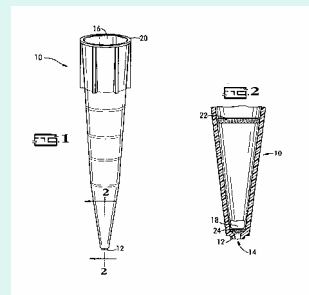


Comparison of Luke Method with Disposable Pipette Extraction of Pesticide Residues

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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 CH₂Cl₂/pet ether
3. Repeat 2 times with 50 mL CH₂Cl₂ 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

DPX (sdvb)

1. Blend 100 g sample w/ 200 mL acetone (from Luke)
2. Transfer 2.5 mL into test tube and add 1 mL satd. NaCl
3. Condition DPX tip with 0.5 mL ethyl acetate (or methanol)
4. Draw solution into DPX tip with air to mix
5. Wait app. 10-20 seconds (layers may separate)
6. Draw in 0.5 mL ethyl acetate and mix with air
7. Allow layers to separate (10 sec), and dispense bottom layer
8. Dispense upper organic layer into clean test tube
9. Elute from TOP with additional 0.5 mL ethyl acetate
10. Pass organic eluent through Na₂SO₄ and/or florisil (ECD) and collect into graduated C-tube
11. Dry to app. 0.5 mL with heat and gas flow (bottom layer—salt)
12. Remove bottom layer and bring to 0.5 mL mark; transfer to GC vial

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

Previous DPX Research v. this Research

2005 Study

- Analyzed acetone extract from the Luke extraction
- Took 5 mL acetone extract and added 10 mL water
- 1 mL final volume
- DPX took app. 20 min. to process up to 12 samples simultaneously (lever press)
- Great recoveries for OC, OP and nonpolar compounds
- Poor recoveries for fungicides

2006 study

- Analyzed methanol extract, so processed samples from scratch
- Took 2.5 mL methanol extract and added 2.5 mL sat'd. NaCl
- 0.5 mL final volume
- DPX took app. 3 min. per sample—processed 1 at a time
- Much better recoveries for fungicides and polar compounds

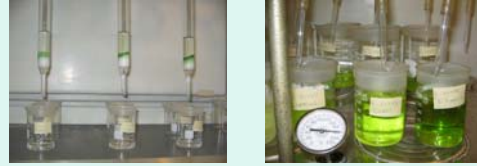
2007 Study

- DPX L/L methodology
- Solid phase-liquid-liquid extraction
- Permits the use of acetone solution
- Direct comparison with Luke Method
- Use NPD and ECD detectors with minimal solvent evaporation
- Very similar chromatograms between 2 methods
- Florisil cleanup tips (Pat. Pend.)

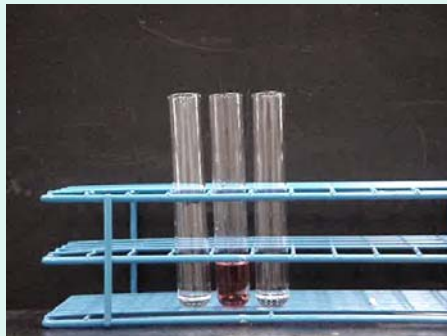
Sample Preparation--Luke



Sample Preparation--Luke



Movie—DPX L/L

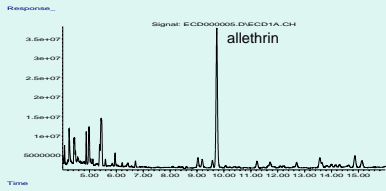


DATE	SAMPLE	COMPOUNDS	DET.	LUKE	DPX	NOTES/TOL.
Preliminary study						
3/15/2007	green bell peppers	monitor	NPD	1.00 ppm	0.91 ppm	over 1 week later
		acephate	NPD	1.42 ppm	0.32 ppm	
		oxamyl	NPD	1.01 ppm	0.21 ppm	
		L. cyhalothrin	ECD	0.08 ppm	0.10 ppm	
		cypermethrin	ECD	0.14 ppm	0.09 ppm	
	sweet potatoes	dicloran	ECD	0.74 ppm	0.50 ppm	over 1 week later
	lettuce (spike)	buprofezin	NPD	0.98 ppm	0.45 ppm	over 1 week later
	spinach	cyfluthrin	ECD	0.60 ppm	0.66 ppm	over 1 week later
		cypermethrin	ECD	1.02 ppm	1.00 ppm	

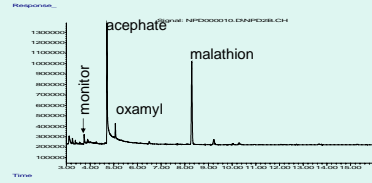
DATE	SAMPLE	COMPOUNDS	DET.	LUKE	DPX	NOTES/TOL.
3/20/2007	lettuce (spike)	acephate	NPD	0.69	0.09	
		dursban	NPD	0.49	0.30	
		thiabendazole	NPD	1.46	0.47	
3/22/2007	lettuce (spike)	acephate	NPD	0.59	0.25	
		dursban	NPD	0.40	0.42	
		thiabendazole	NPD	1.31	0.87	
		chlorothalonil	ECD	0.11	0.40	
		captan	ECD	0.34	0.16	
		L. cyhalothrin	ECD	0.41	0.51	
		dursban	ECD	0.37	0.41	
3/27/2007	cauliflower (spike)	dursban	NPD	0.94	0.78	2 extractions
		fipronil	NPD	0.83	0.62	*

DATE	SAMPLE	COMPOUNDS	DET.	LUKE	DPX	NOTES/TOL.
Methanol conditioning**						
4/4/2007	roma tomatoes (spike)	chlorothalonil	ECD	0.32	1.03	
		allethrin	ECD	0.89	0.98	
		captan	ECD	0.93	0.41	
		bifenthrin	ECD	0.95	1.00	
		L. cyhalothrin	ECD	0.93	1.04	
	butter lettuce	L. cyhalothrin	ECD	0.04 ppm	0.04 ppm	Tot: 2.0 ppm
4/11/2007	tomatoes (spike)	acephate	NPD	0.51	0.07	
		chlorpropham	NPD	1.14	0.85	
		dursban	NPD	0.99	0.98	
		thiabendazole	NPD	1.15	0.60	
		phosmet	NPD	1.05	0.80	
	red apples	DPA	NPD	1.60 ppm	1.18 ppm	Tot: 10.0 ppm
	potatoes	chlorpropham	NPD	6.47 ppm	4.09 ppm	Tot: 50 ppm
	pears	thiabendazole	NPD	0.52 ppm	0.38 ppm	Tot: 10 ppm

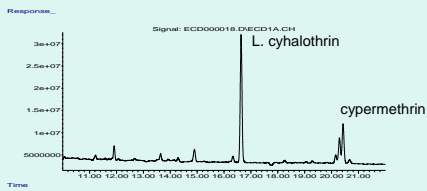
2/09/07 ECD 000005 spiked cucumbers
**early studies—sorbent needed cleaning



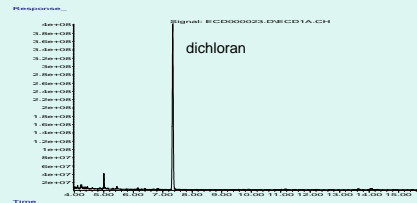
3/15/07 NPD 000010 green bell peppers



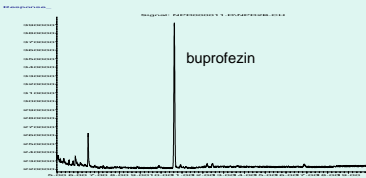
3/15/07 ECD 000018 green bell peppers



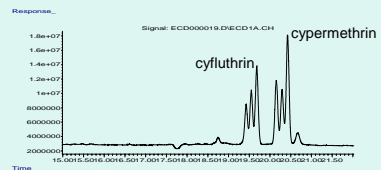
3/15/07 ECD 000023 sweet potatoes

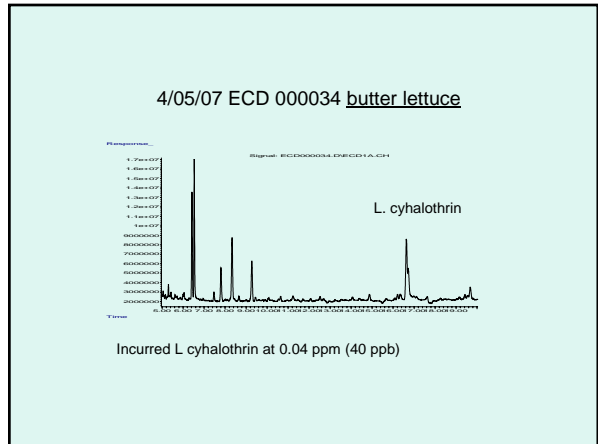
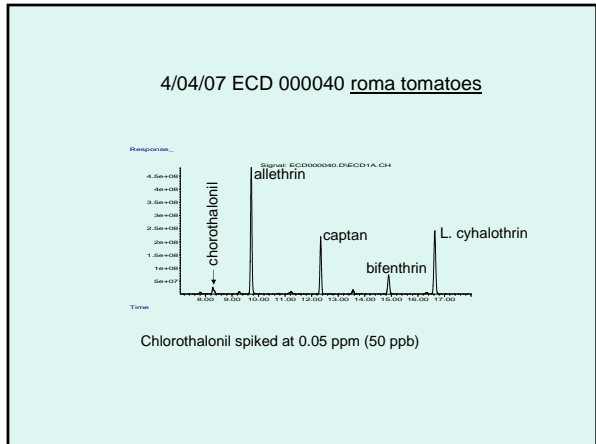
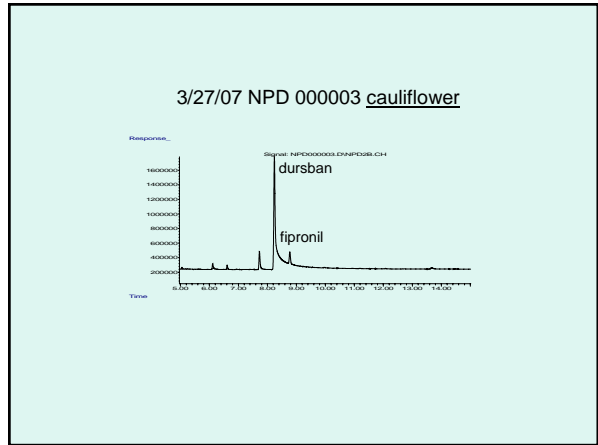
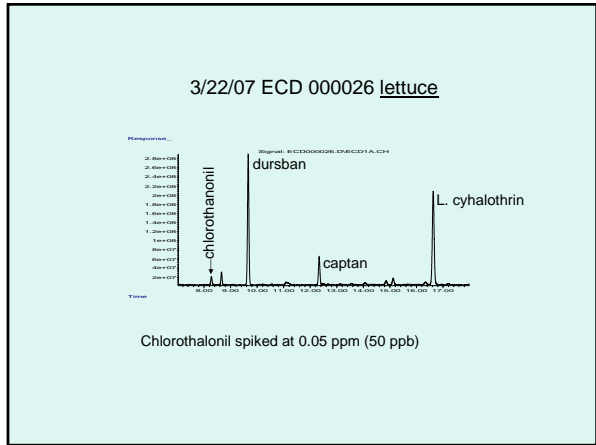
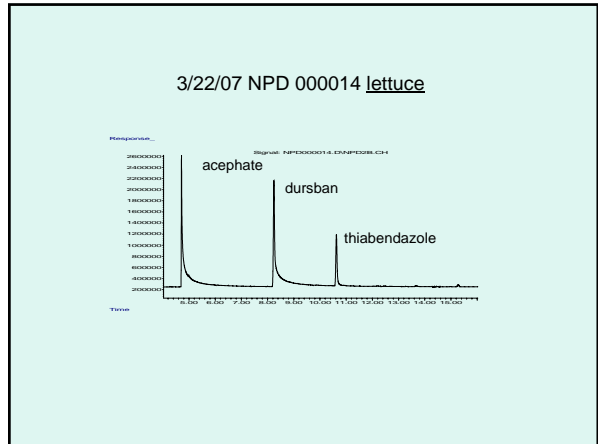
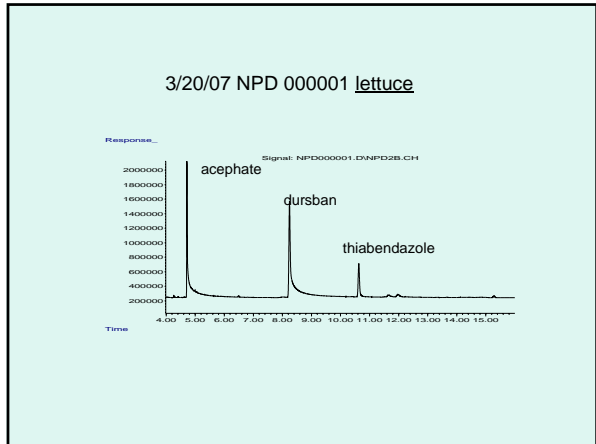


3/15/07 NPD 000011 lettuce



3/15/07 ECD 000019 spinach





CONCLUSIONS

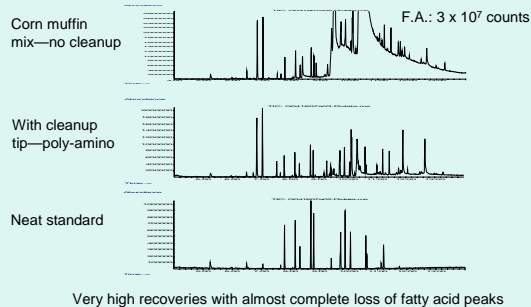
- DPX L/L Method is a viable alternative to the Luke Method
- Great recoveries for nonpolar compounds and pyrethroids in particular
- Better recoveries* for chlorothalonil
- Fair recoveries* for polar compounds (e.g., thiabendazole), and poor recoveries for acephate
- Surprisingly very "CLEAN" chromatograms
- Tomato extracts run on ECD "without" florisil cleanup
- **New: DPX-RP tips with DPX L/L provide great recoveries of chlorothalonil, thiabendazole and captan**

Movie—DPX (polar/nonpolar)



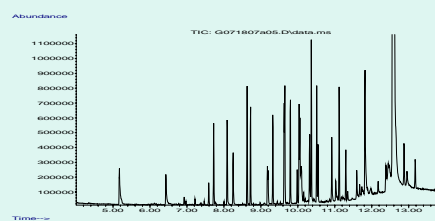
DPX cleanup tip (Pat. Pend.)

GC/MS chromatograms of 0.8 ppm OP mix in acetonitrile extract



DPX Quechers Tip

GC/MS chromatograms of 1 ppm OP mix in acetonitrile extract of muffin mix



Future Research of DPX

- DPX clean up tips (remove fatty acids--PA, PSA)
- Mixed sorbent of polar and sdvb will provide multi-residue analysis—use 2 separate elutions
- Fully automated extraction following initial sample preparation (blending of sample to obtain representative sample)—GERSTEL
- Gerstel automation of Quechers using DPX-Q

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- DPX Labs, LLC, Columbia, SC
- **GERSTEL**

