

Pesticide Residues in Produce Sold in Connecticut: A Comparative Study of Present and QuEChERS Methodology



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Origin of Current Work

- 1962 Purchased and Received GC
- 1962 CAES to Analyze Produce Samples on Behalf of DCP
- 1962 Analyzed 8 Samples

This Relationship Exists in the Current Program

- 1960's - Early 1970's Analyzed an Average of 290 Samples per Year for Pesticide Residues
- Mid 1970's - Early 1980's Focus Shifted Away from Residue Analysis onto Formulation and Food Additive Adulteration

<http://www.ct.gov/caes>

Vegetable Preparation Procedure (VegPrep)

- 1988 Dr. Harry M. Pylypiw - CAES
Currently: Associate Professor of Chemistry - Quinnipiac University
- Developed a Method for the Analysis of OC and OP Pesticides in Fruits and Vegetables
- Focus on NPD, ECD, ELCD Detectors
'...Needs No Modification Based on Sample Matrix...'
- Presented Work in July, 1992 at the 29th FPRW
H.M. Pylypiw, J AOAC Int 76 (1993) 1369-1373
- 1994 - 1999 Residues Confirmed HP 5970 MSD

<http://www.ct.gov/caes>

Summary of Original Work

- 1988 - 1993 22 Pesticides Validated
 - Recoveries 81 - 114 %
 - LOD ECD 0.1 ppm Captan - 0.002 ppm for 11 Others
 - LOD ELCD 0.1 Dicofol - 0.01 ppm for 9 Others
 - LOD FPD 0.05 ppm Phosmet (OP's) - 0.01 ppm Ethion
- 12 Organochlorines Partially Validated on ECD
 - LOD's (0.01 - 0.002 ppm); 88 - 91 % Recoveries
- Method Avoids Co-extractable Plant Compounds
 - Petroleum Ether / 2-Propanol vs Acetone or Acetonitrile
 - No Additional Cleanup Step Required
 - 2-Propanol and Water Soluble Interferences Removed

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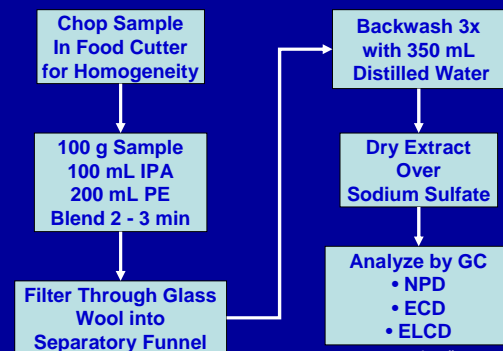
VegPrep Summary 1990 - 2006

- 1999 - Present Screen with μ ECD and 5973 MSD
- 5027 Samples Analyzed for Pesticide Residues
- 4233 Fresh Produce Samples
 - 2306 Fruit (32 Different Commodities)
 - 1927 Vegetable (58 Different Commodities)
- 794 Processed Produce Samples
- 48 Different Pesticides Detected and Quantified

• Organophosphates	7	• Organochlorines	4
• Pyrethroids	6	• Conazoles	5
• Anilides, Carbamates, Cyclodienes 3 each			
• Dinitroanilines, Dicarboxamides, Strobilium 2, 2, 1			
• Others	12		


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VegPrep Method Summary



<http://www.ct.gov/caes>

VegPrep Procedure



Food Samples

Homogenize

Blend w/ Solvent

Backwash

Dry & Bottle

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Top Ten Lists

<u>Fresh Commodities:</u>		<u>Pesticides:</u>	
• Apples	706	• Endosulfan	629
• Strawberries	559	• Captan	373
• Tomatoes	327	• Vinclozolin	166
• Blueberries	276	• Iprodione	144
• Squash, Summer	197	• Chlorothalonil	137
• Peaches	169	• Chlorpyrifos	131
• Peppers	149	• DDE	122
• Cucumbers	134	• Dicofol	83
• Pears	130	• Permethrin	66
• Potatoes	129	• Phosmet	55

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Reluctance to Change...Then...

- VegPrep Robust, Rapid, Easy; Provides Reasonably Wide Pesticide Coverage; Little Instrument Maintenance
- VegPrep Results in a 2 Fold Dilution of Sample

...QuEChERS... (Quick, Easy, Cheap, Effective, Rugged, Safe)

- M. Anastassiades, S.J. Lehotay, D. Stajnbaher and F.J. Schenck, J AOAC Int 86 (2003) 412
- QuEChERS Provides 5 Fold Concentration
- Net Gain of 10 Fold - 1 Order of Magnitude

<http://www.quechers.com/> <http://www.ct.gov/caes>

... and New Instrumentation



- Provides Additional Sensitivity
- QuEChERS Extract Amenable to GC & LC
- VegPrep PE Extract is Not Amenable to LC

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QuEChERS Method Summary

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    graph TD
      A[Chop Sample In Food Cutter for Homogeneity] --> B[15 g Sample 50 mL Tube]
      B --> C[600 ng 13C6-Alachlor (IS) (60 µL 10 ppm Toluene) 200 ng / mL Final Concentration]
      A --> D[6 g MgSO4 1.5 g NaOAc 15 mL CH3CN Shake 1 h]
      D --> E[Centrifuge 3000 rpm, 10 m]
      E --> F[Decant 10 mL 15 mL Tube 1.5 g MgSO4 500 mg PSA 2 mL Toluene Shake 5 m]
      F --> G[Centrifuge 3000 rpm, 10 m]
      G --> H[Decant 6 mL Conc. Tube N2 Blow down < 1 mL; > 0 mL]
      H --> I[Toluene to 1 mL]
      I --> J[Analyze by GC - 5975i LC - LTQ]
  
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QuEChERS Procedure



Homogenize

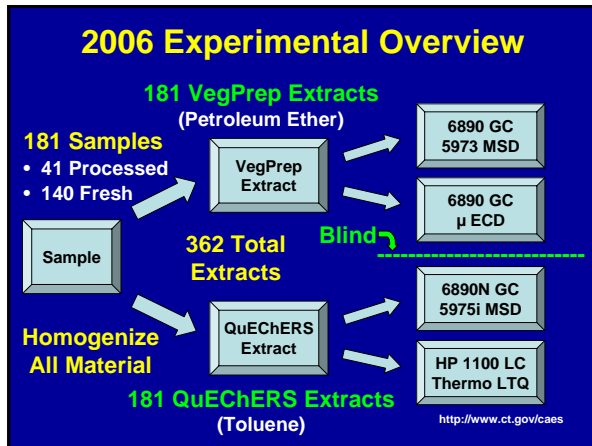
Wrist Action Shaker

Sample Tubes

Centrifuge

N₂ Blow down

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Pesticide Findings Summary

- 181 Fresh and Processed Samples from CT DCP
- 313 Individual Residues Reported
 - 133 Found by VegPrep
 - 180 Found by QuEChERS
- Inter-method Confirmation Not Always Observed
- A Total of 34 Different Pesticides Detected
 - 23 Pesticides Detected by BOTH Methods
 - 5 First Time Reported Pesticides
 - 6 Pesticides Detected Only by QuEChERS
 - 5 Pesticides Detected Only by VegPrep

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23 Found by Both Methods

- Only Those Pesticides Amenable to GC Detection
- Sensitivity of ECD Important at Low Levels

• Boscalid	• DDT & Metabolites	• Imazalil
• Captan	• Dieldrin	• Iprodione
• Chlordane	• Diphenylamine	• Malathion
• Chlorothalonil	• Endosulfan	• Metolachlor
• Chlorpyrifos	• Fenhexamid	• Myclobutanil
• Chlorpropham	• Fenbuconazole	• Phosmet
• Cyhalothrin, <i>lambda</i>	• Fenpropathrin	• Trifloxystrobin
• Cyprodinil	• Fludioxinil	

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QuEChERS

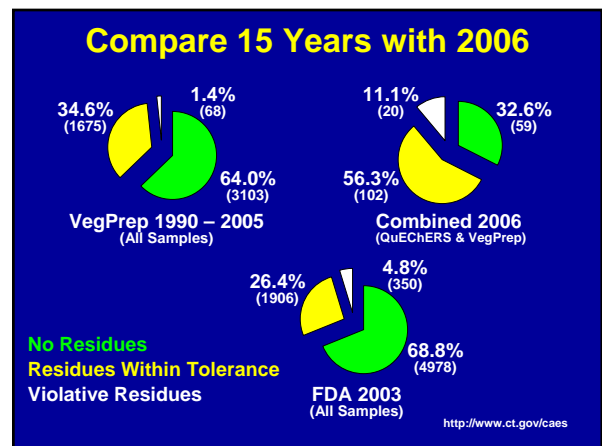
- 5 First Reported Pesticides
 - Acephate (2) 0.030 - 0.033 ppm LTQ
 - Acetamiprid (2) 0.086 - 0.211 ppm LTQ
 - Atrazine (9) 0.0002 - 0.016 ppm **LTQ**
 - Dimethomorph (1) 0.004 ppm LTQ
 - Methomyl (2) 0.001 - 0.078 ppm LTQ
- Carbaryl found 16 times
 - GC/ 5975i (4) 0.053 - 1.1 ppm
 - LTQ (16) 0.0004 - 1.2 ppm
- LTQ Extremely Sensitive at Very Low Levels for Pesticides Complimentary to GC Screen

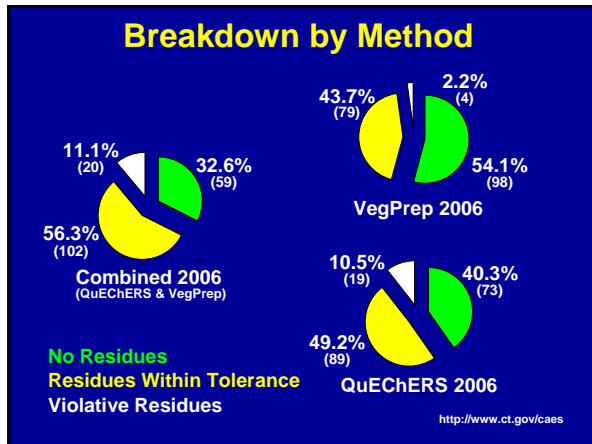
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VegPrep

- 5 Pesticides Found Using VegPrep Exclusive of QuEChERS
 - Bifenthrin (4) 0.004 - 0.041 ppm
 - Cypermethrin (1) 0.019 ppm
 - Fenvalerate (1) 0.06 ppm
 - Permethrin (3) 0.975 - 1.8 ppm
 - Sulfur (5) 0.24 - 12 ppm
- VegPrep Method Better at Detecting Pyrethroids?
 - Both Capable of Extracting These Pesticides
 - Is VegPrep Better at Extracting? - Future
 - ECD Proves Useful Tool

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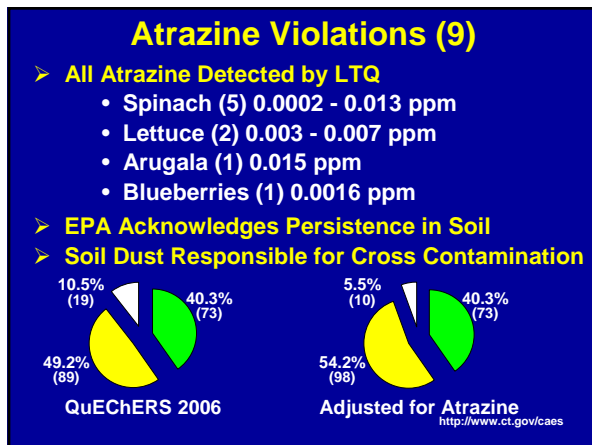




Pesticides Detected by Method

Pesticide	Detected	VegPrep		QuEChERS	LTQ
		μ ECD / 5973	5975i		
Endosulfan	31 (1)	29	7	0	
Phosmet	28 (10)	5	25	27	
Captan	22 (2)	17	18	0	
Cyprodinil	18 (23)	9	5	18	
Carbaryl	16 ND	0	4	16	
Boscalid	12 (38)	3	7	12	
Fenpropathrin	12 (19)	11	5	5	
Chlorothalonil	9 (5)	4	8	5	
Atrazine	9 ND	0	0	9	

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External or Internal Standard

	VegPrep		QuEChERS
	μ ECD / 5973	5975i	LTQ
Apples (CT)			
Phosmet	0.18	0.16	0.15
Fenbuconazole	-	0.002	0.004
Trifloxystrobin	0.14	0.024	0.031
Potatoes (CO)			
Chlorpropham	4.8	3.9	2.1
Strawberries (FL)			
Captan	0.328	0.76	-
Fenhexamid	0.087	0.032	0.033
Cyprodinil	0.009	0.013	0.006

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- ### Summary
- A Blind Study Evaluated the Differences using the QuEChERS Extraction Protocol and New Instrumentation vs Current Method of Analysis
 - Extraction Gains a 10 Fold Increase in Sensitivity
 - Demonstrated Usefulness of Alternate Detectors
 - Most Pesticides Extracted by Both Methods
 - Quantitation Results Similar by Both Methods
 - Demonstrated Usefulness of Internal Standard
 - Atrazine Review Providing Action Levels
- <http://www.ct.gov/caes>

Bulletins

- Published Annually; Reader Friendly Format
- 1998 forward available at: <http://www.ct.gov/caes>
- Please feel free to contact me:
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Special Thanks to: Drs. Brian D. Eitzer and Mary Jane Incorvia Mattina, Terri Arsenault, & The Analytical Chemistry Staff

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