Arsenic in Rice in the Spotlight

The tools needed to measure Arsenic in rice and rice products

September 2012

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Media – Sept, 2012

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NATURE NEWS BLOG

Arsenic in rice stirs US action

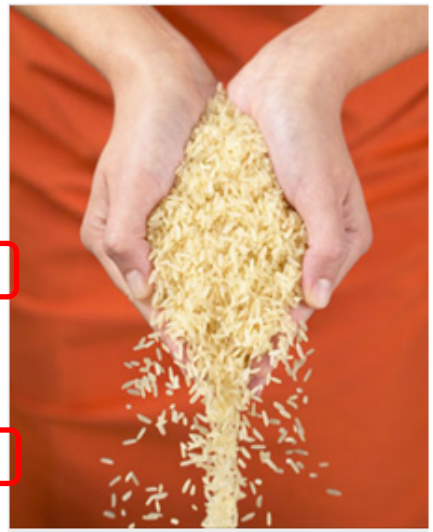
22 Sep 2012 | 00:05 BST | Posted by Helen Shen | Category: Earth, environment & ecology, Health and medicine

On the heels of two reports that have reignited worries about arsenic poisoning from rice, US lawmakers are taking steps to restrict the toxic substance.

On 21 September, US House Representative Rosa DeLauro of Connecticut introduced a bill that would require the Secretary of Health and Human Services to set limits on allowable arsenic levels in rice and rice products. The proposal specifies that the heavy metal — which has been linked to increased risk of certain cancers — should be restricted to levels that would minimize such risks.

Arsenic occurs naturally in soil, and can be taken up by plants such as rice. However, as *Nature* reported in 2005, in the United States, and particularly in some Southern states, arsenic may be concentrated in rice fields once used for cotton farming and treated with arsenic-based pesticides against boll weevils.

For the past year, the US Food and Drug Administration has been studying arsenic in commercially available rice and rice products. The agency released its preliminary findings 19 September.



US RICE FEDERATION

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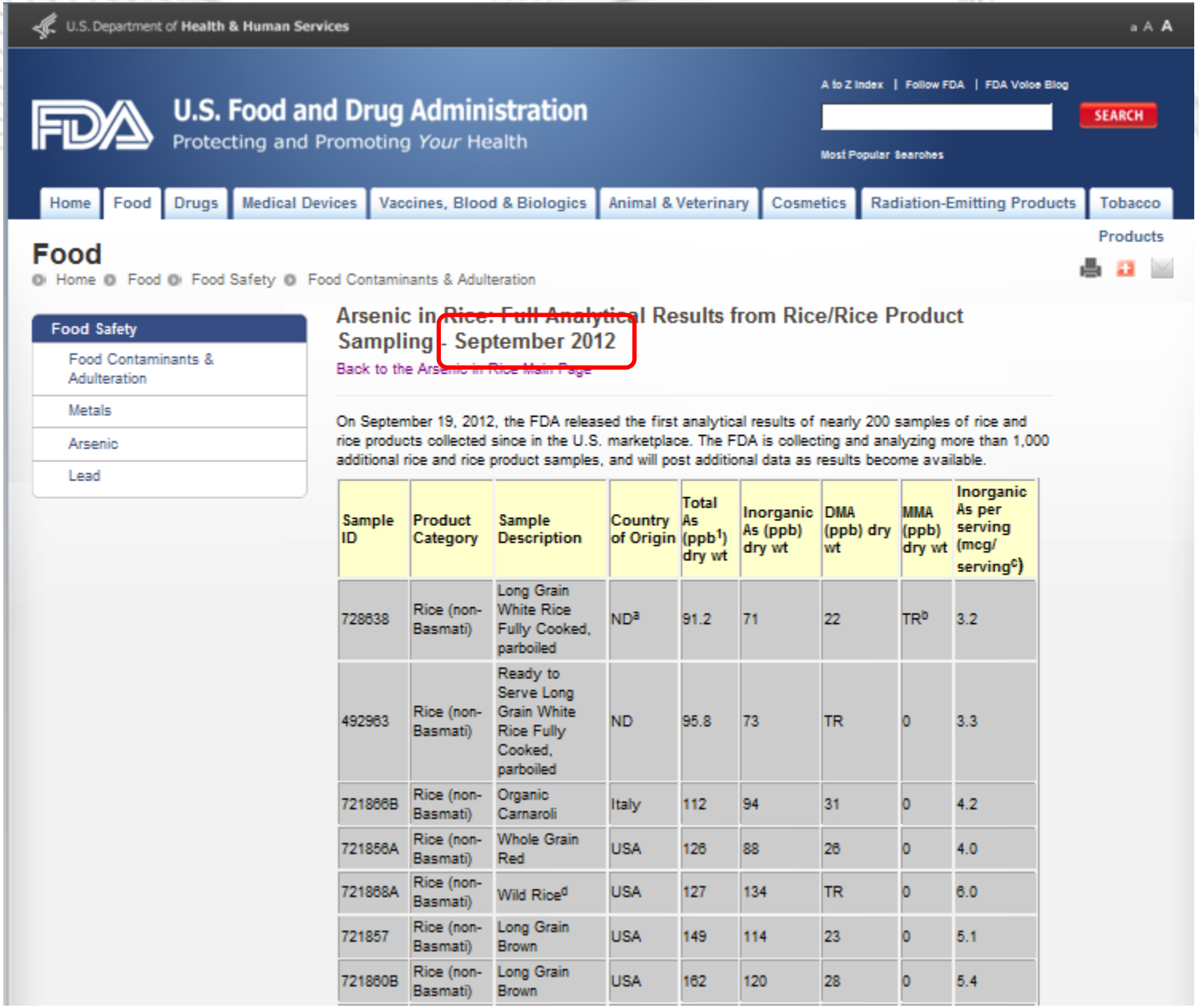

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  - Arsenic
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Arsenic in Rice: Full Analytical Results from Rice/Rice Product Sampling - September 2012

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On September 19, 2012, the FDA released the first analytical results of nearly 200 samples of rice and rice products collected since in the U.S. marketplace. The FDA is collecting and analyzing more than 1,000 additional rice and rice product samples, and will post additional data as results become available.

Sample ID	Product Category	Sample Description	Country of Origin	Total As (ppb[1]) dry wt	Inorganic As (ppb) dry wt	DMA (ppb) dry wt	MMA (ppb) dry wt	Inorganic As per serving (mcg/serving[c])
728838	Rice (non-Basmati)	Long Grain White Rice Fully Cooked, parboiled	ND[a]	91.2	71	22	TR[b]	3.2
492963	Rice (non-Basmati)	Ready to Serve Long Grain White Rice Fully Cooked, parboiled	ND	95.8	73	TR	0	3.3
721866B	Rice (non-Basmati)	Organic Carnaroli	Italy	112	94	31	0	4.2
721856A	Rice (non-Basmati)	Whole Grain Red	USA	126	88	26	0	4.0
721868A	Rice (non-Basmati)	Wild Rice[d]	USA	127	134	TR	0	6.0
721857	Rice (non-Basmati)	Long Grain Brown	USA	149	114	23	0	5.1
721860B	Rice (non-Basmati)	Long Grain Brown	USA	162	120	28	0	5.4

UK food agency 2009 advisory

Food Standards Agency

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Arsenic in rice research published

Thursday 21 May 2009

The Agency has today published results from two studies: arsenic levels in rice drinks and one on cooking methods to reduce arsenic levels in rice. As a result of the rice drink study, the Agency recommends that toddlers and young children should not have rice drinks, often known as rice milk, as a replacement for cows' milk, breast milk or infant formula.

The rice drink study followed concerns about results from a study published last year that measured arsenic levels in these types of drinks. The research published today examined 60 samples of rice drinks and found low levels of arsenic in all of them (see The science behind the story section below).

The level of total arsenic ranged from 0.010 - 0.034 milligram/kilogram and the levels of inorganic – the more harmful – form of arsenic ranged from 0.005 - 0.020 milligram/kilogram. The proportion of inorganic arsenic in the rice drink samples ranged from 48 - 63%. None of the results were over the current legal limit (but see the Current regulations section below).

In the second study, researchers looked at the effect of cooking methods on arsenic content of rice. The Agency is not advising anyone to change the way they cook rice as a result of this study as the impact on the overall dietary intake of arsenic from different cooking methods is minimal.

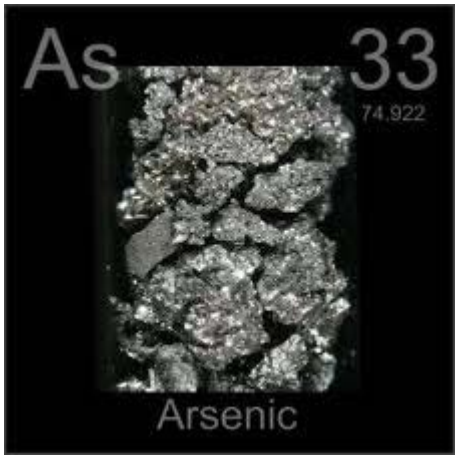
What the Agency advises

As a precaution, toddlers and young children between 1 and 4.5 years old should not have rice drinks as a replacement for cows' milk, breast milk, or infant formula. This is because they will then drink a relatively large amount of it, and their intake of arsenic will be greater than that of older children and adults relative to their bodyweight. This is both on nutritional grounds and because such substitution can increase their intake of inorganic arsenic, which should be kept as low as possible. A daily half pint or 280 millilitres of rice drink could double the amount of the more harmful form of arsenic they consume each day.

There is no immediate risk to children who have been consuming rice drinks and it is unlikely that there would have been any long-term harmful effects but to reduce further exposure to arsenic parents should stop giving these drinks to toddlers and young children.

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.



http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm280202.htm

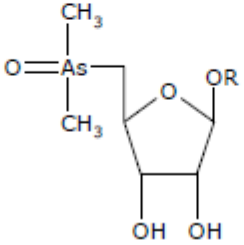
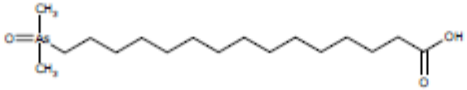
Are there different types of arsenic?

Two types: 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.

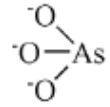
http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm280202.htm

Toxicity of Arsenic

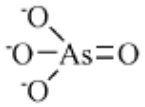
Table 1: Names, abbreviations, and chemical structures for arsenic species referred to in this report (from EFSA Scientific Opinion on Arsenic in Food)

Name	Abbreviation	Chemical structure[a]	Relevance/comment
Inorganic arsenic	iAs		Sum of As(III) and As(V).
Arsenite	As(III)	$As(O^-)_3$	Trace to low levels in most foods; highly toxic.
Arsenate	As(V)	$O{=}As(O^-)_3$	Trace to low levels in most foods; a major form in water; highly toxic.
Arsenobetaine	AB	$(CH_3)_3As^+CH_2COO^-$	Major arsenic species in most seafoods; non-toxic.
Arsenosugars[b]			Major (edible algae) or significant (molluscs) arsenic species in many seafoods.
Arsenolipids[c]		e.g. 	Newly discovered arsenic species present in fish oils and fatty fish; likely to be present in other seafoods as well.
Trimethylarsonio propionate	TMAP	$(CH_3)_3As^+CH_2CH_2COO^-$	Minor arsenic species present in most seafoods.
Methylarsonate	MA	$CH_3AsO(O^-)_2$	Trace arsenic species of some seafoods and terrestrial foods; a significant human urine metabolite of iAs.
Methylarsonite	MA(III)	$CH_3As(O^-)_2$	Not usually detected in foods; detected in some human urine samples as a metabolite of iAs; a toxic species thought to be important for arsenic's mode of toxic action.
Dimethylarsinate	DMA	$(CH_3)_2AsO(O^-)$	Minor arsenic species in seafoods and some terrestrial foods; the major human urine metabolite of iAs, arsenosugars and arsenolipids.
Thio-dimethylarsinate	Thio-DMA	$(CH_3)_2AsS(O^-)$	A minor human urine metabolite of inorganic arsenic and arsenosugars.

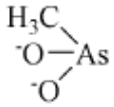
There are a LOT of arsenic species!



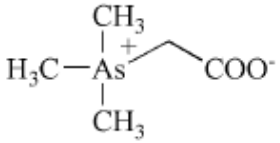
Arsenite
[As(III)]



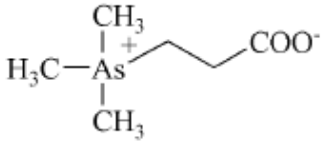
Arsenate
[As(V)]



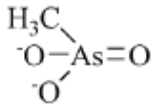
Methylarsonite
[MA(III)]



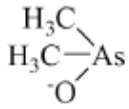
Trimethylarsonioacetate
(Arsenobetaine, AB)



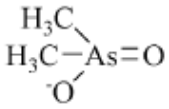
Trimethylarsoniopr
opionate
(TMAP)



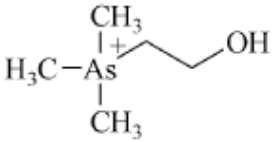
Methylarsonate
(MA)



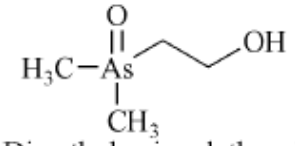
Dimethylarsinite
[DMA(III)]



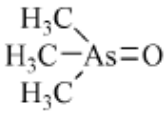
Dimethylarsinate
(DMA)



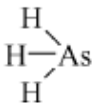
Arsenocholine
(AC)



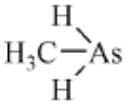
Dimethylarsinoylethanol
(DMAE)



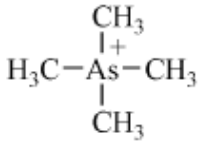
Trimethylarsine oxide
(TMAO)



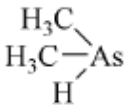
Arsine



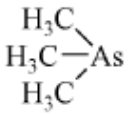
Methylarsine



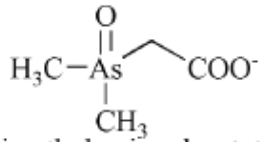
Tetramethylarsonium ion
(TETRA)



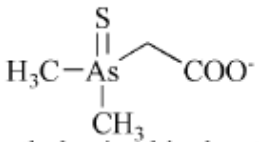
Dimethylarsine



Trimethylarsine



Dimethylarsinoylacetate
(DMAA)

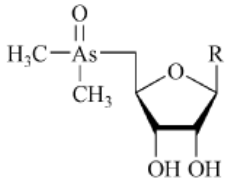


Dimethylarsinothioylacetate

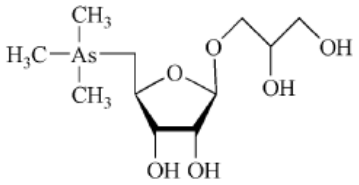
Analyst, 2004, **129**, 373–395

More arsenic species

Dimethylated Arsenosugars:

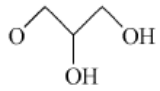


Trimethylated Arsenosugar:

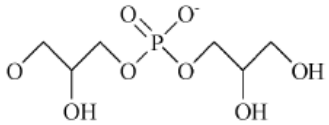


Arsenosugar **9**

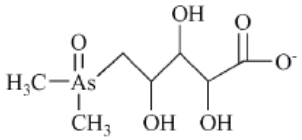
R =



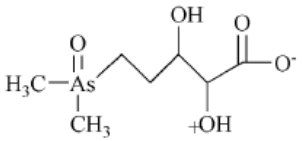
Arsenosugar **1**
(glycerol sugar)



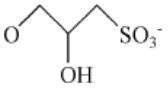
Arsenosugar **2**
(phosphate sugar)



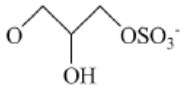
5-Dimethylarsinoyl-2,3,4-trihydroxypentanate



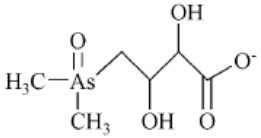
5-Dimethylarsinoyl-2,3-dihydroxypentanate



Arsenosugar **3**
(sulfonate sugar)



Arsenosugar **4**
(sulfate sugar)



4-Dimethylarsinoyl-2,3-dihydroxybutanate

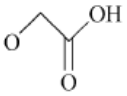
Seleno-bis(S-glutathionyl)arsinium ion
(GS = Glutathione)

H

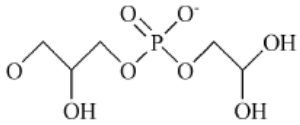
Arsenosugar **5**

OH

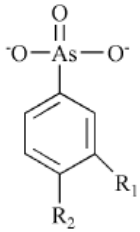
Arsenosugar **6**



Arsenosugar **7**



Arsenosugar **8**

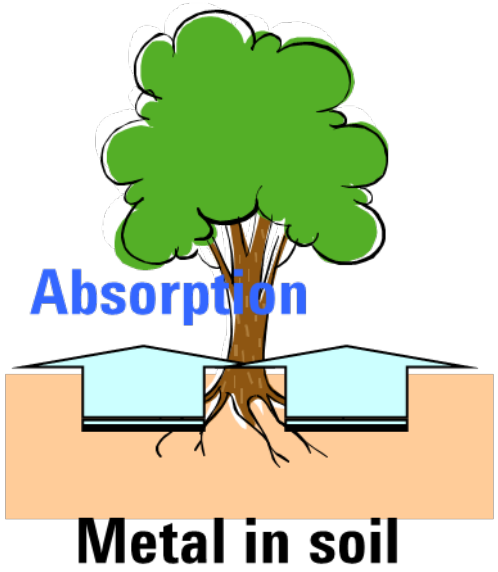


$R_1, R_2 = H$	Phenylarsonate
$R_1 = H, R_2 = NH_2$	p-Arsanilate
$R_1 = NO_2, R_2 = OH$ itrophenylarsonate	4-Hydroxy-3- (Roxarsone)

Analyst, 2004, 129, 373–395

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. Rice is different than most crops because it takes up arsenic from soil and water more readily than other foods.



http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm280202.htm

Schoof et al. 1999, Williams et al. EST 2005, Raab et al. 2004

Arsenic concentration in food varies over 4 orders of magnitude

(slide courtesy J. Feldmann, U. Aberdeen)

0.001

0.005-
0.01

0.05-0.09

0.22-1.1

[Arsenic]

0.5-1,5

>500

3.0

20-200

0.01 mg/kg

0.1 mg/kg

1 mg/kg

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.

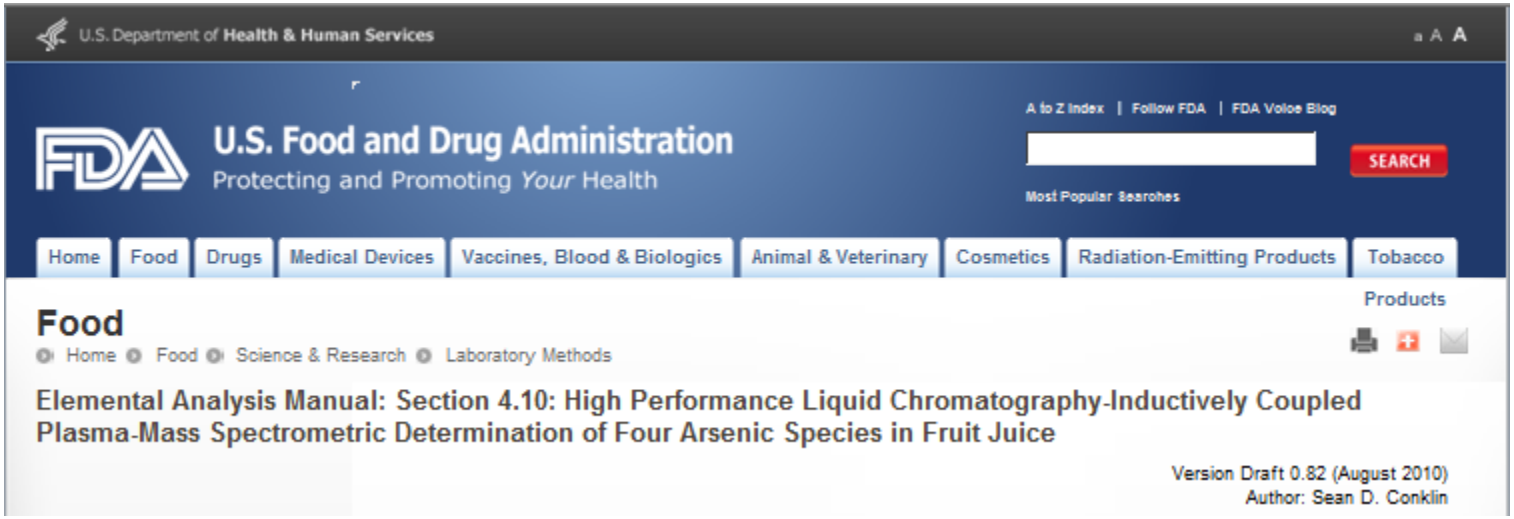
The FDA is currently examining these and other long-term effects.

http://www.nature.com/news/2008/080714/full/454263a.html

http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm280202.htm

Does the FDA test for arsenic in foods?

Yes, the FDA tests for total and inorganic arsenic in a variety of foods. The FDA has published a method for the analysis of arsenic in Apple juice.



The FDA has also shown that they have a method for testing arsenic in Rice as well, but not online yet.

http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm280202.htm

Arsenic in Rice - FDA

U.S. Department of Health & Human Services

U.S. Food and Drug Administration
Protecting and Promoting *Your* Health

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- Metals
- Arsenic
- Lead

Arsenic in Rice

Arsenic Main Page

The FDA has collected and tested rice for total arsenic for about 20 years. On September 19, 2012, the FDA released the **first analytical results of nearly 200 samples of rice and rice products** tested for both total and inorganic arsenic. The FDA is collecting and analyzing more than 1,000 additional rice and rice product samples, and will post additional data as results become available.

Samples included various brands of rice and rice products, such as infant rice cereal, breakfast cereal, rice cakes and rice beverages. FDA scientists tested the samples for total arsenic, inorganic arsenic, and two forms of organic arsenic that may have toxic effects (dimethylarsinic acid, or DMA, and monomethylarsonic acid, or MMA). The sample results also show the amount in micrograms of inorganic arsenic per serving. Serving amounts are based on the Reference Amount Customarily Consumed as defined in the Code of Federal Regulations.

The **table** FDA released shows the micrograms of inorganic arsenic (iAs) per serving for each sample tested. The summary chart below shows the average amounts of iAs in micrograms per serving for each of the product categories, and the range of the amount of inorganic arsenic in micrograms per serving for each product category.

Rice and Rice Products Sample Analysis - September 2012
Average Amounts of Inorganic Arsenic by Product Category in mcg per serving

Product	Average Inorganic Arsenic (iAs) mcg/serving	Range of iAs mcg/serving	Number of Samples
Basmati rice[1]	3.5	1.2 - 9.0	52
Rice cereals	3.5	1.5 - 9.7	32
Rice Beverages[2]	3.8	Trace - 4.1	28
Rice cakes	5.4	3.0 - 8.2	32
Rice (non-Basmati)	6.7	2.2 - 11.1	49

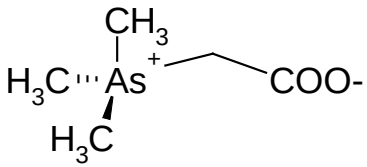
Why analyze concentration of species instead of total elemental concentrations?

The toxicity, bioavailability, and mobility of a given element depends on its form.

- e.g., inorganic arsenic is far more toxic than organic arsenic, but inorganic mercury is far less toxic than organic mercury

Lethal dose of organic arsenic

- LD_{50} of DMA 200-1000 mg per kg body weight
- LD_{50} of Arsenobetaine >10,000 mg per kg body weight



Lethal dose of inorganic arsenic

- LD_{50} of As_2O_3 10 mg per kg body weight
- LD_{50} of As_2O_5 30 mg per kg body weight

Speciation Analysis

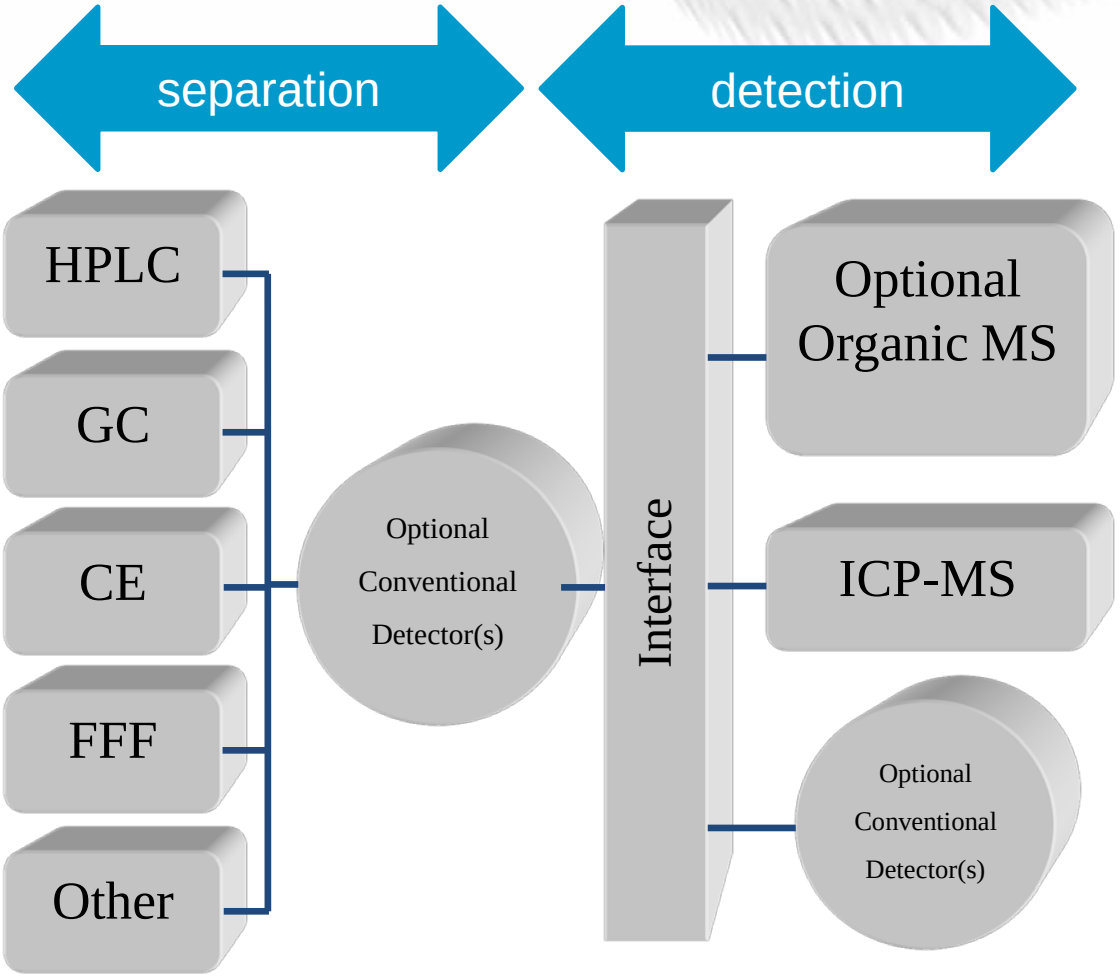
Elemental speciation requires 2 steps

1. Separate the species
2. Identify and quantify the elemental composition of the species

The separation is done chromatographically or electrophoretically.

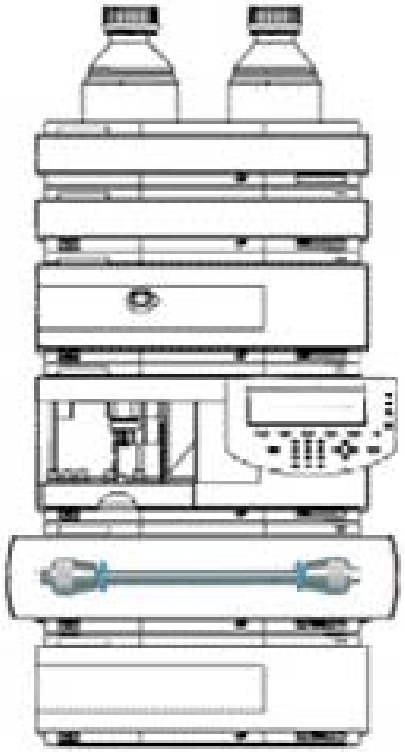
The elemental identification and quantification is performed using ICP-MS coupled to the chromatograph

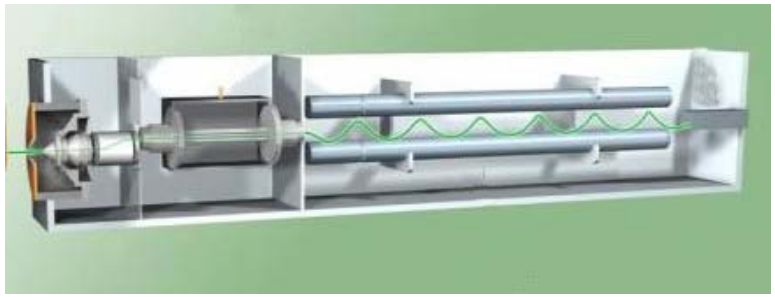
Most common techniques are GC-ICP-MS and HPLC-ICP-MS



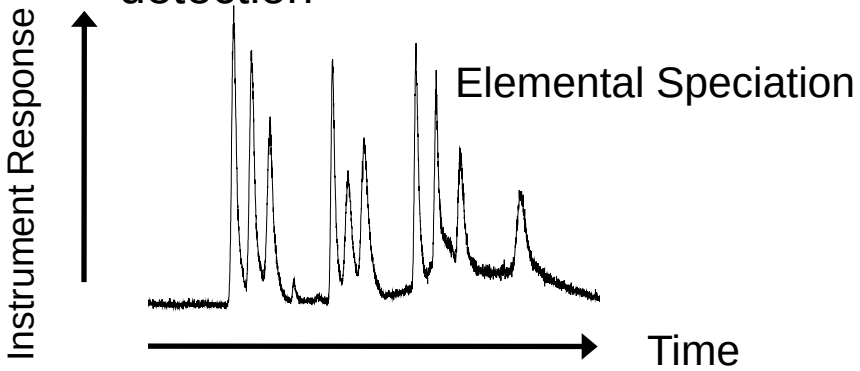
Coupling HPLC to ICP-MS

Sample





ICP-MS for element specific detection

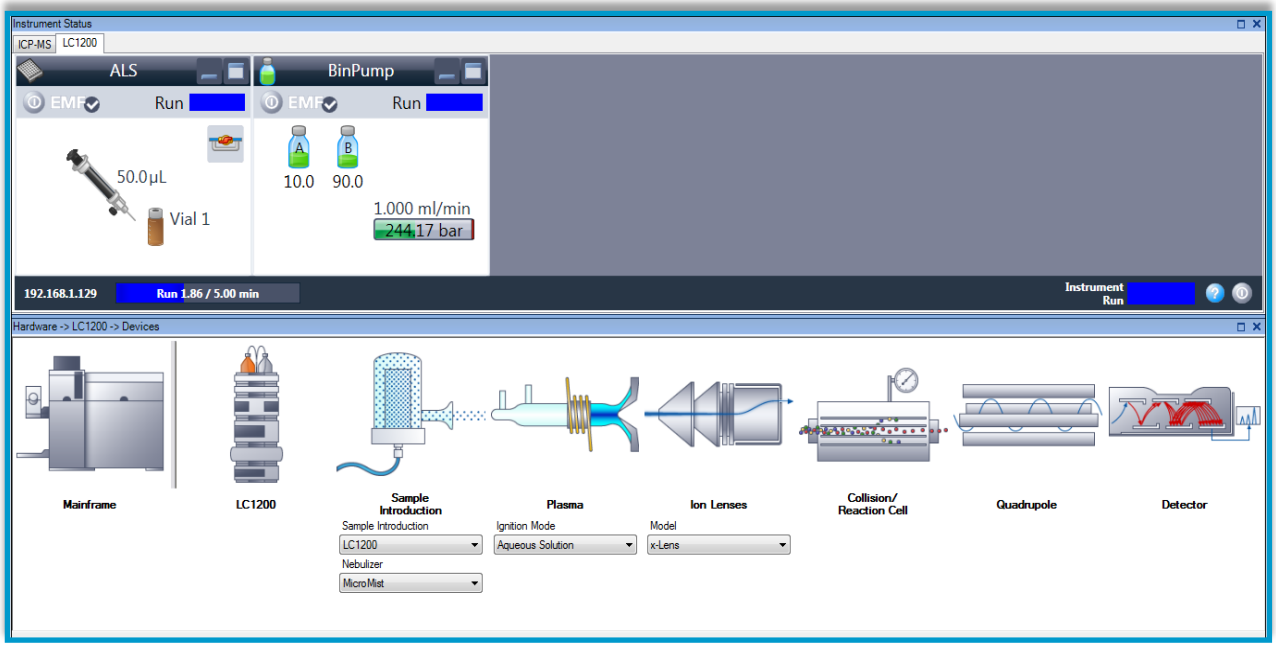


HPLC-ICP-MS

Simple set-up

ICP-MS MassHunter software controls LC and ICP-MS as a fully integrated analytical system

Agilent LC connection kit provides complete hardware connectivity



ICP-MS MassHunter software screenshot showing details of the HPLC-ICP-MS configuration

ICP-MS as an elemental detector for speciation analysis

Strengths:

- Extremely sensitive (ppt or better detection limits)
- Nearly universal elemental coverage
- Capable of isotope dilution quantification
- Compound independent response
- Excellent matrix tolerance
- Very wide linear dynamic range (9 orders of magnitude)

ICP-MS as an elemental detector for speciation analysis

Limitations:

No molecular (structural) information*

Relatively expensive

*Molecular identification needs to be established by another means:

- Retention time matching
- In parallel with molecular MS

ICP-MS is capable of compound-independent quantification – specific standards not required

Elemental response in ICP-MS is independent of the form or species of the element.

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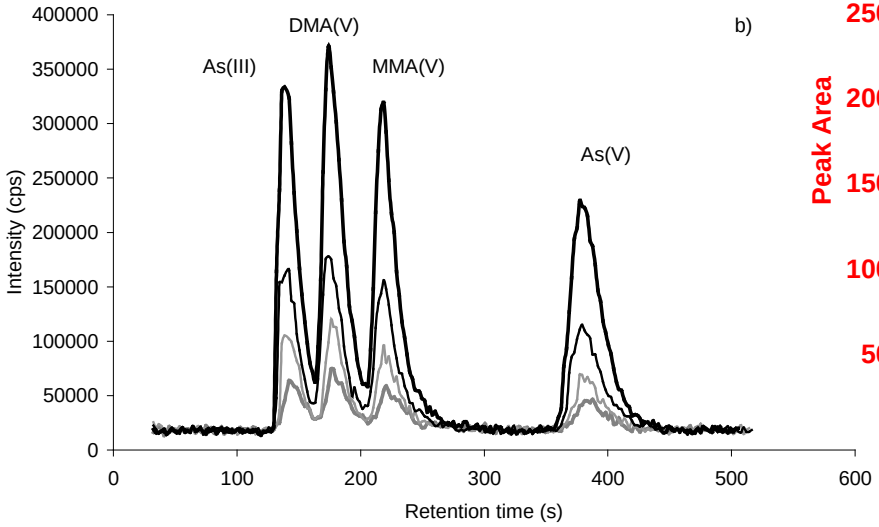
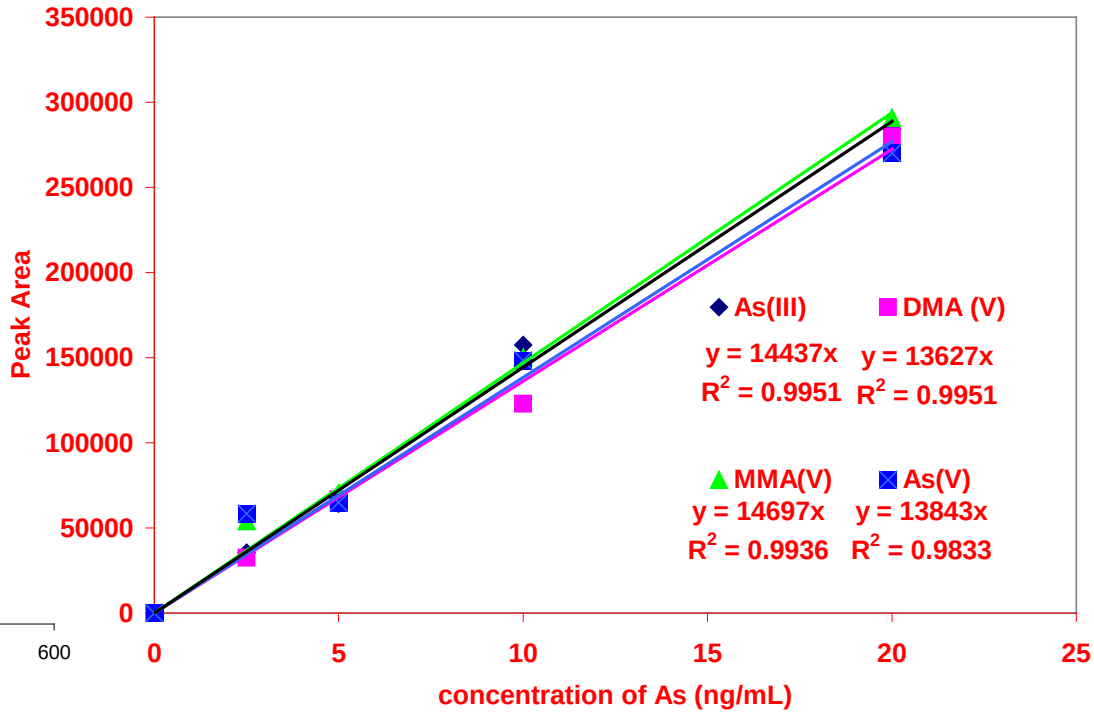




Arsenic in rice – Is it toxic, or not…

Variation in Arsenic Speciation and Concentration in Paddy Rice Related to Dietary Exposure

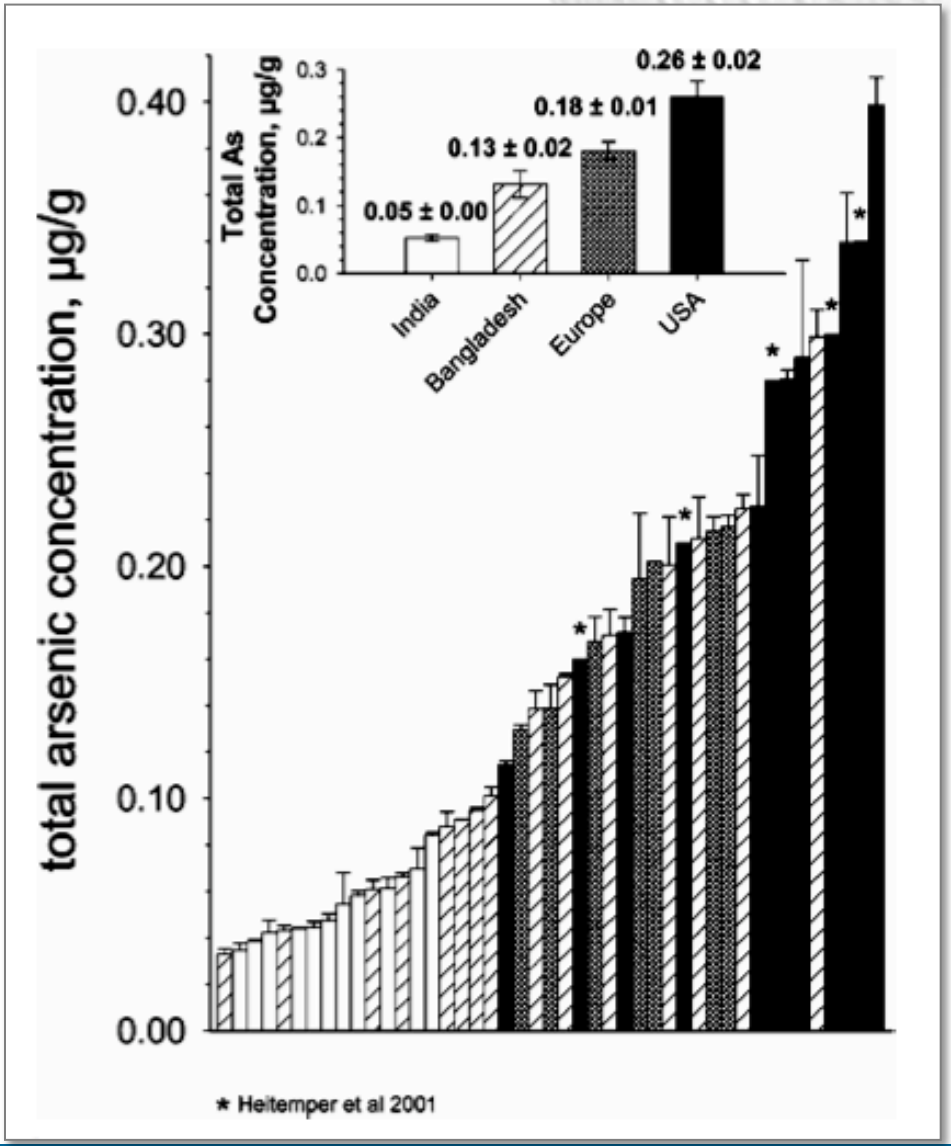
P. N. WILLIAMS,[†] A. H. PRICE,[†] A. RAAB,[‡] S. A. HOSSAIN,[†,§] J. FELDMANN,[‡] AND A. A. MEHARG*[,†]

School of Biological Sciences, University of Aberdeen, Aberdeen, AB24 3UU, UK, and Department of Chemistry, University of Aberdeen, Aberdeen, AB24 3UE, UK

"USA long grain rice had the highest mean arsenic level in the grain at 0.26 µg As g^{-1}"

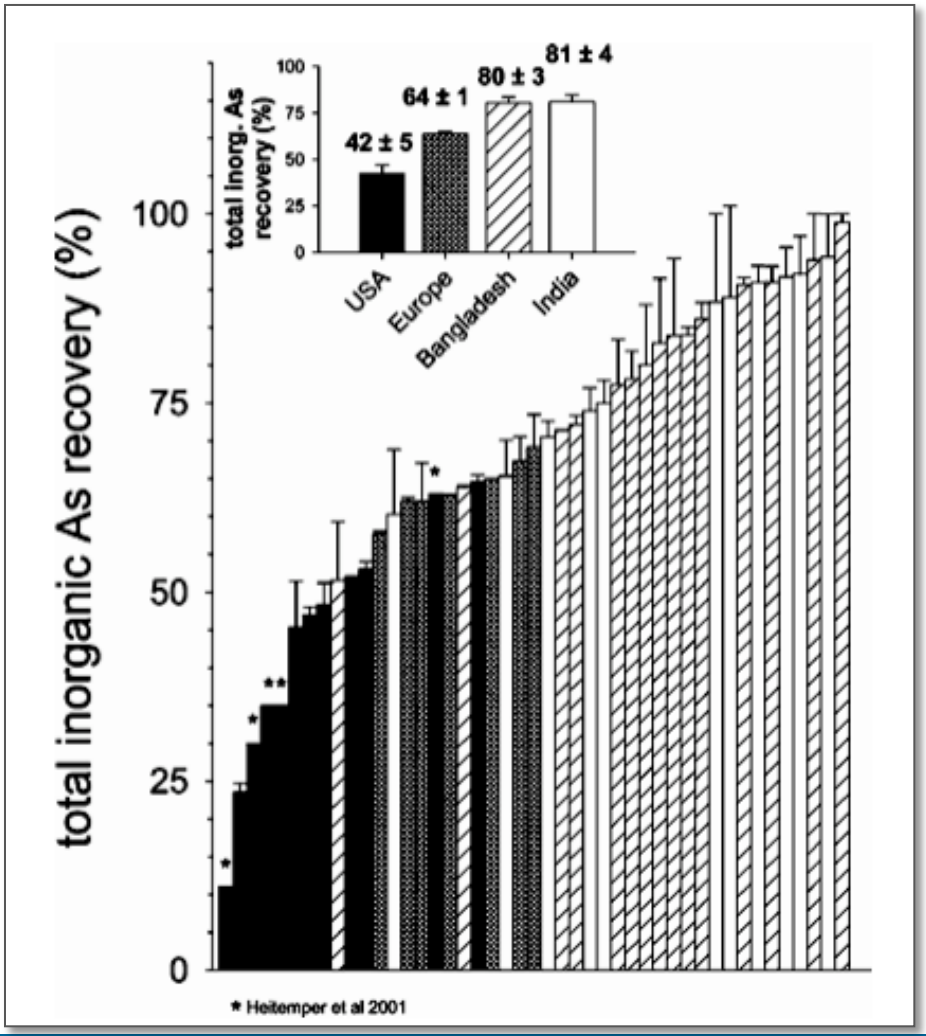
"arsenic in rice contributes considerably to arsenic ingestion in subsistence rice diets"

Williams et al ES&T 39: 2005



Arsenic speciation in rice

Percentage inorganic As in market rice.



Arsenic speciation in the grain differs between rice cultivars grown on the same soil

'genetic variation accounts for differences in uptake and speciation'

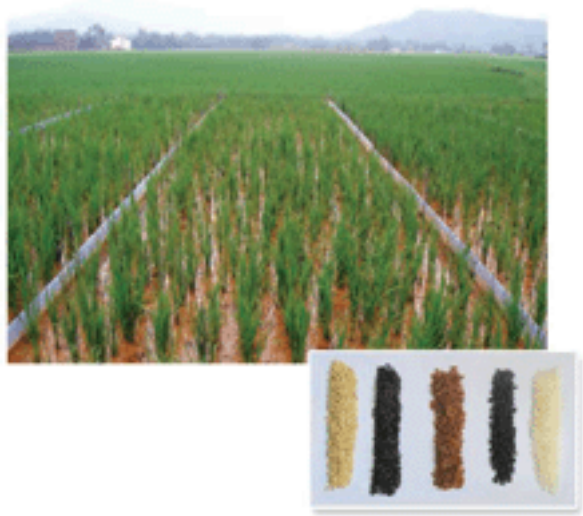
DMA is main form of arsenic in US rice: Is this legacy arsenic from DMA use as a pesticide?

Williams et al ES&T 39: 2005

Arsenic and Paddy Rice: A Neglected Cancer Risk?

- Three sets of findings reporting elevated As in rice and products such as rice bran and rice crackers
- Speciation: inorganic – oxides As^{V} and As^{III}

- China regulates As levels in food: recently reduced 'safe' level from 700 to 150 µg kg^{-1}
- US and EU have not set limits for As in food
- Rice contain 10 fold more As than wheat or other cereals



Field trials of low-As rice:
Zhu Yong-Guan's group.
Grain levels ranged from 63-421 µg kg^{-1}

Science 11 July 2008 Volume 321

Research

New Phytologist

Variation in grain arsenic assessed in a diverse panel of rice (*Oryza sativa*) grown in multiple sites

Gareth J. Norton[1], Shannon R. M. Pinson[2], Jill Alexander[1], Susan Mckay[1], Helle Hansen[1], Gui-Lan Duan[3], M. Rafiqul Islam[4], Shofiqul Islam[4], Jacqueline L. Stroud[5], Fang-Jie Zhao[5], Steve P. McGrath[5], Yong-Guan Zhu[3], Brett Lahner[6], Elena Yakubova[6], Mary Lou Guerinot[7], Lee Tarpley[8], Georgia C. Eizenga[9], David E. Salt[6], Andrew A. Meharg[1] and Adam H. Price[1]

- 300 common cultivars grown at 4 sites (China, Bangladesh, Arkansas, Texas)
- 3 – 34 fold range in arsenic concentrations within a field
- Total As strongly correlated with inorganic As for China and Bangladesh
- Cultivar was major factor determining variation in As uptake
- Year, location and flooding management also important in explaining As variation

Arsenic in food: Recent Dartmouth papers

PNAS

Rice consumption contributes to arsenic exposure in US women

Diane Gilbert-Diamond[a,b,1,2], Kathryn L. Cottingham[a,c,1], Joann F. Gruber[a,b], Tracy Punshon[a,c], Vicki Sayarath[a,b], A. Jay Gandolfi[d], Emily R. Baker[a,e], Brian P. Jackson[f], Carol L. Folt[a,c], and Margaret R. Karagas[a,b]

[a]Children's Environmental Health and Disease Prevention Center at Dartmouth, Hanover, NH 03755; [b]Section of Biostatistics and Epidemiology, Department of Community and Family Medicine, Dartmouth Medical School, Hanover, NH 03756; [c]Department of Biological Sciences, Dartmouth College, Hanover, NH 03755; [d]Department of Pharmacology and Toxicology, University of Arizona, Tucson, AZ 85721; [e]Dartmouth Hitchcock Medical Center, Lebanon, NH 03756; and [f]Trace Element Analysis Laboratory, Department of Earth Sciences, Dartmouth College, Hanover, NH 03755

Edited by Jerome Nriagu, University of Michigan, Ann Arbor, MI, and accepted by the Editorial Board October 17, 2011 (received for review June 7, 2011)

New Hampshire birth cohort

229 women gave urine sample at 6 month prenatal visit

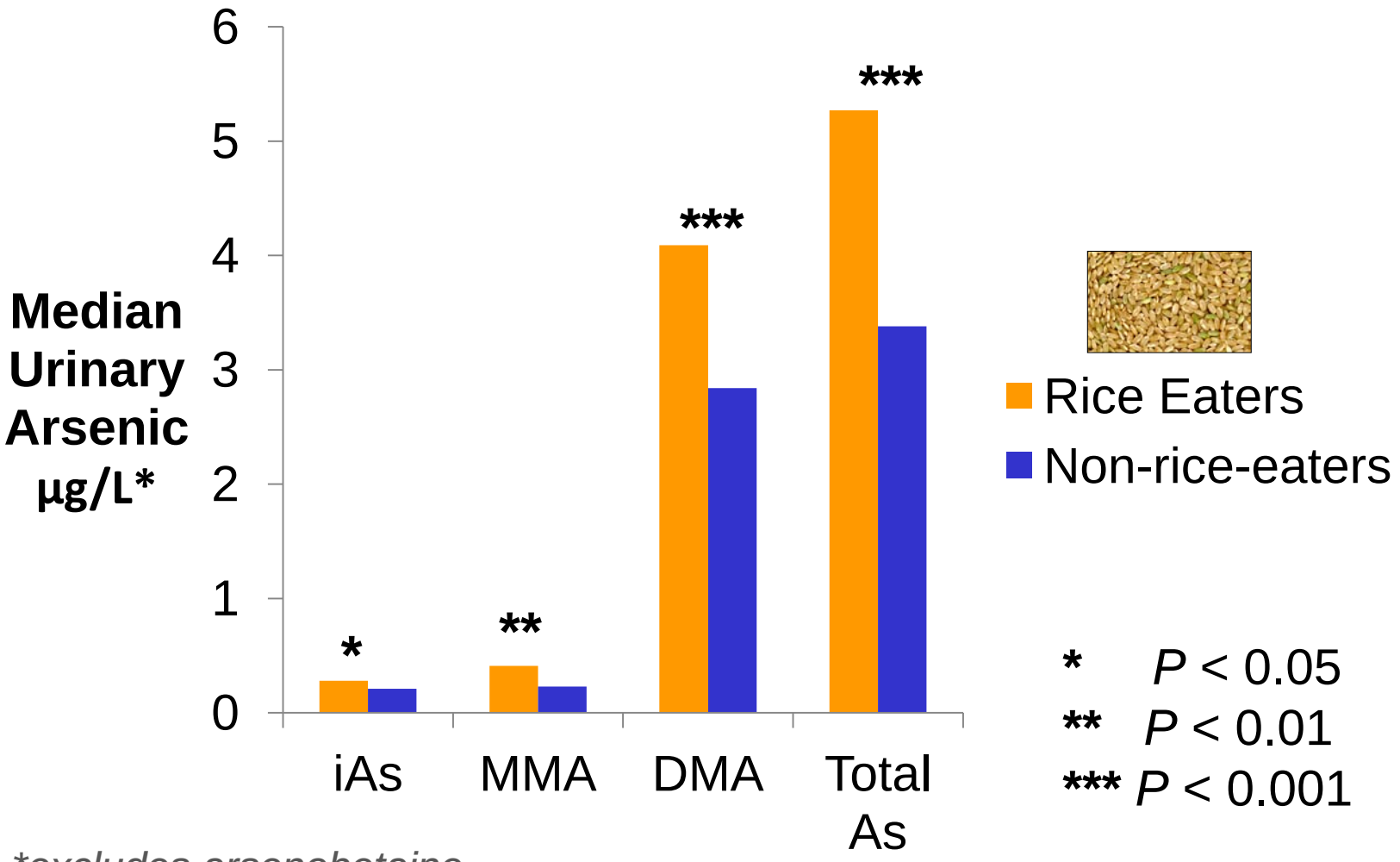
3 day dietary record.

73 women reported rice intake

Urine measured for total As and speciation

Tap water measured for As

Results of As in US Women study



*excludes arsenobetaine

Arsenic in infant formulas and first foods*

- Phone questionnaire up to 4 months
  - Formula, breastfed, both?
  - What kind(s) of formula?
  - How is formula prepared?
- Analyze As in diet items and estimate intake
- Compare to toenail As at 4 months
- Written food frequency questionnaire at 12 months
- Analyze As in diet items and estimate intake
  - First foods (stage 1)
  - Weaning foods (stage 2)
  - Use existing data for “adult” foods as needed
- Compare to toenail As at 12 months

*Pure Appl. Chem., Vol. 84, No. 2, pp. 215–223, 2012

http://medical.gerber.com/nirf/cm2/upload/25C6EA68-1933-4FC1-A14E-2242F60283AD/category_infant_purees.jpg

http://www.hechoparamama.com/wp-content/uploads/2009/10/earthsbest1-300x200.jpg

Total arsenic in 15 baby formula samples

Total As (ng g^{-1})	Dairy	contains rice starch	Speciated	species recovery	% inorganic As
5.36 ± 0.21	YES	NO	NO		
11.27 ± 0.35	NO	NO	YES	88.20%	100%
9.29 ± 0.43	NO	NO	YES	88.61%	100%
11.89 ± 0.64	NO	YES	YES	66.76%	100%
5.76 ± 0.4	YES	NO	NO		
6.95 ± 0.43	NO	NO	YES	102.84%	100%
11.43 ± 1.09	NO	NO	YES	84.25%	100%
6.02 ± 0.26	YES	YES	NO		
8.19 ± 0.63	YES	YES	YES	54.48%	100%
8.14 ± 0.77	YES	NO	YES	55.31%	100%
9.38 ± 0.31	YES	NO	YES	62.75%	100%
2.92 ± 0.33	YES	NO	NO		
9.62 ± 1.35	NO	NO	YES	77.58%	100%
3.42± 0.2	YES	NO	NO		
2.6 ± 0.44	YES	NO	NO		

Statistics

Rice starch versus no rice starch:
$p = 0.9008$

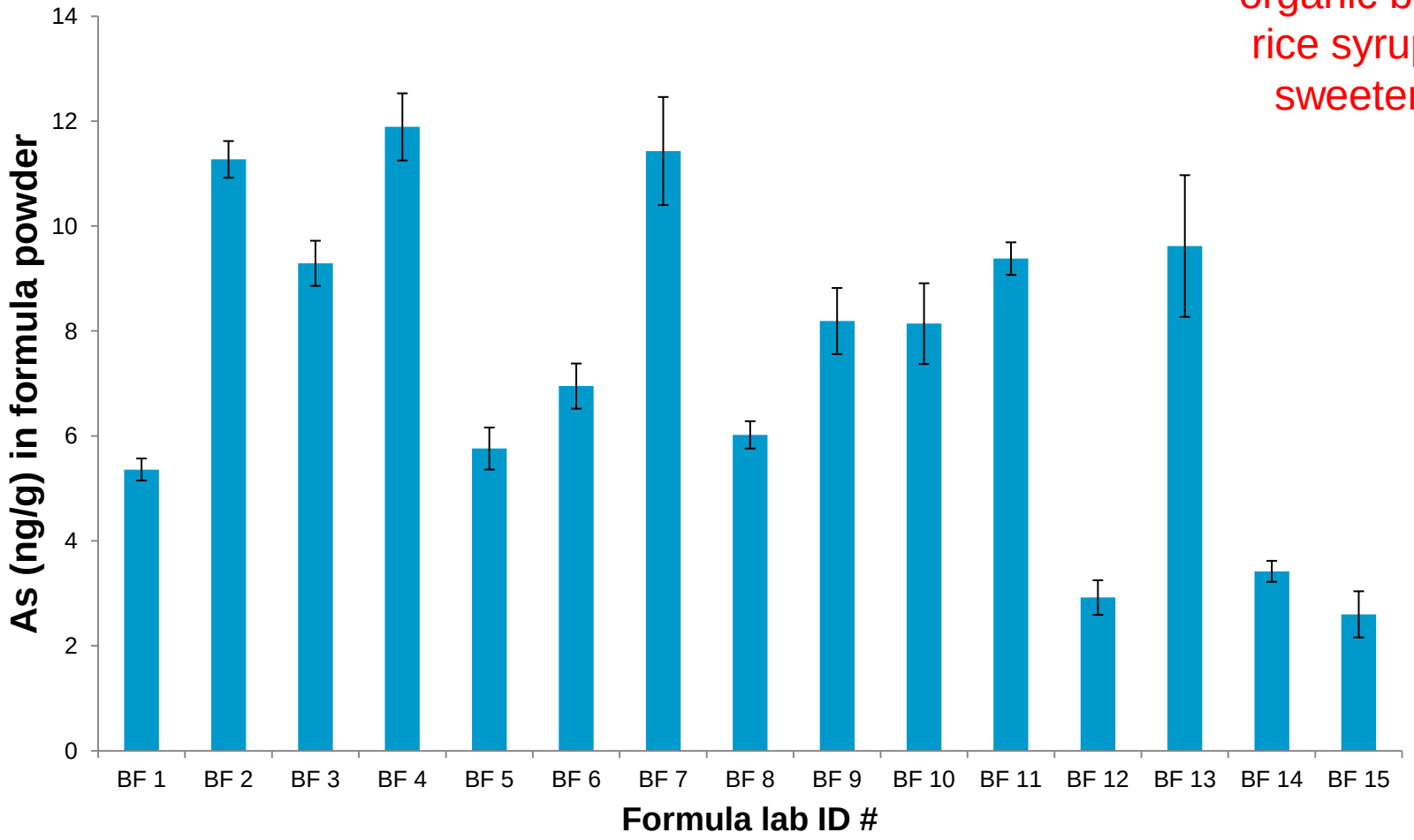
Dairy versus non-dairy:
$p = 0.015$

Reconstituting infant formula involves a 7X dilution

For water with 0 As concentration formulas will have <1 – 1.7 µg/l

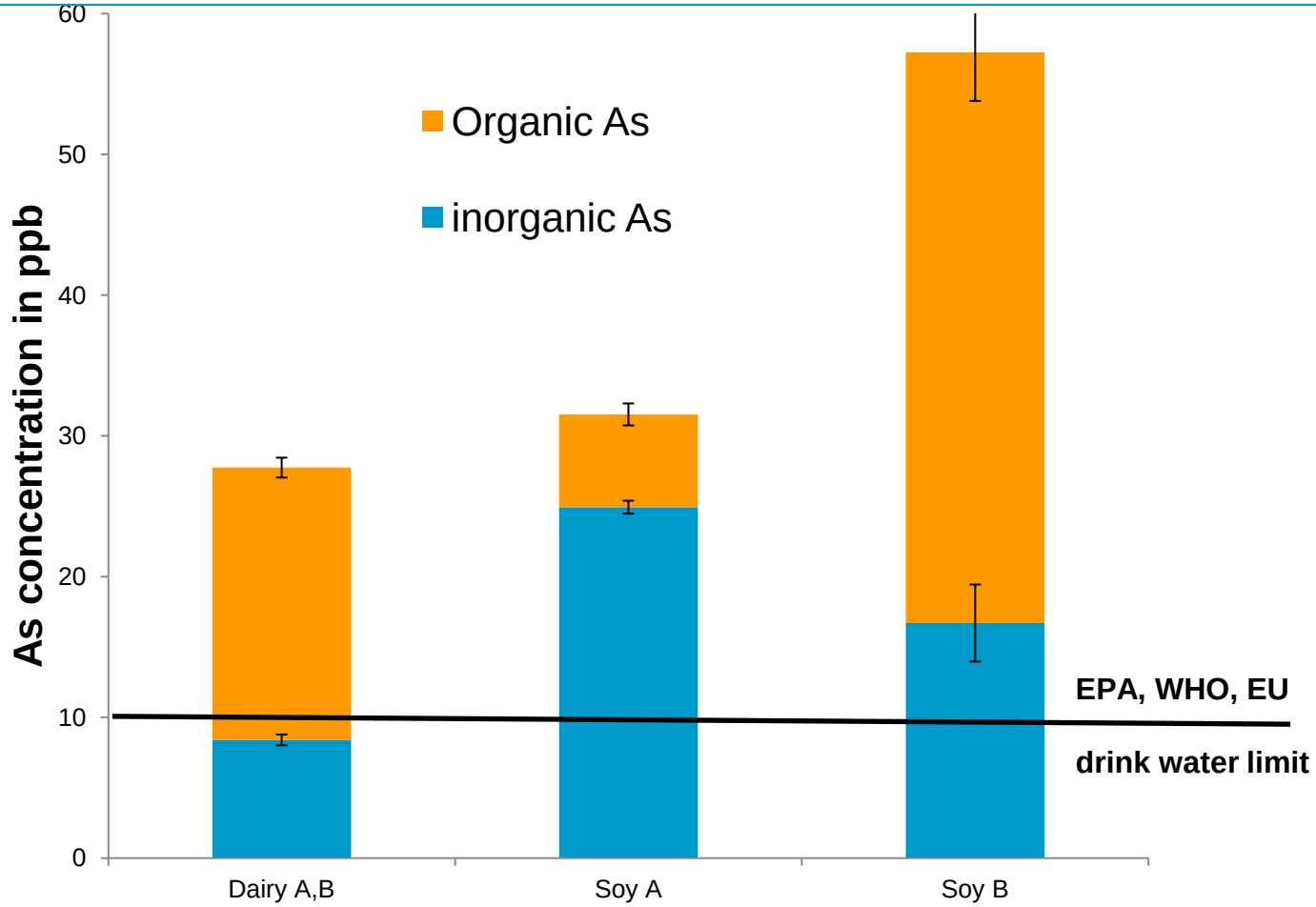
Arsenic in baby formulas

Toddler formulas using organic brown rice syrup as sweetener

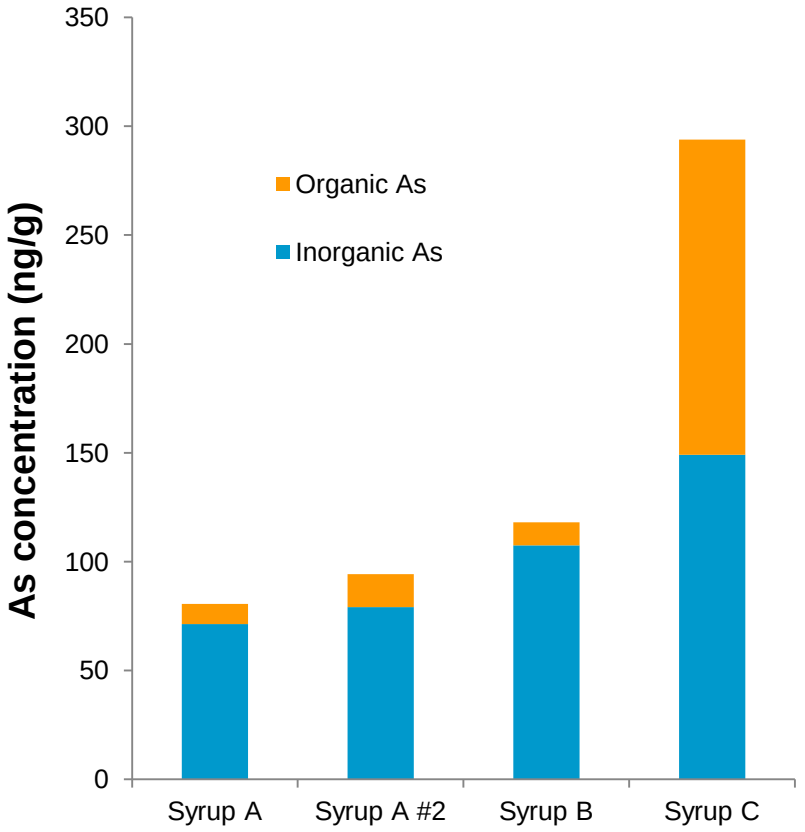


Toddler formula using brown rice syrup

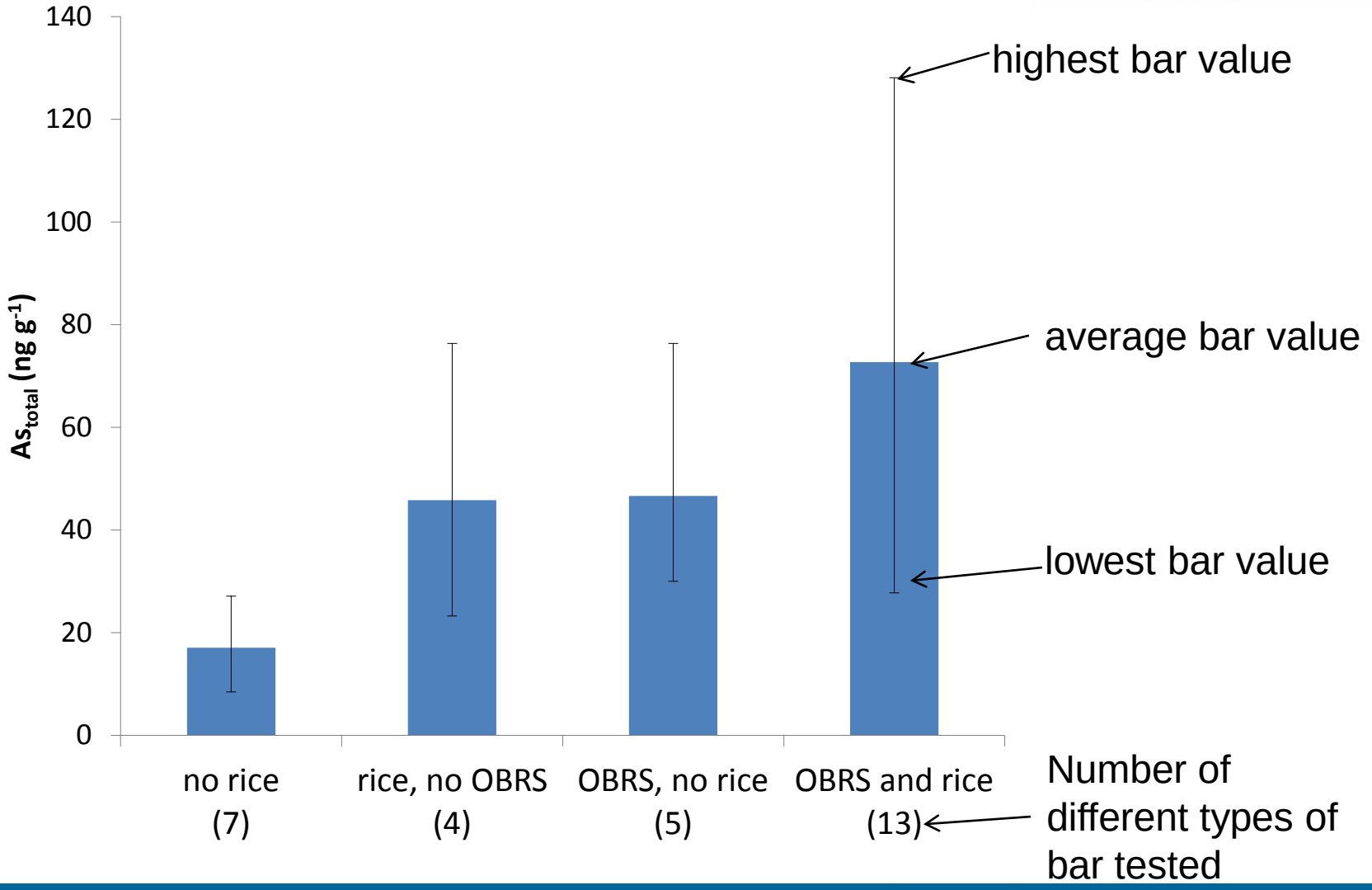
As concentration in reconstituted formula fed to baby, assumes no As contribution from water used to make formula



Organic brown rice syrups



Arsenic in cereal bars
(OBRS = organic brown rice syrup)

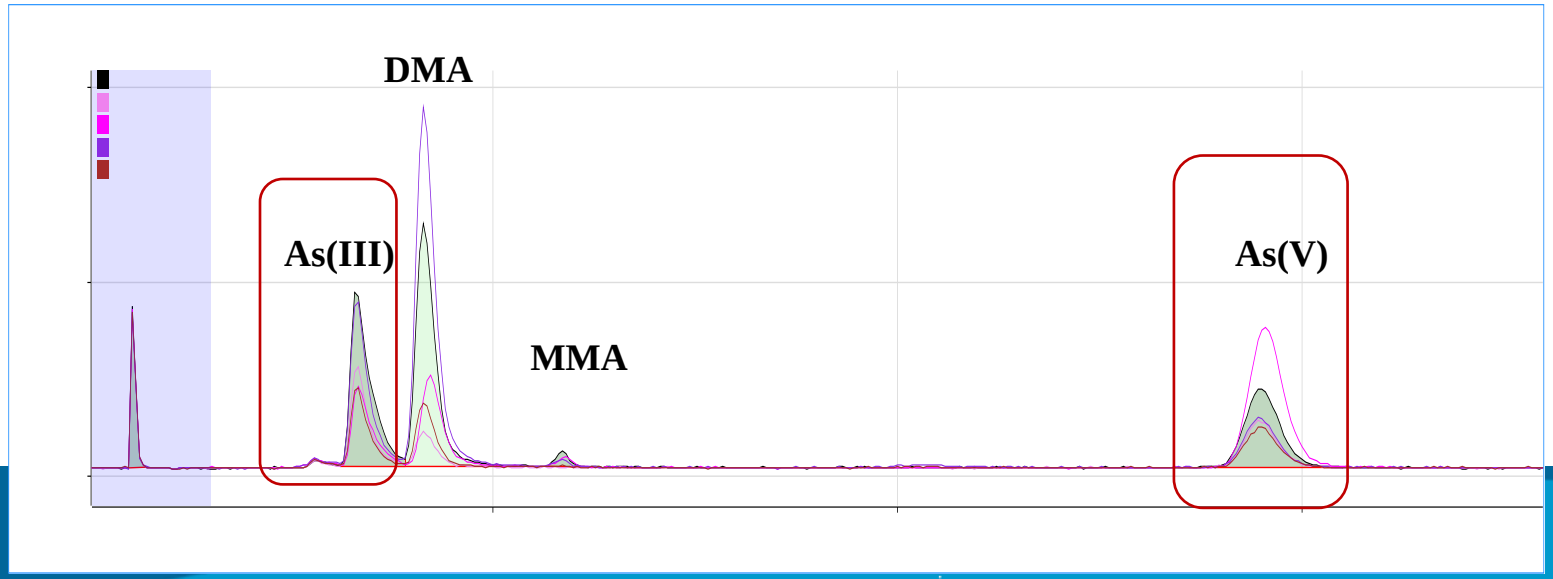


Arsenic Speciation in Infant Rice Cereals using HPLC-ICP-MS

Rima Juskelis[1] ; Katarzyna Banaszewski[1]; Jenny Nelson[2]; Jack C. Cappozzo[1]
[1]IFSH/ ITT, Bedford Park, IL; [2]Agilent Technologies, Santa Clara, CA

Innovation Through Collaboration
IFSH INSTITUTE FOR FOOD SAFETY AND HEALTH

Species	RT (min)	Sensitivity (peak area)	ASDL (ng/g)	ASQL (ng/g)	Method LOD µg/kg	Method LOQ µg/kg
75 As(III)	3.6	48162	0.03	0.26	1.7	13
75 DMA	4.4	69264	0.02	0.14	0.9	7
75 MMA	6.1	71551	0.02	0.18	1.2	9
75 As(V)	14.1	84219	0.04	0.27	1.8	14



Profiling Trace Metals in Food

Date/Time: October 9 at 11:00 a.m. EDT

Speaker: Jack Cappozzo, Director of Chemistry, Institute for Food Safety & Health at ITT

In recent years, food safety has become a major focus for the general public, food industry and government agencies. The US government has taken steps to increase food safety by implementing HACCP (Hazard Analysis and Critical Control Points) a few years back and recently passing the Food Safety Modernization Act (FSMA).

Register to Attend

THANK YOU