Comparison of Multiresidue Extraction Methods for Pesticides in Produce

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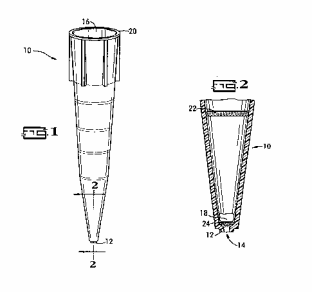
Disposable Pipette Extraction (DPX)



William E. Brewer, US patent 6,566,145 B2

Comparison of Multiresidue Extraction Methods

LUKE METHOD

1. Blend 100 g sample with 200 mL acetone and filter
2. 50 mL extracted with 100 mL CH_2Cl_2/pet ether
3. Repeat 2 times with 50 mL CH_2Cl_2 after addition of NaCl
4. Organic layer diluted to 240 mL with acetone
5. 2-120 mL portions split and concentrated—OC and OP
6. OP: solvent exchanged to 5 mL acetone—***GC-NPD***
7. OC: florisil column cleanup (several steps!)
8. OC: solvent exchanged to 5 mL iso-octane—***GC-ECD***

Note: 5:1 conc. factor or app. 1.7 g/mL sample equiv.

Comparison of Multiresidue Extraction Methods

Quechers

1. Blend 100 g sample w/ 100 mL CH_3CN
2. Add 3 g salt to 15 mL of extract in a 15 mL centrifuge tube
3. Vortex/shake 1 min.
4. Centrifuge for 2 to 5 min.
5. Transfer organic layer to c-tube containing 0.3 g PSA and 0.9 g MgSO4
6. Add 1 mL toluene and vortex
7. Centrifuge 5 min.
8. Transfer exactly 4 mL (3.75 g of sample) to graduated c-tube
9. Add 3:1 acetone/toluene to 10 mL mark
10. Evaporate to 0.5 mL twice with washings using 3:1 acetone/toluene
11. Dilute to final volume of 2 mL

Note: 3.75 g/2 mL = 1.88 g/mL injected

Comparison of Multiresidue Extraction Methods

DPX (sdvb)

1. Blend 100 g sample w/ 200 mL acetone or methanol
2. Transfer 2.5 mL into test tube and add 2.5 mL satd. NaCl
3. Draw 2.5 mL of solution into DPX tip with air to mix
4. Wait 30 sec. and dispense to waste
5. Draw in remainder of solution into DPX tip and mix w/ air
6. Wait 30 sec. and dispense to waste
7. Draw in 0.3 mL hexane-ethyl acetate (50/50) and mix
8. Elute into graduated GC vial
9. Repeat elution with additional 0.3 mL hexane-ethyl acetate
10. Elute into corresponding GC vial
11. Remove water layer and bring to 0.5 mL mark (if needed)

Note: 5:1 conc. factor or app. 1.7 g/mL sample equiv.

Previous DPX Research v. this Research

Previous	This study
• Analyzed acetone extract from the Luke extraction	• Analyzed methanol extract, so processed samples from scratch
• Took 5 mL acetone extract and added 10 mL water	• Took 2.5 mL methanol extract and added 2.5 mL sat'd. NaCl
• 1 mL final volume	• 0.5 mL final volume
• DPX took app. 20 min. to process up to 12 samples simultaneously (lever press)	• DPX took app. 3 min. per sample—processed 1 at a time
• Great recoveries for OC, OP and nonpolar compounds	• Much better recoveries for fungicides and polar compounds
• Poor recoveries for fungicides	

Differences between Quechers and DPX

- Quechers uses salt to separate organic layer from aqueous layer—provides high recovery
- Quechers uses PSA to remove fatty acid components
- Quechers may incorporate additional clean up procedures
- Quechers (SCDA) concentrates sample extract using solvent evaporation/exchange

- DPX uses sorbent for the analytes of interest to "adsorb/partition"—provides selectivity
- DPX has "built-in" concentration factor and does not require solvent evaporation

Comparison of Multiresidue Extraction Methods

The Ten Matrices tested each week:

1. Iceberg Lettuce (blank)
2. Yellow Squash
3. Granny Smith Apples
4. Strawberries
5. Peaches
6. White Grapes
7. Red Grapes
8. Tomatoes
9. Green Beans
10. Sweet Potatoes

Sample Preparation--Luke




Sample Preparation--Luke


Sample Preparation--Quechers




Sample Preparation--DPX




Week 1 Results:

SAMPLE I.D.	LUKE PPM	DPX (PPM) Acetone/Methanol	Quech. PPM	COMPOUND (det.)	TOL. PPM
Yellow Squash	0.027	0.0180 / 0.0158	0.0167	Endo I (ECD)	2.0
	0.0068	0.0061 / 0.0048	0.0050	Endo II (ECD)	2.0
	0.0413	0.0295 / 0.0306	0.0329	Endo Sulfate (ECD)	2.0
Iceburg Lettuce	0.0149	0.0132 / 0.0149	0.0162	Endo Sulfate (ECD)	2.0
Granny Smith Apples	0.5196	NR / 0.2061	NR	Thiabendazole (NPD)	10.0
Strawberries	9.5988	2.0681 / 2.2659	2.0846	Captan (ECD)	25.0
Peaches	0.5041	1.4268 / 1.6187	1.8901	Iprodione (ECD)	20.0
	2.1294	2.3670 / 1.4017	1.2349	Iprodione (NPD)	20.0
White Grapes	3.0540	0.3095 / 0.3477	0.0487	Captan (ECD)	50.0
Red Grapes	1.4859	0.2095 / 0.6540	0.0119	Captan (ECD)	50.0
Sweet Potatoes	1.009	0.7272 / Mat. Int.	0.7242	Dicloran (ECD)	10.0
Lettuce spike @ 1.0 ppm	0.0789	0.2949 / 0.4008	0.0358	Chlorothalonil (ECD)	
@ 2.0 p	1.5381	0.9703 / 1.271	0.1432	Dursban (ECD)	
@ 1.0 p	0.79	0.4600 / 0.6296	0.114	Cyfluthrin (ECD)	
@ 5.0 p	6.263	1.8008 / 6.3472	0.2649	Prometon (NPD)	
@ 2.0 p	2.493	1.4632 / 2.6702	0.1008	Dursban (NPD)	
@ 4.0 p	6.067	0.3803 / 4.9492	NR	Thiabendazole (NPD)	

Note: Quechers was performed using an original procedure with less solvent and no blending.

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Strawberries	9.5988	2.0681 / 2.2659	2.0846	Captan (ECD)	25.0
Peaches	0.5041	1.4268 / 1.6187	1.8901	Iprodione (ECD)	20.0
	2.1294	2.3670 / 1.4017	1.2349	Iprodione (NPD)	20.0
White Grapes	3.0540	0.3095 / 0.3477	0.0487	Captan (ECD)	50.0
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@ 2.0 p	2.493	1.4632 / 2.6702	0.1008	Dursban (NPD)	
@ 4.0 p	6.067	0.3803 / 4.9492	NR	Thiabendazole (NPD)	

Note: Quechers was performed using an original procedure with less solvent and no blending.

Week 2 Results:

SAMPLE I.D.	LUKE PPM	DPX (PPM) METHANOL	Quech. PPM	COMPOUND (det.)	TOL. PPM
Yellow Squash	0.0136	0.0129	0.01476	Endo I (ECD)	2.0
	0.0043	0.0042	0.0038	Endo II (ECD)	2.0
	0.0266	0.0227	0.0352	Endo Sulfate (ECD)	2.0
	0.0012	NR	0.0023 *	Dieldrin (ECD)	NT
Lettuce	0.0015	0.0011	0.0019	Endo I (ECD)	2.0
	0.0015	NR	NR	Endo II (ECD)	2.0
	0.0087	0.0082	0.0154	Endo Sulfate (ECD)	2.0
G. S. Apples	0.3906	NR	0.4547	Thiabendazole (NPD)	10.0
Strawberries	1.79	0.5264	0.7044	Captan (ECD)	25.0
Peaches	0.0057	NR	0.0096	Dursban (ECD)	0.05
	1.1803	1.3733	1.1529	Iprodione (ECD)	20.0
	2.7440	2.1751	1.1957	Iprodione (NPD)	20.0
White Grapes	0.5184	0.2182	0.0437 **	Captan (ECD)	50.0
Red Grapes	0.4411	0.1741	0.0135 **	Captan (ECD)	50.0
Sweet Pot.	0.4115	0.3247	0.5505	Dicloran (ECD)	10.0
Lettuce spike @ 1.0ppm	0.048	0.3883	0.6784	Chlorothalonil (ECD)	
@ 1.0	0.827	0.5987	0.8166	Dursban (ECD)	
@ 1.0	0.9889	0.8183	0.7956	Dursban (NPD)	
@ 5.0	7.7878	2.5839	3.8147	Thiabendazole (NPD)	

Note: **Quechers still being developed; possibly extracted wrong portion.

Week 3 Results:

SAMPLE I.D.	LUKE PPM	DPX PPM	Quechers PPM	COMPOUND (det.)	TOL. PPM
Yellow Squash	0.0076	0.0025	0.005	Endo I (ECD)	2.0
	0.0134	0.0103	0.0457	Endo Sulfate (ECD)	2.0
Lettuce				Negative	
G. S. Apples				Negative	
Strawberries	3.4518	1.9274 *	3.3204	Captan (ECD)	25.0
Peaches	0.0152	NR *	0.0094	Captan (ECD)	50.0
	5.8357	2.9150	7.9723	Iprodione (ECD)	20.0
	0.0328	0.0191	0.0309	Dursban (ECD)	0.05
	0.1243	0.0891	0.0961	Azinphos - methyl (ECD)	2.0
	18.5668	8.0567	7.6867	Iprodione (NPD)	20.0
	0.0182	NR	NR	Dursban (NPD)	0.05
	0.0883	0.0482	0.0678	Azinphos - methyl (NPD)	2.0
White Grapes	0.0033	0.9280 *	NR *	Captan (ECD)	50.0
Red Grapes	0.5600	0.3469 *	0.49577 *	Captan (ECD)	50.0
	0.0038	NR	0.0066	Dursban (ECD)	0.5

Week 3 Results (cont'd):

SAMPLE I.D.	LUKE PPM	DPX PPM	Quechers PPM	COMPOUND (det.)	TOL. PPM
Tomatoes	0.0282	0.0075	0.0999	Dursban (ECD)	0.05
	0.0026	NR	0.0017	Endo I (ECD)	2.0
	0.0038	NR	0.0035	Endo II (ECD)	2.0
	0.0048	NR	0.0062	Endo Sulfate (ECD)	2.0
	0.0146	0.0008	NR	Captan (ECD)	25.0
Green Beans	0.0161	0.0053	0.0102	Endo I (ECD)	2.0
	0.0052	0.0021	0.0044	Endo II (ECD)	2.0
	0.0208	0.0141	0.0388	Endo Sulfate (ECD)	2.0
			0.0037	Chlorothalonil (ECD)	5.0
Sweet Potatoes	0.647	0.2231	0.3136	Dicloran (ECD)	10.0
Lettuce spike @ 1.0ppm	0.09665	0.3181	0.6515	Chlorothalonil (ECD)	
@1.0 ppm	0.7525	0.5839	0.76	Dursban (ECD)	
@1.0ppm	1.0048	0.8764	0.6947	Dursban (NPD)	
@5.0ppm	7.1257	3.479	3.8998	Thiabendazole (NPD)	

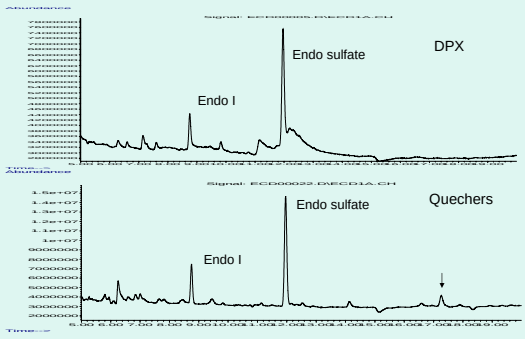
Week 4 Results:

SAMPLE I.D.	LUKE PPM	DPX PPM	Quech. PPM	COMPOUND (det.)	TOL. PPM
Yellow Squash	0.0026	0.0019	0.0045	Endo I (ECD)	2.0
	0.0191	0.0179	0.0317	Endo Sulfate (ECD)	2.0
Lettuce				Negative	
G. S. Apples	0.3957	NR	0.2064	Thiabendazole (NPD)	10.0
Strawberries	3.3918	2.3359	2.0179	Captan (ECD)	25.0
Peaches	0.0306	0.0173	0.0361	Dursban (ECD)	0.05
	4.1178	1.296	4.500	Iprodione (ECD)	20.0
	0.0114	NR	NR	Captan (ECD)	50.0
	NR	0.0672	NR	Azinphos - Methyl (ECD)	2.0
	0.1158	0.0746	0.1402	Azinphos - Methyl (NPD)	2.0
	0.0147	0.0122	0.0151	Dursban (NPD)	0.05
	11.7864	4.4621	8.1997	Iprodione (NPD)	20.0
Red Grapes	0.3035	0.3575	0.1506	Captan (ECD)	50.0
Tomatoes	0.0128	0.0647	0.0869	Dursban (ECD)	0.05
	0.0032	0.0034	0.0037	Endo II (ECD)	2.0
	0.0048	0.0048	0.0054	Endo Sulfate (ECD)	2.0
	NR	0.0012	0.0015	Endo I (ECD)	2.0
	NR	0.0265	0.0378	Dursban (NPD)	0.05

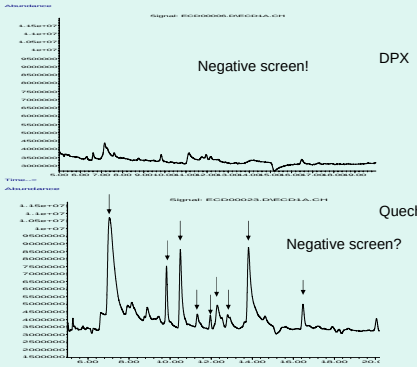
Week 4 Results (cont'd):

SAMPLE I.D.	LUKE	DPX	Quech.	COMPOUND (det.)	TOL.
	PPM	PPM	PPM		PPM
Green Beans	0.0089	0.0061	0.0119	Endo I (ECD)	2.0
	0.0050	0.0026	0.0047	Endo II (ECD)	2.0
	0.0280	0.0262	0.0407	Endo Sulfate (ECD)	2.0
Sweet Potatoes	0.2302	0.1695	0.4025	Dicloran (ECD)	10.0
Lettuce spike @ 1.0ppm	0.1383	0.3032	0.6232	Cholorothalonil (ECD)	
@ 1.0ppm	0.8693	0.5231	0.8895	Dursban (ECD)	
@ 1.0ppm	0.7991	0.8335	0.838	Dursban (NPD)	
@ 5.0ppm	7.4264	2.9731	5.922	Thiabendazole (NPD)	

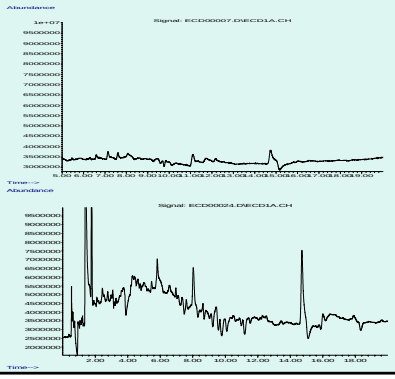
GC-ECD Chromatograms—DPX v. Quechers Yellow Squash



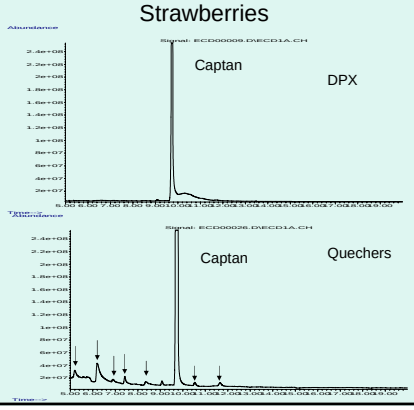
GC-ECD Chromatograms—DPX v. Quechers Lettuce



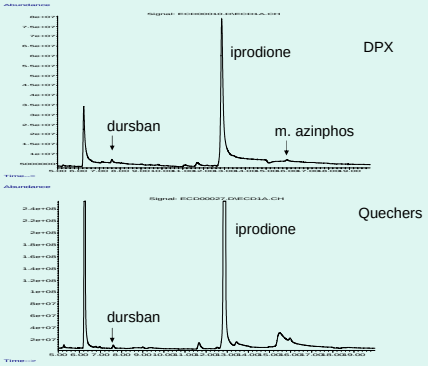
GC-ECD Chromatograms—DPX v. Quechers Granny Smith Apples



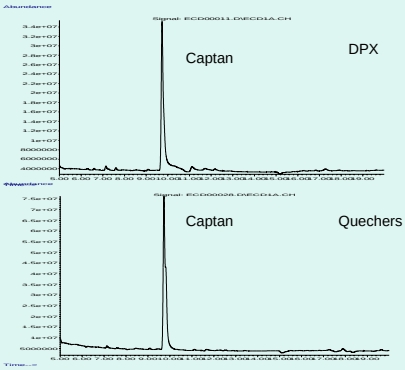
GC-ECD Chromatograms—DPX v. Quechers Strawberries



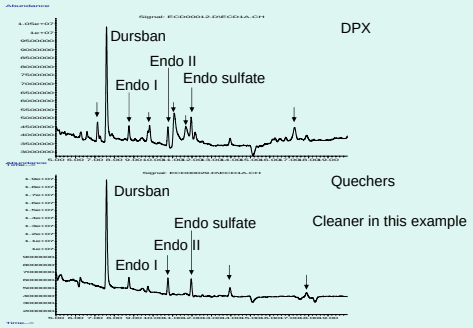
GC-ECD Chromatograms—DPX v. Quechers Peaches



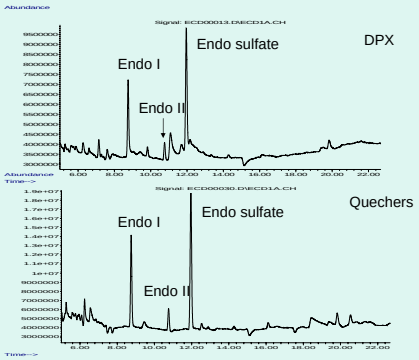
GC-ECD Chromatograms—DPX v. Quechers
Red Grapes



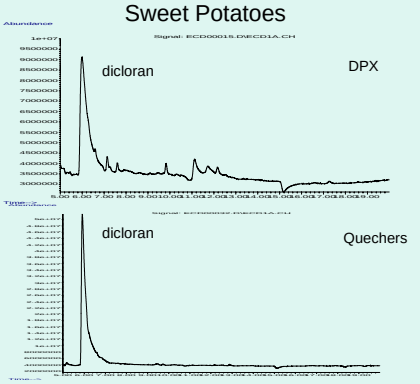
GC-ECD Chromatograms—DPX v. Quechers
Tomatoes



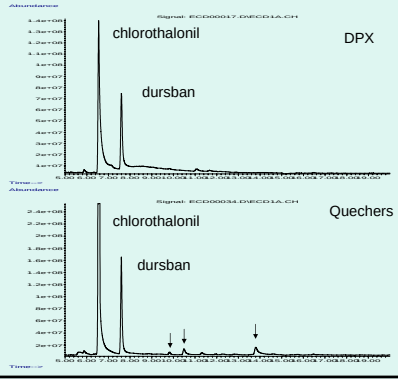
GC-ECD Chromatograms—DPX v. Quechers
Green Beans



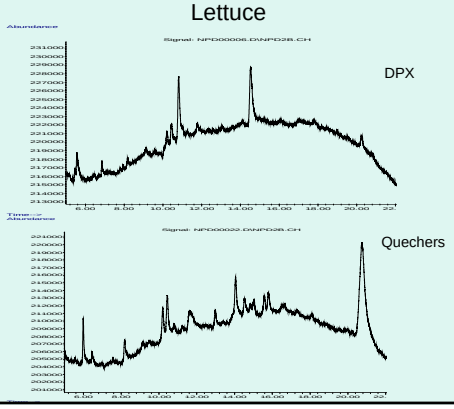
GC-ECD Chromatograms—DPX v. Quechers
Sweet Potatoes



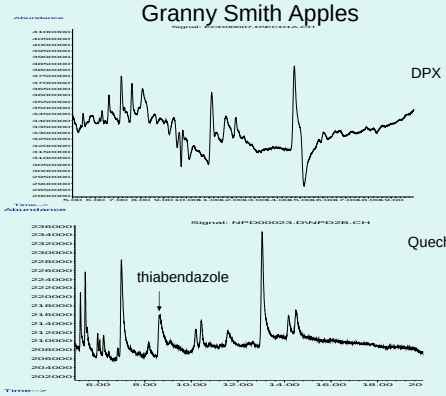
GC-NPD Chromatograms—DPX v. Quechers
Lettuce Spike



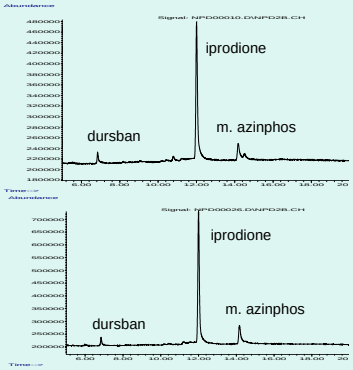
GC-NPD Chromatograms—DPX v. Quechers
Lettuce



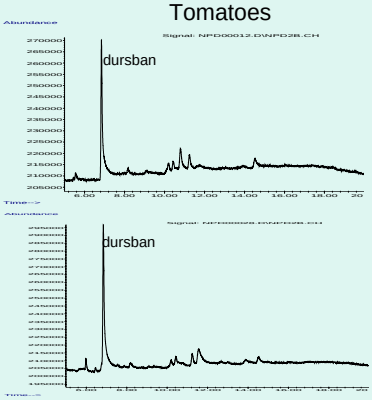
GC-NPD Chromatograms—DPX v. Quechers Granny Smith Apples



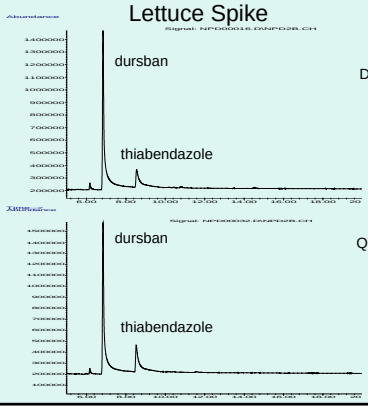
GC-NPD Chromatograms—DPX v. Quechers Peaches



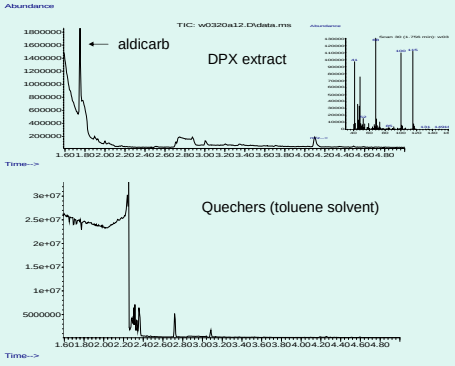
GC-NPD Chromatograms—DPX v. Quechers Tomatoes



GC-NPD Chromatograms—DPX v. Quechers Lettuce Spike



Quechers solvent "front" in GC/MS



Conclusions of Quechers and DPX

Adv. Quechers-SCDA

- Fast extractions
- High recoveries**
- OC, OP, fungicides (others?)

Disadv. Quechers-SCDA

- Matrix interferences
- Solvent exchange req.
- Use of toluene or iso-octane (aldicarb int.)

Adv. DPX

- Very fast extractions
- No solvent evaporation
- Easily automated
- High throughput
- OC, OP, fungicides, pyrethrins (& carbamates)
- Portable

Disadv. DPX

- "fair" recoveries** (pend.)
- Matrix interferences—cleanup DPX tip (feed)

Future Research of DPX

- Commercialization of DPX
- Polar sorbent (proprietary) will permit use of acetone to improve recoveries
- Mixed sorbent of polar and sdvb will provide multi-residue analysis in one extract
- Fully automated extraction following initial sample preparation (blending of sample to obtain representative sample)

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