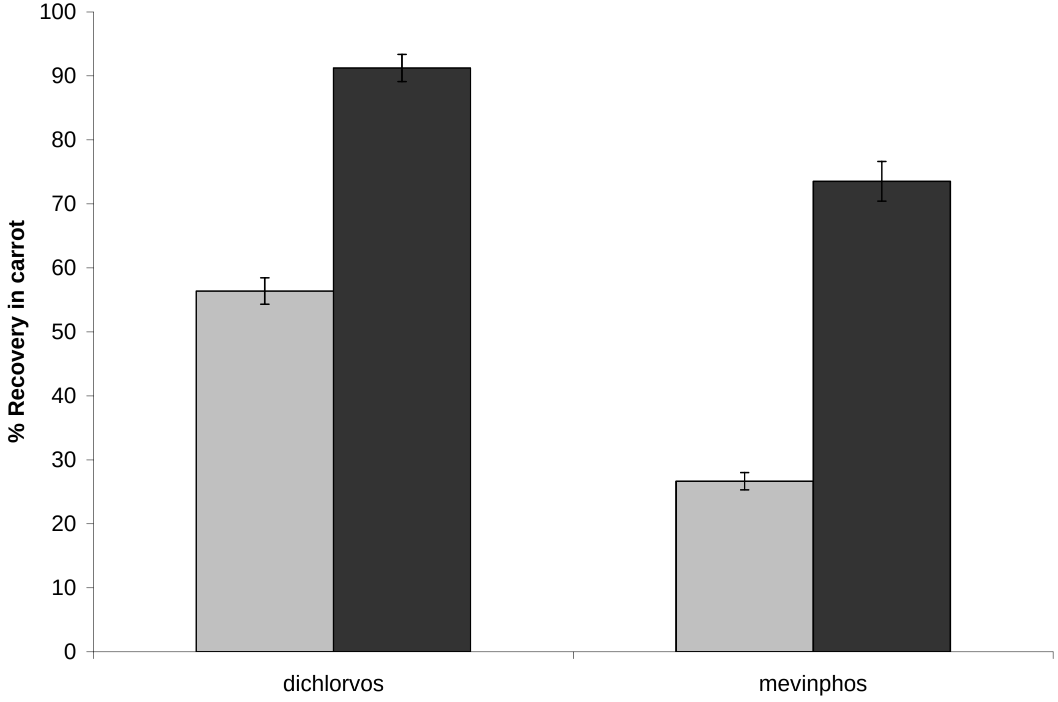
Database: U.S. National Library of Medicine.http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?CHEM

Results and discussion

What did we do to improve recoveries for polar OPs ?

Adding large volume of DI H_2O to "breakthrough solution"



OP extraction using 2.4 mL DI H2O, (n=4)

Extraction of "breakthrough" solution by adding extra 8 mL DI H_2O, (n=4)

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Linearity and LOD for studied OCs

Pesticide	r^2		LOD (ppm)	
	carrot	orange	carrot	orange
Aldrin	0.9979	0.9984	0.0172	0.0308
Alpha-BHC	0.9988	0.9988	0.0072	0.0216
Beta-BHC	0.9991	0.9986	0.0069	0.0234
Delta-BHC	0.9990	0.9983	0.0329	0.0333
Gamma-BHC	0.9991	0.9987	0.0100	0.0119
4,4’-DDD	0.9986	0.9968	0.0039	0.0741
4,4’-DDE	0.9955	0.9981	0.0141	0.0324
4,4’-DDT	0.9974	0.9957	0.0220	0.0629
Dieldrin	0.9991	0.9990	0.0170	0.0388
Endosulfan I	0.9990	0.9987	0.0099	0.0334
Endosulfan II	0.9974	0.9984	0.0136	0.0592
Endosulfan sulfate	0.9990	0.9954	0.0182	0.0806
Endrin	0.9992	0.9986	0.0246	0.0624
Endrin aldehyde	0.9980	0.9987	0.0481	0.0272
Heptachlor	0.9984	0.9984	0.0116	0.0460
Heptachlor epoxide	0.9978	0.9986	0.0224	0.0221
Methoxychlor	0.9982	0.9965	0.0051	0.0506

r^2: coefficient of determination, LOD: limit of detection.

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Linearity and LOD for studied OPs

Pesticide	r^2		LOD (ppm)	
	carrot	orange	carrot	orange
Bolstar	0.9977	0.9983	0.0061	0.0277
Chlorpyrifos	0.9990	0.9996	0.0134	0.0374
Coumaphos	0.9976	0.9984	0.0066	0.0576
Demeton-S	0.9972	0.9995	0.0201	0.0201
Diazinon	0.9996	0.9997	0.0331	0.0213
Dichlorvos	0.9984	0.9967	0.0120	0.0153
Disulfoton	0.9995	0.9978	0.0101	0.0128
Ethoprophos	0.9997	0.9992	0.0143	0.0246
Fenthion	0.9990	0.9995	0.0051	0.0227
Fensulfothion	0.9977	0.9990	0.0093	0.0270
Methyl parathion	0.9991	0.9978	0.0139	0.0187
Mevinphos	0.9945	0.9989	0.0228	0.0352
Phorate	0.9996	0.9990	0.0049	0.0208
Ronnel	0.9993	0.9995	0.0058	0.0213
Stirofos	0.9992	0.9956	0.0224	0.0718
Tokuthion	0.9988	0.9983	0.0129	0.0355
Trichloronat	0.9994	0.9993	0.0189	0.0141

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DPX-Q for polar OP's (GC/MS)

Pesticides	Vegetable/fruit	Spiked conc. (ppm)	DPX method	% recovery (n=4)	%RSD (n=4)
Acephate	Spinach	5.0	$GCB/MgSO_4/PSA$[a]	99.88	3.92
	Orange	5.0		109.5	1.38
Dichlorphos	Spinach	0.5	$GCB/MgSO_4/PSA$[a]	91.56	2.09
	Orange	0.5		100.55	2.00
Mevinphos	Spinach	0.5	$GCB/MgSO_4/PSA$[a]	90.38	1.86
	Orange	0.5		94.51	3.79
Methamidophos	Spinach	2.0	$GCB/MgSO_4/PSA$[a]	96.32	9.60
	Orange	2.0		103.06	2.59

Procedures:

•1ml acetonitrile solution, add 300μL of toluene (total 1.3 mL sample solution).

•Draw in DPX (150 mg mixed $GCB/MgSO_4/PSA$) three times from the bottom to remove sample matrix.

•Dispense and collect after cleanup (total about 1 mL).

•Add "external" standard.

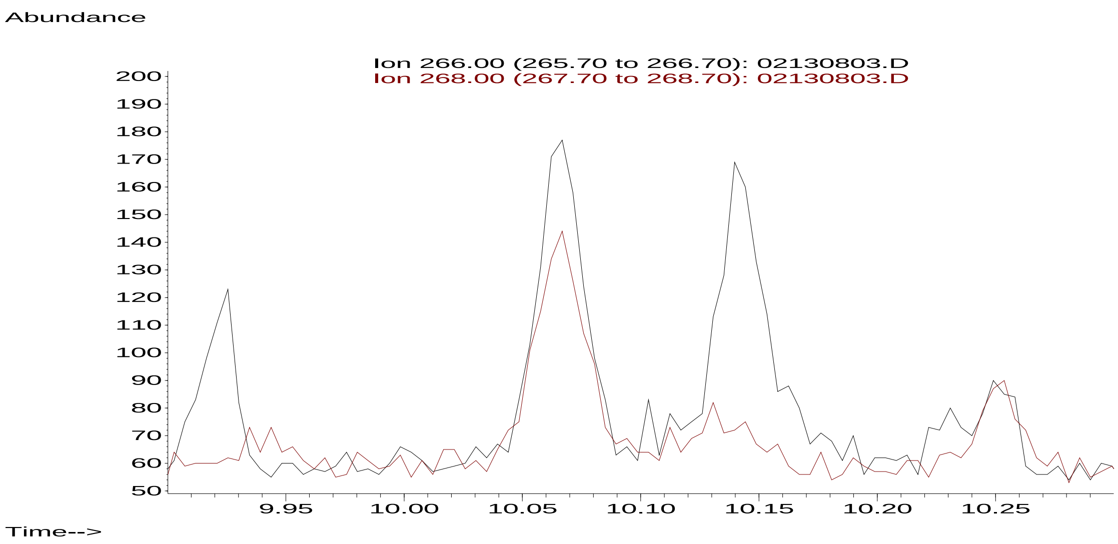
•Dry down to 0.5 mL.

•Inject.

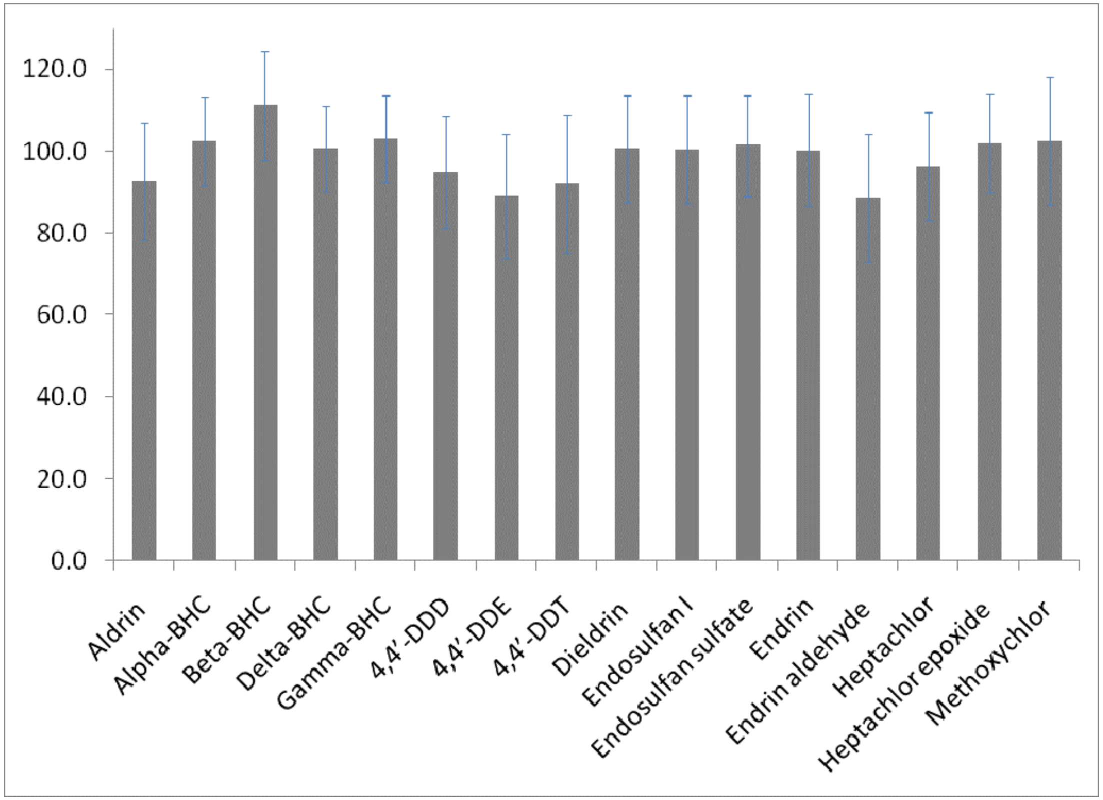
DPX-RP for captan and chlorothalonil

pesticides	Vegetable/fruit	Spiked conc. (ppm	DPX method	%recovery	% RSD
Captan	Spinach	2.0	SDVB	104.48	1.19
	Orange	2.0	SDVB	91.81	5.35
chlorothalonil	Spinach	0.5	SDVB	113.57	1.91
	Orange	0.5	SDVB	115.28	9.80

10 ppb chlorothalonil extracted by DPX-RP using GC/MS (SIM)



% Recovery of OCs in carrot extracted using automated DPX with GERSTEL MPS=2



OCs: spiked 0.5ppm in carrot

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DPX -- GERSTELIZED

Conclusions

DPX-RP provided “cleaner” extracts than QuEChERS (modified) for GC-ECD data.

High recoveries were achieved for all of the studied pesticides by combining DPX-RP and DPX-Q, with %RSD lower than 10%. This indicates a good accuracy and precision of the current method.

DPX method is more environmentally friendly.

Average coefficient of determination, $r^2 > 0.995$, indicates a good linearity of the current DPX method.

Current research focuses on full automation of DPX using GERSTEL MPS with:

- Large volume injection (LVI, GERSTEL PTV)
- fast GC (ECD, FPD)
- HPLC/MS/MS

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Acknowledgments

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GERSTEL, MPS-2

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University of South Carolina, Dept. of Chemistry and Biochemistry