

# ***Food Safety Research in the Department of Analytical Chemistry: Surveillance of Fresh and Manufactured Foods for Chemical Contamination***



**Jason C. White, Ph.D.**

**Department of Analytical Chemistry**

**The Connecticut Agricultural Experiment Station**



# CAES and Food Safety

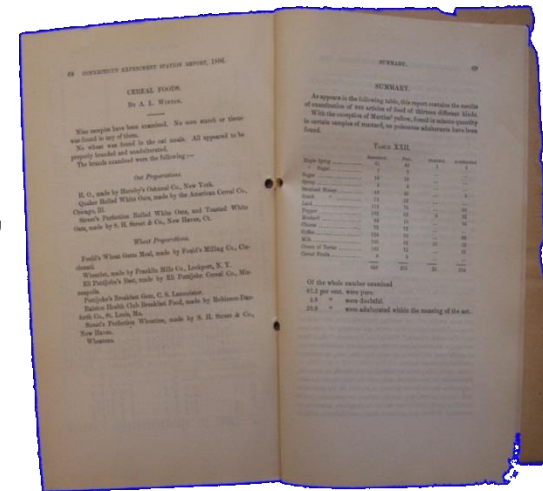
- The CAES was founded in 1875 with a \$2800 appropriation from the Legislature.
- The Station was to provide the CT farmer with scientific information and to conduct research in agriculture, with an immediate focus on fertilizer purity and safety.
- In January 1895, “An Act Regulating the Manufacture and Sale of Food Products” was passed by the Legislature.
- Section 4 reads as “The Connecticut Agricultural Experiment Station shall make analysis of food products on sale in Connecticut suspected of being adulterated...”

Samuel Johnson  
First CAES Director



# CAES and Food Safety

- The results of the first food safety study were published in 1896 (Bulletin 123).
- 848 food samples were analyzed; 14 categories.
- 67% pure; 30% adulterated; 3% “doubtful.”
- Commodities of interest-
  - Maple syrup- 61 samples; 8 violations.
  - Honey- 48 samples; 5 Violations.
  - Coffee- 64 samples, 58 violations.
- 50,595 food samples analyzed between 1896-1930.



# Part I: The Market Basket Survey

- Since 1964, CAES has conducted a Market Basket study with the CT Department of Consumer Protection (DCP).
- Designed as a surveillance program for pesticide residues in the CT foods.
- In 2005, the Department was selected to join the FDA Food Emergency Response Network (FERN).
- We now screen 200+ food samples annually for pesticides, toxins/poisons and other agents of concern for chemical terrorism.





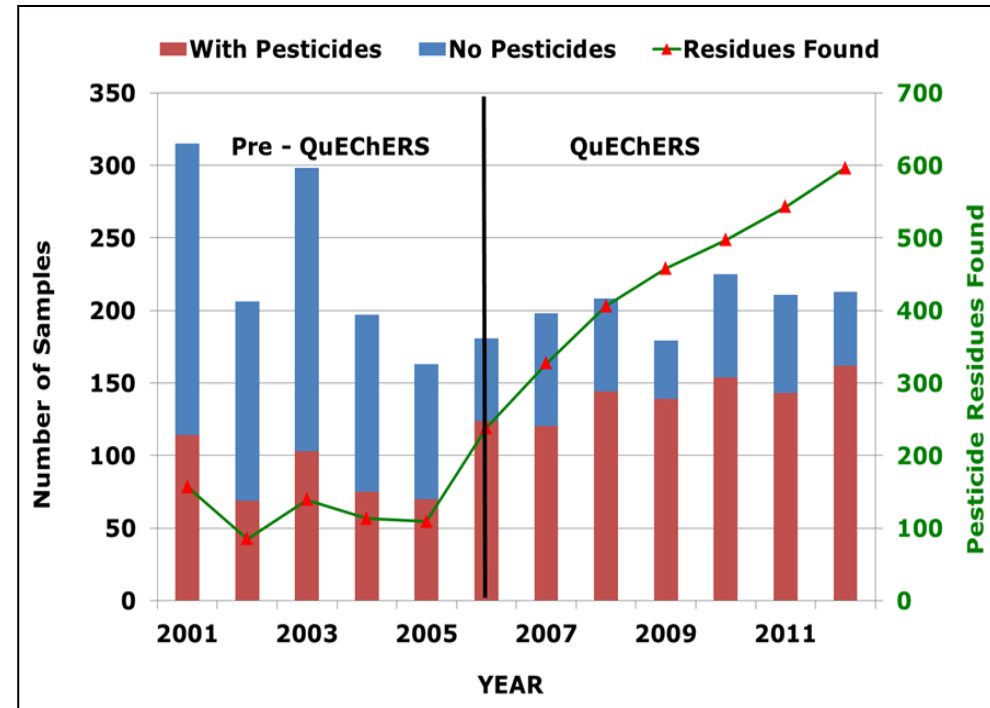
# Part I: The Market Basket Survey

- As a result of the robustness of our program, the FDA and USDA do not sample CT foods for pesticides.
- FDA FERN supplies highly sensitive equipment for the chemical terrorism grant that we also use for our state program.
- DCP or FDA select foods for analysis.
- The program expanded in 2010 with CT Department of Public Health; simultaneous analysis for chemicals and bacteria.



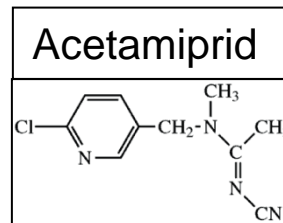
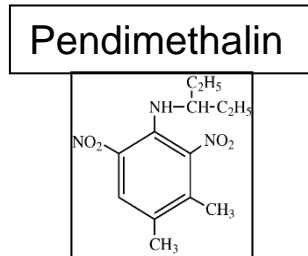
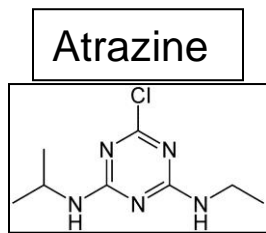
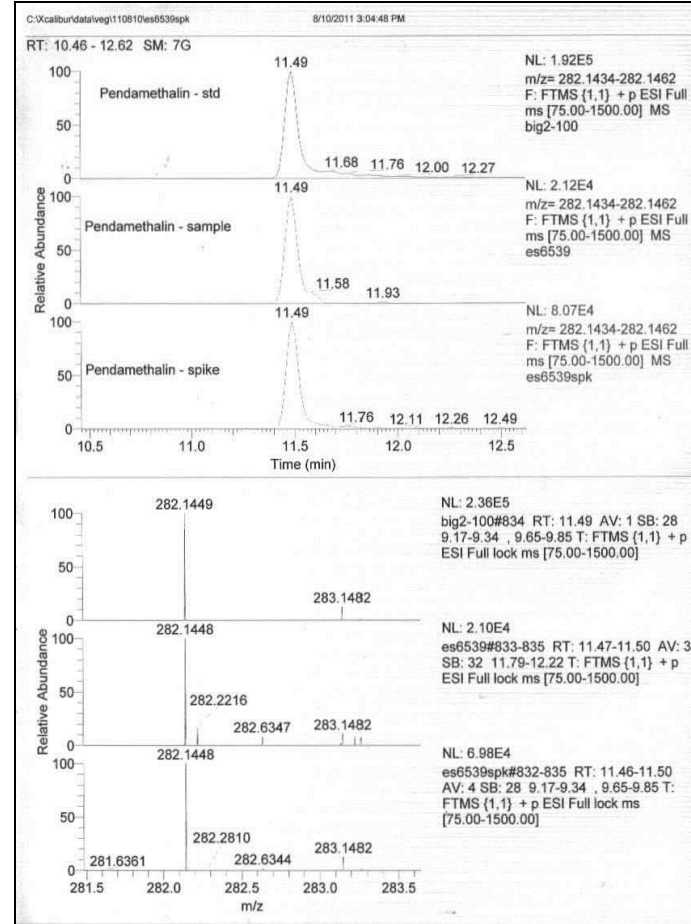
# The Market Basket - CAES Improvements

- In 2006, CAES switched to our current methods.
- Pre-2006, 40% of samples contained residues. Since 2006, greater sensitivity has revealed 65% of foods have residues and a greater number of residue types are present. CT violation rates have doubled from 3-4% to 7-8% per year.



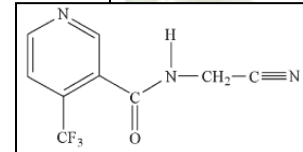
# The Market Basket Survey- Herbs

- Some pesticides are allowed in food.
- Violations come in two flavors:
  - Residue with no EPA tolerance.
  - Residue above the EPA tolerance.
- DCP collected fresh cilantro and parsley in January 2011.
  - The parsley had 6 residues but no violations.
  - The cilantro had 3 violations; none had tolerances (33 ppb acetamiprid- I, 21 ppb pendimethalin- H, and 8 ppb atrazine-H).



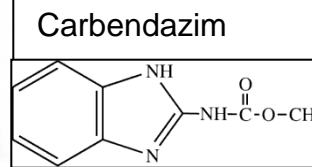
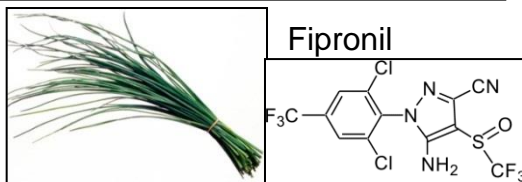
# The Market Basket Survey- Herbs

- As a follow up, **12** fresh samples were collected from May to July 2011.
- All 12 had violations, including...
- Organic tarragon with 7 violations: 1.5ppm cypermethrin (I) and 10ppm propinconazole (F).
- Chives with 5 violations: 0.17ppm fipronil (I) and 0.68ppm carbendazim (F).
- Thyme with 5 violations: 0.21ppm phosmet (I) and 16ppm carbendazim (F).
- A blended sample contained **13** violations: 0.8ppm oxamyl (I), 0.31ppm pyraclostrobin (F), 0.30ppm cyromazine (I), and 0.28ppm flonicamid (I).



Flonicamid


- **RESIDUES AT THESE LEVELS ARE NOT AN IMMINENT PUBLIC HEALTH CONCERN.**





# USDA Pesticide Data Program

- Separately the USDA collected 189 cilantro samples in May 2011; 44% contained violations. Chicago Tribune article on May 31, 2011 “USDA testing finds 30-plus unapproved pesticides on the herb cilantro.”
- Herbs/spices are not commodities the USDA, FDA or the CAES Market Basket survey have focused on.
- USDA/FDA go for commodities consumed in large quantities.
- CAES goes for a cross-section of the market basket but haven't looked at these before.


**The Connecticut Agricultural Experiment Station**  
 123 HUNTINGTON STREET, P.O. BOX 1106, NEW HAVEN, CONNECTICUT 06504  
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**ES6500B - SAMPLE REPORT -**      7/11/11

Sample Number	Commodity	Reported Value (ppm)	Found	CFR Number	Tolerance (ppm)	Violation ??
ES6500B	Holiday Ham Blend (Thyme, Rosemary, Parsely)	0.104	Dinotefuran	40CFR180.603	0	YES
		0.076	Thiamethoxam	40CFR180.565	0	YES
		0.013	Clothianidin	40CFR180.586	0	YES
		0.005	Imidacloprid & Metabolites	40CFR180.472	48	NO
		0.049	Prinamidine	40CFR180.317	0	YES
		0.01	Boscalid	40CFR180.589	0	YES
		0.01	Azoxystrobin	40CFR180.507	260	NO
		0.182	Profenofos	40CFR180.404	0	YES
		0.275	Fonicamid	40CFR180.613	0	YES
		0.203	2,6 Dichlorobenzamide	none see 231, 627	0	YES
			Dichlobenil*	40CFR180.231	0	YES
			Fluopicolide*	40CFR180.627	0	YES
		0.812	Oxamyl	40CFR180.303	0	YES
		0.342	Cyprodinil	40CFR180.532	170	NO
		0.025	Fludioxonil	40CFR180.516	65	NO
0.305	Pyraclostrobin	40CFR180.582	0	YES		
0.1	Carbendazim	none 294, 371	0	YES		
	Benomyl*	40CFR180.294	0	YES		
	Thiophanate Methyl*	40CFR180.371	0	YES		
0.219	Flutriafol	40CFR180.629	0	YES		
0.295	Cyromazine	40CFR180.414	0	YES		
	*** Pesticides Listed in Red are Violations***					

\*Parent is a metabolite of these pesticides.  
 If these pesticides are allowed, the metabolite is also allowed.  
 Otherwise the finding of the metabolite is a violation.

Phone: (203) 974-8500      Fax: (203) 974-8502  
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# And the Dried Herbs?

- DCP collected 24 dried herbs/spices.
- Manufacturers included Spice Classics, Nutmeg Spice, Gel Spice Co., McCormick,...
- Of the 24, 19 had violations; including organic parsley and thyme.
- Residues were in the ppb range.
- Two dried parsleys had 6 and 11 violations (11.6ppm methoxyfenozide [I]).
- Two dried chives had 11 and 12 violations (3.3ppm thiophenate methyl [F]).
- Dried tarragon contained 5 violations (10ppm propinconazole [F]).




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9/21/11

**ES6590 SAMPLE REPORT**

Sample Number	Commodity	Reported Value (ppm)	Found	CFR Number	Tolerance (ppm)	Violation ??
ES6590	Chives, Dried	0.221	Acetamipris	40CFR180.678	0	YES
		0.208	Imidacloprid & Metabolites	40CFR180.472	48	NO
		0.063	Carbofuran	40CFR180.254	0	YES
		0.023	Metaxyl	40CFR180.408	0	YES
		0.285	Dimethomorph	40CFR180.493	0	YES
		0.121	Difenoconazole	40CFR180.475	0	YES
		0.063	Chlorpyrifos	40CFR180.342	0	YES
		0.144	Acephate & Metabolites	40CFR180.108	0	YES
		3.700	Thiophenate Methyl & Metabolites	40CFR180.371	0	YES
		0.017	Methomyl	40CFR180.253	0	YES
		0.031	Oxadixyl	Revoked 7/02 Effective 9/03	0	YES
		0.296	Iprodione	40CFR180.399	0	YES
0.011	Propiconazole	40CFR180.434	0	YES		
0.619	Pyrimethanil	40CFR180.516	0	YES		

**VIOLATIONS ARE RED**

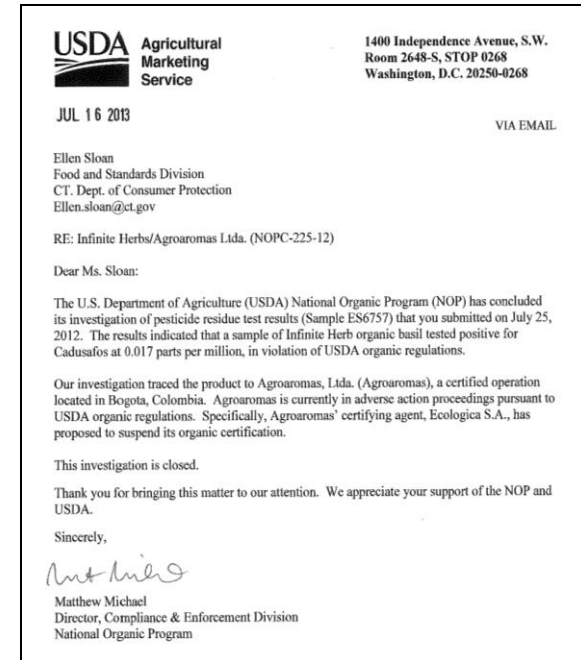
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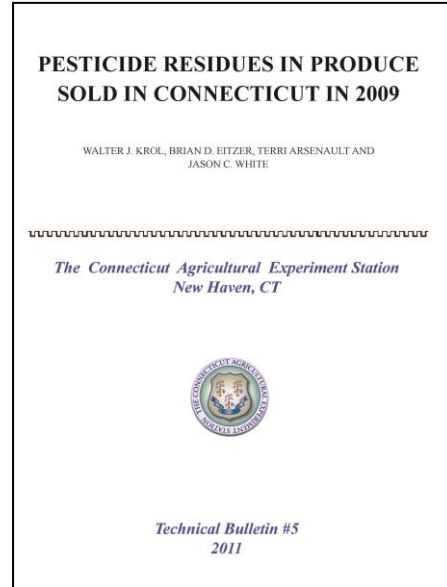
# Regulatory Response

- 43 fresh/dried herbs tested; 35 or 82% are violations. Our normal rate is 7-8%.
- FDA and USDA (organic foods) have regulatory authority (grown outside CT; most in US)
- FDA is investigating but has noted that this is not a public health concern and they focus on “sample commodities of dietary importance such as foods consumed in large amounts...”
- For violations, ppb levels (most) may be spray drift or incidental contamination; ppm levels suggest direct application.

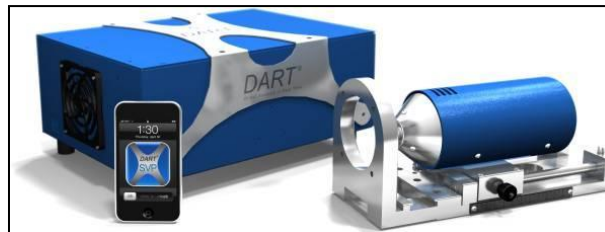


# What is CAES doing?

- Our Market Basket report is published each year; for 2011 we will publish 2 reports (one on herbs).
- We are working with the FDA to validate the DART (Direct Analysis in Real Time) on these herb samples. The DART is a field portable mass spectrometer.
- The DART could be deployed with Customs and Border Protection to test food prior to entry into the country. This validation has been presented at scientific meetings.



[www.ct.gov/caes](http://www.ct.gov/caes)

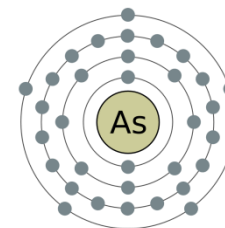


CAES- Plant Science Day 2013



# Part II: Arsenic in Apple Juice

- In September 2011, Dr. Mehmet Oz drew criticism for a show focusing on the “dangers” of arsenic in apple juice.
- An independent laboratory found 10 samples over 10 ppb, the arsenic drinking water limit.
- Public response was strong; one school district took apple juice off its menu
- However, only total arsenic was measured; several forms of arsenic exist and some are considered harmless.
- There was no regulatory level for arsenic in juice at the time. Focusing on the 10 ppb is problematic because it's based on water consumption (2-3 quarts per day).





# What is Arsenic?

- Arsenic occurs naturally but can also result from contamination by human activity.
- There are two types: organic and inorganic. Inorganic arsenic is harmful; organic arsenic is regarded as harmless.
- Both forms of arsenic found in soil and ground water; small amounts may be found in food/beverages
- The FDA has been testing for arsenic in apple juice and other foods for decades.
- The vast majority of apple juice tested contains low arsenic levels; the FDA is confident in the overall safety of apple juice consumed in this country.



The screenshot shows the FDA website page for Arsenic. The page is titled "Arsenic" and is part of the "Food" section. It includes a navigation menu with options like Home, Food, Drugs, Medical Devices, Radiation-Emitting Products, Vaccines, Blood & Biologics, Animal & Veterinary, Cosmetics, and Tobacco Products. The main content area is titled "Arsenic" and contains the following text:

**En Español (Spanish)**  
**中国 (Chinese)**

Arsenic is present in the environment as a naturally occurring substance or as a result of contamination from human activity. It is found in water, air, food, and soil in organic and inorganic forms.

The FDA has been measuring total arsenic concentrations in foods, including rice and juices, through its Total Diet Study program since 1991. The agency also monitors toxic elements, including arsenic, in a variety of domestic and imported foods under the Toxic Elements Program, with emphasis is placed on foods that children are likely to eat or drink, such as juices.

- Questions & Answers on Arsenic
- Information on Arsenic in Specific Products
- Method for Measuring Arsenic, Cadmium, Chromium, Mercury and Lead in Foods

**Questions & Answers on Arsenic**

**What is Arsenic?**

Arsenic is a chemical element present in the environment from both natural and human sources, including erosion of arsenic-containing rocks, volcanic eruptions, contamination from mining and smelting ores, and previous or current use of arsenic-containing pesticides.

**Are there different types of arsenic?**

There are two types of arsenic compounds in water, food, air, and soil: organic and inorganic (these together are referred to as "total arsenic"). The inorganic forms of arsenic are the forms that have been associated with long term health effects. Because both forms of arsenic have been found in soil and ground water for many years, some arsenic may be found in certain food and beverage products, including rice, fruit juices and juice concentrates.

**How does arsenic get into foods? Do all foods have arsenic?**

Arsenic may be present in many foods including grains, fruits, and vegetables where it is present due to absorption through the soil and water. While most crops don't readily take up much arsenic from the ground, rice is different because it takes up arsenic from soil and water more readily than other grains. In addition, some seafood has high levels of less toxic organic arsenic.

**Do organic foods have less arsenic than non-organic foods?**

Because arsenic is naturally found in the soil and water, it is absorbed by plants regardless of whether they are grown under conventional or organic farming practices.

**What are the health risks associated with arsenic exposure?**

Long-term exposure to high levels of arsenic is associated with higher rates of skin, bladder, and lung cancers, as well as heart disease. The FDA is currently examining these and other long-term effects.



# What is Arsenic?

- The maximum level allowed in drinking water is 10 ppb **total** arsenic.
- There was not a regulatory level for juice; there was a level of concern (LOC) of 23 ppb **inorganic** arsenic.
- July 12, 2013- The FDA has proposed creating an action level to 10 ppb **inorganic** arsenic.

U.S. Department of Health & Human Services

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### FDA NEWS RELEASE

For Immediate Release: July 12, 2013  
Media Inquiries: Theresa Eisenman, 301-796-2805, [theresa.eisenman@fda.hhs.gov](mailto:theresa.eisenman@fda.hhs.gov)  
Consumer Inquiries: 888-INFO-FDA

[En Español](#)

#### FDA proposes “action level” for arsenic in apple juice

*Agency testing and analysis confirm overall safety of apple juice*

The U.S. Food and Drug Administration today proposed an “action level” of 10 parts per billion (ppb) for inorganic arsenic in apple juice. This is the same level set by the U.S. Environmental Protection Agency (EPA) for arsenic in drinking water.

“The FDA is committed to ensuring the safety of the American food supply and to doing what is necessary to protect public health,” said FDA Commissioner Margaret A. Hamburg, M.D. “We have been studying this issue comprehensively, and based on the agency’s data and analytical work, the FDA is confident in the overall safety of apple juice for children and adults.”

“While the levels of arsenic in apple juice are very low, the FDA is proposing an action level to help prevent public exposure to the occasional lots of apple juice with arsenic levels above those permitted in drinking water,” said Michael R. Taylor, the FDA’s deputy commissioner for foods and veterinary medicine.

The FDA is establishing this threshold to provide guidance to industry. The agency takes the action level into account when considering an enforcement action, if it finds a food product exceeds the threshold.

The FDA has been monitoring the presence of arsenic in apple juice for the past 20 years and has consistently found that samples contain levels of arsenic that are low, with few exceptions. New tools, however, have allowed the agency to better understand the breakdown between organic and inorganic arsenic levels. Last year the FDA released findings from its latest data collection and analysis of 94 samples of arsenic in apple juice. The analysis showed that 95 percent of the apple juice samples tested were below 10 ppb total arsenic; 100 percent of the samples were below 10 ppb for inorganic arsenic, the carcinogenic form of arsenic.

The proposed level of 10 ppb takes into account this sampling data plus a recently completed, peer-reviewed risk assessment of inorganic arsenic in apple juice conducted by FDA scientists. The assessment is based on lifetime exposure.

Inorganic arsenic may be found in foods because it is present in the environment, both as a naturally occurring mineral and because of activity such as past use of arsenic-containing pesticides. A known carcinogen, inorganic arsenic also has been associated with skin lesions, developmental effects, cardiovascular disease, neurotoxicity, and diabetes.

In conducting its new assessment on apple juice, the FDA was able to use data from two studies published in 2010, as well as a 2011 evaluation by the Joint Expert Committee on Food Additives and Contaminants of the Food and Agriculture Organization, part of the United Nations and the World Health Organization.

The agency will accept public comments on the proposed action level and the risk assessment for 60 days.



# Consumer Reports Follow Up



- January 2012 *Consumer Reports*- “Arsenic in your juice”
- 88 samples of apple and grape juice tested (19 brands)
- 90% were lower than 10 ppb total arsenic
- CR had the arsenic speciated; “most” was inorganic
- Of 555 parents surveyed, 88% of children consume less than 16 ounces/per day (0.5 quarts).
- The drinking water value for arsenic is based on 2-3 quarts per day.

Country-of-origin labeling (COOL)	Juice type (RTD = ready-to-drink package)	Package type	Size (fl. oz.)	Lot #	Total arsenic (ppb)	Total inorganic arsenic species (ppb) <sup>1</sup>	Total organic arsenic species (ppb) <sup>1</sup>	Total lead (ppb)
Turkey, Argentina, New Zealand	RTD	Plastic bottle	64	1	7.11	5.89	0.60	3.49
Argentina	RTD	Plastic bottle	64	2	7.00	6.74	0.71	3.79
China	RTD	Plastic bottle	64	1	1.67	1.03	0.55	1.40
China	RTD	Plastic bottle	64	2	4.37 <sup>2</sup>	3.85 <sup>2</sup>	0.94 <sup>2</sup>	5.56 <sup>2</sup>
China	RTD	Plastic bottle	64	3	1.37	0.60	0.51	0.50
USA, Argentina, China	RTD	Juice box(es)	8 x 6.75	1	5.02	2.49	1.88	2.05
USA, Argentina, China	RTD	Juice box(es)	8 x 6.75	2	5.30	3.06	2.23	3.44
USA, Argentina, China	RTD	Juice box(es)	8 x 6.75	3	10.5	4.13	4.85	1.90
Argentina	RTD	Plastic bottle(s)	4 x 4	1	9.69	10.48	0.92	13.6
Argentina	RTD	Plastic bottle(s)	4 x 4	2	8.66	7.65	0.88	7.08
Argentina	RTD	Plastic bottle(s)	4 x 4	3	5.82	3.48	0.69	3.41
Argentina	RTD	Plastic bottle(s)	4 x 4	1	5.74	4.44	0.90	2.21
Argentina	RTD	Plastic bottle(s)	4 x 4	2	5.68	4.55	0.95	2.28
Argentina	RTD	Plastic bottle(s)	4 x 4	3	5.47	3.89	0.78	2.23
China	RTD	Plastic bottle	64	1	3.14	2.05	0.69	2.87
China	RTD	Plastic bottle	64	2	9.38	4.99 <sup>3</sup>	3.94 <sup>3</sup>	5.57
China	RTD	Plastic bottle	64	3	8.56	5.44	3.61	4.84





## FDA website- March 2012

- 94 apple juice samples (many brands) collected in late 2011
- Test results for total arsenic, inorganic arsenic, DMA and MMA.
- 95% of the samples tested below 10 ppb total arsenic; however, most was inorganic arsenic.
- The FDA has concluded that the very low levels detected are not a public health risk and the juice products are safe for consumption.



Sample ID	Total Arsenic Analysis*	Arsenic Speciation Analysis**		
	Total As Concentration (µg/kg, ppb)	Inorganic As Concentration (AsIII + AsV) (µg/kg, ppb)	DMA Concentration (µg/kg, ppb)	MMA Concentration (µg/kg, ppb)
561799	5.6	5.2	TR	0
561800	36	8.3	TR	19
592030	7.5	5.4	TR	0
606077	4.1	TR	TR	0
606078	6.6	3.9	0	0
615659	1.3	TR	0	0
629367	6.9	5.0	TR	0
629368	10	8.1	TR	0
645508	30	8.4	TR	20
645509	5.5	TR	0	TR
645510	1.4	TR	0	0
657385	TR	0	TR	0
658160	2.6	TR	0	0
658161	5.1	TR	0	0
658162	7.2	4.0	TR	TR

# Next Steps

- Establishing a new action level: 10ppb inorganic arsenic.
- Enhanced surveillance of apple juice. Results on the FDA website.
- Continue to test juice from China; 95% < 10ppb.
- Enhanced surveillance of other juices, such as grape, pear, apricot, ... Involves FDA FERN Labs such as the CAES.
- Work with the juice industry to determine arsenic sources.
- Enhanced surveillance of arsenic in other foods (rice).



CAES- Plant Science Day 2013

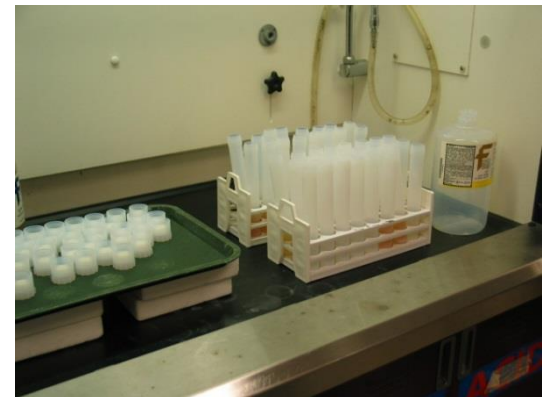


[www.ct.gov/caes](http://www.ct.gov/caes)



# Arsenic Analysis in CT: ICP-MS

- FDA method: 40 minutes, 200°C microwave digestion in concentrated acid
- ICP-MS gives dozens of elements in 3 minutes
- Detecting 50 ppt (part per trillion!)
- The problem: ICP-MS only gives total arsenic



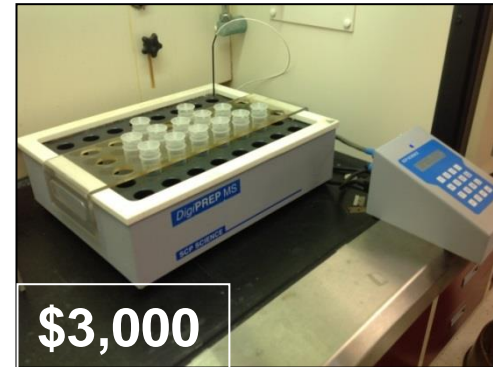
\$162,000



\$28,000

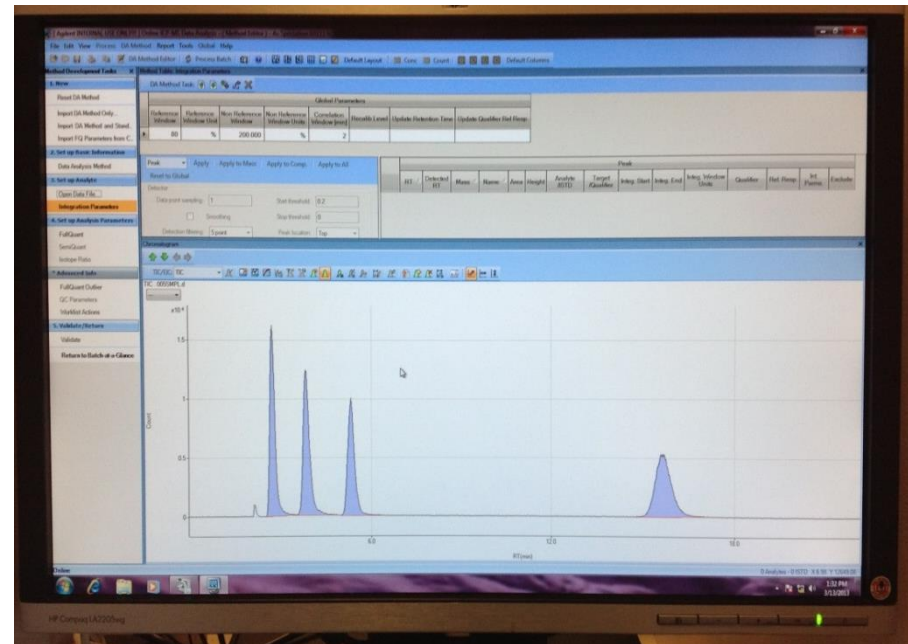
# Analytical Issues: Total Arsenic

- We need arsenic species; not total arsenic
- LC-ICP-MS- It is still ICP-MS
- The LC allows separation of organic and inorganic species
- An extraction; dilute acid on a hot block at 90°C.
  - Separation first; each run is 22 minutes
  - Looks for arsenic only over the whole run



# CT-FDA FERN Activities

- Running an FDA validation for arsenic species in food
- CT agencies (DoAg, DCP, DPH) also interested in arsenic in seaweed, rice, rice-based formula,...







**Jason C. White, Ph.D.**  
Department of Analytical Chemistry  
123 Huntington Street  
P. O. Box 1106  
New Haven, CT 06504



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Phone: 203.974.8523  
Email: [Jason.White@ct.gov](mailto:Jason.White@ct.gov)  
Website: [www.ct.gov/caes](http://www.ct.gov/caes)

