Analysis of Arsenic Species and Low-Level Heavy Metals in Rice

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Introduction

Rice is a staple food for vast numbers of people worldwide, and the issue of potentially toxic contaminants present in rice has recently become an extremely hot topic. There have been few studies published pertaining to the heavy metals content of rice at low parts-per-billion (ppb) concentrations, and even fewer that have evaluated the different forms of arsenic species present in rice samples. However, recently there has been a growing awareness of the need for the testing of foods for heavy metals and inorganic arsenic to ensure product safety for consumers.

For this research, a wide variety of rice samples grown in nine different countries were analyzed using a low-level methodology for four heavy metals: arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg). In addition, the samples were also analyzed for arsenic speciation by determining inorganic arsenic [As(Inorg)], arsenite [As(III)], and arsenate [As(III)] concentrations.

For all analyses, the limit of quantification (LOQ) was less than or equal to 10 ppb. Additionally, all samples were further evaluated for total metals in both the native and rinsed states, as rinsing has been reported to significantly reduce the levels of some metals in rice. The produced data was validated through the use of the NIST SRM 1568a – Rice Flour.

Preparation & Analytical Methods

Prior to analysis for As, Cd, Hg, and Pb by inductively coupled plasma – mass spectroscopy (ICP-MS) using a Perkin-Elmer ELAN DRC II, a gold and lutetium solution was added to 0.5 g aliquots of each sample for the stabilization of the mercury content (0.1 mL of a 50 mg/L solution) and then microwave-digested with 4 mL of 16 M nitric acid and 1 mL of 30% hydrogen peroxide. Digestates were diluted to a final volume of 20 mL and then diluted again 4x at the instrument.

The samples were prepared and analyzed for arsenic speciation by hydride generation – cryogenic trapping – atomic absorption spectrometry (HG-CT-AAS), as described in EPA Method 1632a, using a customized Buck Scientific AAS. Sample aliquots of 0.5 g were extracted overnight at 80 °C with 2 M HCl. Aliquots of digestate for the determination of As(Inorg) are adjusted to pH 1.5 prior to analysis, while sample aliquots for As(III) are adjusted to pH 6. Samples are then analyzed by hydride generation with $NaBH_4$ reduction, cryogenic trap precollection, H_2/air flame quartz furnace decomposition, and atomic absorption detection. As(V) is calculated as the difference between As(Inorg) and As(III) concentrations.

Microwave Digestion Parameters
(Berghof Speedwave Four)

Step	Power (W)	Temp (°C)	Pressure (bar)	Ramp Time (min)	Hold Time (min)
1	870	145	40	1	1
2	870	50	40	1	1
3	1160	145	40	1	1
4	1160	170	40	1	10
5	1160	190	40	1	10

Analytical Instrument Parameters
(PerkinElmer Elan II)

RF Power (W)	1500
Plasma Gas Flow (L/min)	17 .00
Nebulizer Gas Flow (L/min)	1.05
Analog Stage Voltage (V)	-1600
Pulse Stage Voltage (V)	800

Method Performance

For analyses by ICP-MS, limits of detection (LOD) and limits of quantitation (LOQ) were determined through the analysis of 23 method blanks. The LOD was calculated as three times the standard deviation of the results of the blanks and the LOQ was calculated as two times the value of the LOD, except where the resulting LOQ would be less than the lowest calibration standard, in which case the LOQ was set at the lowest calibration point and the LOD was calculated as 1/3 of the LOQ. All ICP-MS LODs were < 5 ppb and all ICP-MS LOQs were < 10 ppb; therefore, for ease of reporting the LODs and LOQs were raised to 5 ppb and 10 ppb, respectively. For analyses by HG-CT-AAS, LODs were determined by 40 CFR Part 136 B (8 replicate blank spikes) and LOQs were set at the concentration of the lowest calibration standard. The LODs of all three species were determined to be 4 ppb and the LOQs of all three species were set at 10 ppb.

NIST SRM 1568a – Rice Flour was prepared and analyzed in conjunction with the samples. Certified values (ppb) for As, Cd, Hg, and Pb are provided; however this material is not certified for the concentrations of different arsenic species. The "true values" of As(III) and As(V) are taken from the literature (peer-review journal articles). In order further to demonstrate method accuracy and precision, method duplicates and matrix spikes were prepared and analyzed in conjuction with the samples.

NIST SRM-1568a

Analyte	Result	True Value	Recovery
As	285	290	98%
As(III)	58	63	91%
As(V)	52	50	102%
Cd	21	22	97%
Hg	7	6	115%
Pb	6	<10	N/C

Method Spikes

Analyte	Mean Recovery	n
As	91%	5
As(Inorg)	96%	10
As(III)	70%	4
Cd	90%	5
Hg	94%	5
Pb	100%	5

Matrix Duplicates

Analyte	Mean RPD	n
As	17%	5
As(Inorg)	5%	9
As(III)	15%	4
Cd	17%	4
Hg	18%	3
Pb	28%	3

Sample Types and Results for Arsenic/Arsenic Speciation

Twenty-four rice products were selected from retail outlets in Seattle, Washington (*Safeway, Fred Meyer, Trader Joe's*, and *Uwajimaya*). In addition, one sample was obtained from a grocery store in Shanghai, China. All results were corrected for the mean concentration of the method blanks, are reported on an as-received basis (not a dry weight basis), and are provided in units of parts per billion (ppb).

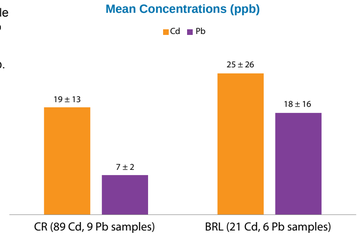
ID	Type of Rice	Origin	As	As(Inorg)	As(III)	As(V)
1	White, Jasmine, Long Grain, Organic	USA (Texas)	395	115	96	19
2	Brown, Long Grain	USA	216	155	92	63
3	White, Short Grain, Sweet	Japan	128	81	64	17
4	White, Jasmine, Long Grain	Thailand	138	81	66	15
5	Red, Himalayan	Nepal	168	88	59	29
6	White, Basmati, Long Grain	India	46	32	22	10
7	Brown, Tinawon Heirloom	Philippines	81	90	55	35
8	Brown, Organic	Taiwan	176	153	104	49
9	White, Long Grain, Enriched	USA	195	106	64	42
10	Red	China	105	107	55	52
11	White, Arborio	Italy	96	67	53	14
12	White, Jasmine, Long Grain, Organic	Thailand	112	80	62	18
13	White, Extra Long Grain, Enriched	USA (Texas)	230	104	65	39
14	Brown, Whole Grain	USA	94	73	60	13
15	White, Medium Grain, Enriched	USA	241	156	76	80
16	White, Jasmine	Thailand	108	85	65	20
17	White, Basmati	India	69	65	55	10
18	Brown, Jasmine	Thailand	176	136	94	42
19	Brown, Basmati	India	125	110	64	46
20	White, Arborio	Italy	146	115	87	28
21	Black	Thailand	187	159	105	54
22	White, Medium Grain, Silver Pearl	USA	103	62	52	10
23	White, Medium Grain, Calrose	USA	113	78	69	9
24	White, Basmati	India	40	34	35	< 4
25	White, Short Grain	China	145	83	60	23

Results for Cadmium, Lead, and Mercury

Of the 25 samples analyzed, 21 had detectable levels of Cd, 6 had detectable levels of Pb, and only 3 had detectable levels of Hg (greater than or equal to the LOD).

- Of the Cd results, 14 exceeded the LOQ and ranged from 11 – 106 ppb.
- Of the Pb results, only 3 exceeded the LOQ and ranged from 12 – 43 ppb.
- None of the Hg results exceeded the LOQ.

The Cd and Pb results from this study (BRL) were compared to the results from a very recent study published by the magazine Consumer Reports (CR) that also had numerous rice samples analyzed for heavy metals. In the CR Study of 91 samples, 89 had detectable levels of Cd while only 9 of the samples had detectable levels of Pb. The mean concentrations of both studies are compared in the adjacent chart.

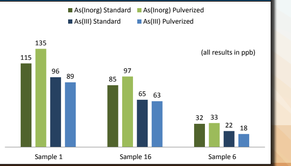


Pulverizing to Improve Extraction Efficiency

To evaluate the effect of sample pulverization on the extraction efficiency for arsenic species, additional aliquots of three of the rice samples were ground to a fine powder in a ball mill prior to digestion.

The resulting data comparison indicates that sample pulverization could have an overall effect of improving the extraction of the As(Inorg) from the sample by as much as approximately 20%.

However, a similar increase in the results for the pulverized samples was not found when the samples were analyzed for As(III).

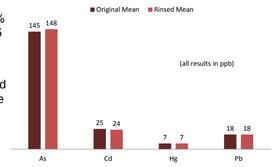


Rinsing to Remove Contaminants

Several researchers have reported that rinsing raw rice thoroughly may remove up to 10-28% of the arsenic content. To evaluate the effect of rinsing of rice prior to sample digestion, all 25 samples were prepared both rinsed and un-rinsed.

Approximately 100 g of rice was placed in a 1-L HDPE jar, and 800 mL of reagent water was added to each jar. The jars were capped and swirled to mix, and then the water was decanted from each jar. This rinsing procedure was repeated two additional times for each sample. The jars were placed uncapped in an oven set at 85 °C to dry the rice.

There was no significant difference in the results between the rinsed and unrinsed rice samples. Results that were less than the LOD were omitted when calculating the mean results adjacent.



Comparisons to FDA and Consumer Reports Data

The results from this study (BRL) were compared to the rice results from two recent studies published by the US Food and Drug Administration[1] (FDA) and the magazine Consumer Reports[2] (CR). The mean total and inorganic arsenic results from our study compare well with the results from the FDA and CR studies.

Our results were lower overall, but this is likely due to the high number of samples in our study from outside of the US.

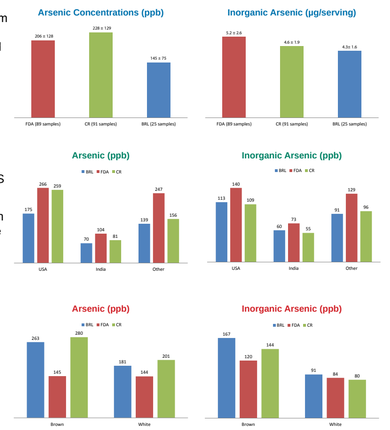
When comparing the mean total and inorganic arsenic results from the USA, India, and other countries, the BRL data confirmed the trend that rice from USA is about 2-3 times higher than rice from India. The mean of the data from other countries were generally lower than the US means for all three studies.

When comparing the mean total and inorganic arsenic results for brown rice versus white rice, the BRL data confirmed the trend that brown rice is higher in total and inorganic arsenic.

For the purpose of this comparison, data for cooked (parboiled) and instant rice was omitted as this process will lower arsenic content. In addition, data in the CR Study report for blind duplicates was omitted. Data for wild rice from the FDA Study was also omitted, as wild rice is not really a rice.

1. "Arsenic in Rice: Full Analytical Results from Rice/Rice Product Sampling - September 2012"(released on 09/19/2012) http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Metals/ucm319916.htm

2. Arsenic in your food: Our findings show a real need for federal standards for this toxin, Consumer Reports Magazine, November 2012 (released on www.ConsumerReports.org on 09/19/12 http://www.consumerreports.org/cro/arsenic1112.htm)



Conclusions

Brooks Rand Labs' methods for the determination of heavy metals (As, Cd, Hg, and Pb) and different arsenic species have produced reliable, accurate, and precise data for concentrations in rice samples.

Our data indicates that pulverizing the rice samples may increase the extraction efficiency of inorganic arsenic by up to 20%; however, this result is inconclusive based on the limited sample set and variability of the observed results. Rinsing the samples with cool water was not shown to have any effect in lowering heavy metals contaminants.

While regulations on the levels of these metals in foods are not yet established, the European Union (EU) has established a maximum level of Cd in food at 200 ppb, China has set a maximum level of inorganic arsenic in rice at 150 ppb, and the World Health Organization and the EU are discussing a limit of 200 ppb for inorganic arsenic in white rice.

While none of the samples tested in this study revealed concentrations of Cd, Pb, or Hg that would be considered above current levels of concern, several of the samples contained levels of inorganic arsenic that could exceed proposed regulations, demonstrating the need for robust and reliable analytical methods.