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2014 Brooks Applied Labs (Formerly Brooks Rand Labs) International Interlaboratory Comparison Study for Arsenic Speciation in Food

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Introduction

The Brooks Applied Labs (formerly Brooks Rand Labs) International Interlaboratory Comparison Study for Arsenic Speciation in Food was initiated in 2013 to provide a reliable means for laboratories to evaluate their competency in the analysis of arsenic species in these matrices, as well as a metric for assessing the intercomparability of data generated by different laboratories and methods. In its second year, this study continued to be one of the largest interlaboratory comparison studies for arsenic speciation in food conducted. This report summarizes where the methods are successful at providing reproducible data and where more research and method development is needed. As demonstrated by the data, this kind of comparison study is vitally important for establishing and maintaining best practices for the arsenic speciation analyses of food and supplements.

The 2014 study again used white rice flour as one of the study materials, but also introduced some more complex matrices including a seasoned seaweed snack, cocoa powder, fin fish muscle tissue (tuna), and shellfish tissue. Participants were asked to analyze the samples for arsenic (As) species using the methods that are commonly used in their laboratory. Participants were asked to report results for as many of the following analytes as possible, based on their analytical methodology: total As in the sample, total As in the speciation extract, inorganic As, and dimethylarsinic acid (DMAs). Participants were asked to measure and report the total arsenic concentration in the sample and in their speciation extract for the purpose of determining extraction efficiency. A sufficient number of participants reported results for monomethylarsonic acid (MMAs) and arsenobetaine (AsB) to allow for most probable values (MPV) to be calculated for these parameters as well. Only participants who reported at least one result for at least one arsenic species (i.e., not just total arsenic) were included in this study report. Lab 26 did not report any speciation results; therefore, their data was omitted from this report.

Some of the key features of the study were a broad invitation to join; a large group of participating laboratories from around the world; anonymous data submission, analysis, and reporting; and the inclusion of analytical method reporting. A small participation fee was collected to cover the cost of materials and shipping to participants, and additional funding or materials were provided by several study sponsors. Thirty laboratories from ten countries registered to participate and were sent the study materials, and twenty-nine datasets were received from twenty-eight different laboratories (one laboratory submitted two different datasets

from different departments within their organization). By requesting laboratories to report detailed information about their analytical methods, this study was again able to assess the efficacy of specific protocols, reagents, and equipment.

Methods

Sample Collection and Distribution

Five different study materials were sourced: white rice flour, a seasoned seaweed snack, cocoa powder, fin fish muscle tissue, and shellfish tissue. All materials were sourced and homogenized by Brooks Rand Labs, and subsequently screened for an acceptable total As concentration of greater than 5 parts-per-billion (ppb), or µg/kg.

Sample 1: Cocoa Powder

Cocoa powder mixed with alkalized cocoa powder was purchased commercially on-line by Brooks Rand Labs. Each participant was sent approximately 20-25 g of sample. Screening data indicated the total As content to be approximately 50 µg/kg and the percent moisture to be < 5%.

Sample 2: Fin Fish Tissue

The fin fish tissue was a certified reference material (CRM) for tuna fish. Dried, homogenized, and sterilized tuna fish muscle tissue is offered as CRM BCR-627 by the Community Bureau of Reference (BCR), the former reference materials program of the European Commission. The certificate has been revised under responsibility of the Institute for Reference Materials and Measurements (IRMM). Each participant was sent approximately 3 g of sample. This CRM has certified values for total As (4800 µg/kg), DMAs (150 µg/kg), and AsB (3896 µg/kg). Screening data indicated the percent moisture to be less than 15%.

Sample 3: Seasoned Seaweed Snack

The seasoned seaweed snack was purchased commercially on-line by Brooks Rand Labs. The seaweed product is roasted, lightly salted, and contains corn oil, grapeseed oil, and sesame oil. The seaweed was ground to a homogenous paste and well homogenized prior to distribution. Each participant was sent approximately 20-25 g of sample. Screening data indicated the total As content to be approximately 10,000 – 20,000 µg/kg and the percent moisture to be < 5%.

Sample 4: Shellfish Tissue

Geoducks (*Panopea generosa*) from the Puget Sound in Washington State, USA, were donated to Brooks Rand Labs by Taylor Shellfish Farms (Shelton, WA). Geoducks are a species of very large, edible, saltwater clams. Upon receipt at Brooks Rand Labs, the geoducks were shucked, frozen, and shipped to Apex Lyo, Inc. (Eugene, OR) for freeze-drying. The lyophilized tissue was returned to Brooks Rand Labs for homogenization. Each participant was sent approximately 15 g of sample. Screening indicated the total As content to be approximately 5,000 – 10,000 µg/kg and the percent moisture to be < 10%.

Sample 5: Rice Flour

The rice flour was a standard reference material (SRM) provided by the National Institute of Standards and Technology (NIST) – NIST SRM 1568b. The rice flour was produced from 100% long grain river rice grown in Arkansas. Each participant was sent approximately 5 g of sample. This CRM has certified values for total As (285 µg/kg), inorganic As (92 µg/kg), DMAs (180 µg/kg), and MMAs (11.6 µg/kg). Screening indicated the percent moisture to be < 10%.

All homogenized intercomparison study samples were placed in 20-mL borosilicate glass vials. Vials were pre-tested and found to be from a lot that was low in total arsenic concentration. Vials were labeled, individually double-bagged in zip-type bags, and stored in cardboard shipping boxes.

Samples were shipped to the participating laboratories during the week of August 4, 2014. Participating laboratories were asked to analyze samples for total arsenic and arsenic species as previously described in accordance with their standard operating procedures, and were given no further guidance on analytical methodology. All results were originally requested to be reported by Tuesday, September 30, 2014, approximately 7 weeks after participants first began receiving samples; however, based on requests from some study participants, this deadline was extended to Sunday, October 5, 2014.

All results were reported to an independent third party, EcoChem, Inc. (Seattle, Washington, USA), a data validation company who had no role in the study other than data management. At EcoChem, the dataset was compiled, and a unique identifier was assigned to each laboratory, before it was transmitted to Brooks Rand Labs. Concurrent with delivery of this report, each participating laboratory received an e-mail containing their own unique identifier, but identifiers

were not disclosed to any other parties, including Brooks Applied Labs. This research design ensured there would be no bias by the preparers of this report against any participating laboratory and that participants could submit data with the comfort of anonymity.

Data Analysis and Calculations

Each laboratory was asked to report an analytical result, detection limit, and date analyzed for each sample and analyte. These data are the basis of the calculated most probable values (MPV) and scores in this report. In addition, each laboratory reported information on sample preparation, analytical methodology, and equipment. These data were used to compile assessments of the performance of various analytical methods, but were not used in laboratory scoring.

Due to the large number of results that were reported below the laboratories' detection limit (non-detects), statistical data analysis for the calculation of the MPVs for applicable analyte/matrix combinations was performed using the Kaplan–Meier method (**Ref. 1**), calculated with the Non-detects and Data Analysis (NADA) Cenfit method of the software program R (**Ref. 2**). This method was chosen because it more appropriately takes non-detects (data censored to the detection limit) into account, rather than just omitting them. The Cenfit method computes an estimate of median for censored data using the Kaplan-Meier method as the nonparametric maximum likelihood of the MPV without assuming any specific distribution.

Statistical data analysis for the calculation of laboratory scores was performed following the method favored by the United States Geological Society's Standard Reference Sample Project (**Ref. 3**). Data are evaluated using nonparametric statistics (**Ref. 4**). This statistical approach was chosen because it is resistant to undue influence of outliers on the median.

The absolute z-value for each result is calculated using the following equations:

$$Z = |(X-M)|/F$$

and

$$F = Q/1.349$$

Where:

Z = absolute Z-value assigned to each result for the purpose of assigning a rating

X = reported value

M = median value reported by all laboratories (excluding values below the reported detection limit)

F = F-pseudosigma (approximates the standard deviation of traditional statistics when the data has a Gaussian distribution); calculated by dividing the interquartile range (or fourth-spread) by 1.349. The 1.349 value is derived from the number of standard deviations that encompasses 50% of the data.

Q = Interquartile range (the difference between the first quartile and third quartile of a set of data)

Participating laboratories were requested to report undetected values as being less than their detection limit. If a value was less than that laboratory's reported detection limit, then that value was omitted and the "u" qualifier was added. For these samples, performance was not rated unless the laboratory's detection limit was less than the MPV (potential false negative) and has a z-value greater than 2. In this case, the laboratory would receive a rating of 0 for that analyte.

In order to assign a score to each laboratory's performance, ratings were assigned based on each laboratory's absolute Z-value for each analyte, as listed in **Table 1**.

Table 1. Descriptions of ratings assigned to each result based on the calculated absolute Z-value.

Rating	Absolute Z-value
4 (Excellent)	0.00 – 0.50
3 (Good)	0.51 – 1.00
2 (Marginal)	1.01 – 1.50
1 (Poor)	1.51 – 2.00
0 (Unacceptable)	Greater than 2.00

Scores were not assigned if the overall number of data points (omitting values that were less than the reported detection limit) was less than seven or when the calculated F-pseudosigma value (F) was greater than the median value (M).

Results

The results reported by each laboratory for each of the material types can be found in Appendix A, along with the MPV, median value (M), mean value, F-psuedosigma (F) value, and number of laboratories reporting results above their detection limit (n) for each parameter. If a laboratory reported a potential false negative (result reported is less than the detection limit and the detection limit is less than M), then the rating of "0" is highlighted in red. If the data is not scored due to the F value being greater than the M value, then the F value is highlighted in red. If the data is not scored because the n value is less than 7, then the n value is highlighted red.

The MPV values for each parameter are listed in **Table 2**. Values highlighted in red were associated with F values that were greater than the M values; therefore, the variability in the data was too high. In addition, datasets with less than seven results were considered too small to use the M value as a consensus value for the purpose of scoring the individual laboratories' results.

Table 2. Summary of Most Probable Values (MPV) for each parameter for each study material.

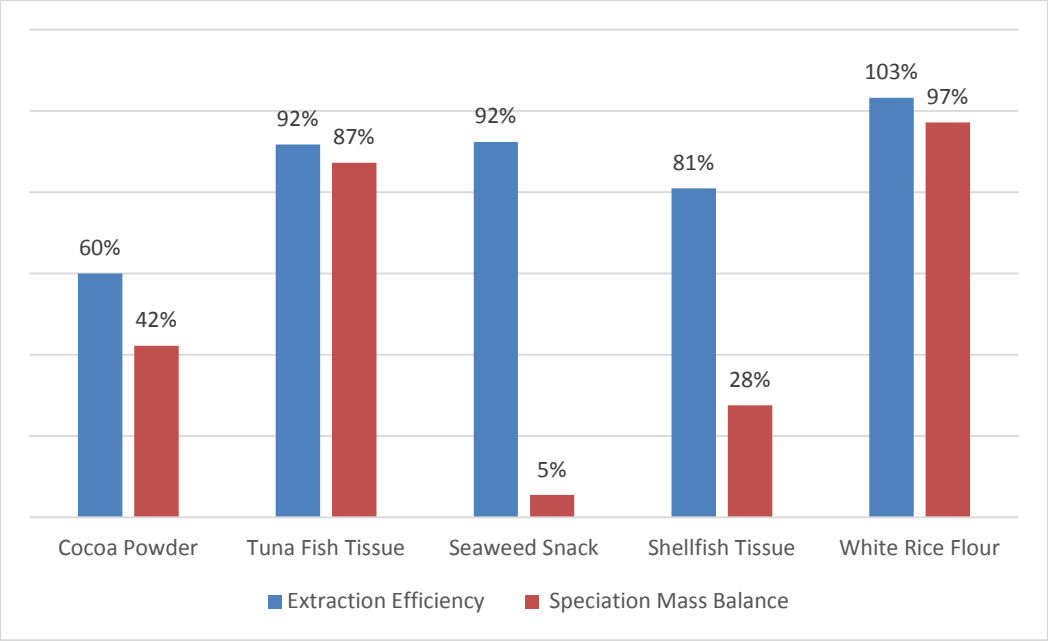
Matrix	Inorg As (µg/kg)	MMAs (µg/kg)	DMAs (µg/kg)	AsB (µg/kg)	Total As in Sample (µg/kg)	Total As in Extract (µg/kg)
Cocoa Powder	19	ISD	ISD	ISD	45	27
Tuna Fish Tissue	39	6.1	140	4000	4800	4400
Certified Values	-	-	*150*	*3896*	*4800*	-
Seaweed Snack	11	ISD	140	560	13000	12000
Shellfish Tissue	120	11	640	1100	6800	5500
White Rice Flour	110	11	180	ISD	310	320
Certified Values	*92*	*12*	*180*	-	*285*	-

ISD = insufficient data for calculation of the MPV

In order to assess the extraction efficiency of the sample preparation method used for the speciation analyses of each sample, laboratories were asked to measure the total arsenic concentration in both the sample and the speciation extract. The total arsenic extraction efficiency was then calculated by dividing the MPV result for total arsenic in the extract by the MPV result for total arsenic in the sample. Most of the participating laboratories complied with the request and sixteen datasets were submitted with results for at least one sample for both total As in the sample and in the speciation extract.

The extraction efficiencies and mass balance calculations based on MPV's for all intercomparison samples are shown in **Graph 1**. The average extraction efficiency for all results reported for the solid samples was 86%. However, the performance of the different extraction procedures varied significantly between laboratories. The speciation mass balances in Graph 1 clearly demonstrate the need to develop additional and more effective extraction methods to be used for diverse matrices.

Graph 1. Speciation Extraction Efficiency by Sample



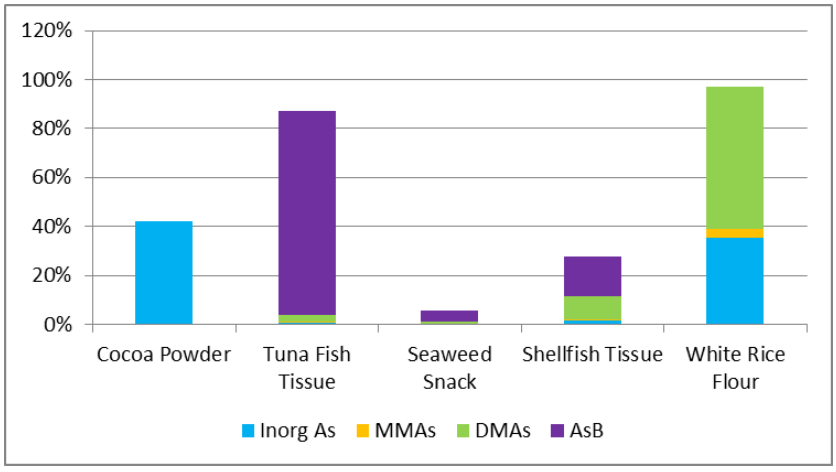
The majority of the laboratories that reported results for both total arsenic in the sample and total arsenic in the extract used some form of nitric acid extraction method. Many of these laboratories followed the procedure described by the FDA (EAM 4.11). With the exception of the highest and the lowest values, all extraction efficiencies for samples prepared with a nitric acid extraction method were between 75-110%. In contrast, extraction efficiencies for samples prepared with a methanol based extraction were typically higher (89% and 94%). The two methanol extractions were considerably different with regards to both time (1 hour and 16 hours) and temperature (ambient and 37 ^{o}C, respectively). The extraction efficiencies were excellent and within experimental error from each other indicating the selection of extraction solutions played a key role in the performance of the approach. Laboratories 08 and 11 applied HCl as the extraction

solution which yielded a similar spread of results as compared to the nitric acid approach (96% and 129%). The extraction temperature, heating method, concentration of HCl, and inclusion of peroxide during extraction did not have an appreciable impact on the extraction efficiency for the two laboratories using HCl as the extraction solution which indicates, as with the methanol extractions, the selection of extraction solutions played a key role in the performance of the approach.

In reviewing the detailed descriptions of the sample preparation methods provided by the laboratories, nearly all variables associated with an extraction method varied significantly. Laboratories 05, 06, 09, 10, 12, 13, 19, 23, and 28 referenced FDA Method 4.11 as the extraction method; however, the temperature, inclusion of peroxide, method of heating (hotblock or microwave), and application of a buffering agent were different between most laboratories.

The MPV arsenic speciation results as a fraction of the MPV total arsenic in the samples are shown in **Graph 2**. The mass balance (sum of arsenic species divided by the total arsenic results) for the cocoa powder averaged 42% with inorganic arsenic as the predominant arsenic species. The range of mass balance varied significantly between laboratories (26% - 97%). The average mass balance for extractions applying nitric acid was 47% indicating the extraction solution was incompatible with the sample matrix. The highest mass balance for the cocoa powder was achieved by Laboratory 22 (97%); however, the extraction method was listed as “other” which negates the possibility of correlating extraction solutions and conditions to the results.

Graph 2. Arsenic Speciation Results as a Fraction of the Total Arsenic Calculated from the MPVs



The overall mass balance for the tuna fish tissue was excellent (87%) throughout the laboratories. The mass balance for eight laboratories (Laboratories 01, 02, 03, 08, 11, 16, 18, 20) was below 10%. The low mass balances are attributed to the limited species that were reported (total inorganic arsenic). The majority of arsenic associated with the tuna fish tissue was arsenobetaine, which explains the low mass balances.

The seaweed snack sample resulted in the lowest mass balance out of all of the intercomparison samples (5%). The low recoveries are attributed to the limited number of arsenic species that were reported for calculating the mass balance (arsenite, arsenate, MMAs, DMAs, and AsB). As part of the intercomparison study laboratories were also requested to report unidentified arsenic species. When taking all other arsenic species into consideration the average mass balance increases to 53% with four laboratories reporting a mass balance of greater than 90% (Laboratories 12, 17, 22, 23). Certain sources of seaweed have been documented to contain copious amounts of arsenosugars. When arsenosugars and unidentified arsenic species are not taken into consideration for organisms with more complex metabolic systems low mass balances are to be expected.

For the shellfish sample the MPV sum of species totaled 28% of the total arsenic MPV. As stated above, the low recoveries are attributed to the limited number of arsenic species that were reported for calculating the mass balance (arsenite, arsenate, MMAs, DMAs, and AsB). When taking all other known arsenic species into consideration the average mass balance increases to 38%. When the additional unknown arsenic species are taken into consideration, as reported from two laboratories, the mass balance is greater than 80% (Laboratories 17 and 22). Additional arsenic species such as tetramethylarsonium, arsenocholine, trimethylarsine, arsenosugars, and multiple unknown arsenic species have been documented to be present in shellfish, which the low mass balances may be attributed to (**Ref. 5**).

For the white rice flour sample, the sum of the MPV arsenic species totaled 97% of the arsenic as compared to the MPV total arsenic concentration. The white rice flour was a NIST certified reference material and was primarily composed of carbohydrates. The simplicity of the sample matrix makes it more amenable to higher extraction efficiencies. Few certified reference materials are available for arsenic speciation analyses, making this CRM a likely candidate for

laboratories offering or pursuing arsenic speciation analyses to use for the purpose of method development and validation processes.

Discussion

Participation

A similar distribution of participating labs from North America, Europe, and other countries was encountered as compared to the 2013 study, as can be seen in **Table 4**.

Of the 30 laboratories that registered to participate in this study, 29 received the study materials. Of the 29 laboratories that received the study materials, 28 of them reported results. The list of the participating laboratories can be found in **Table 3**.

Of the participating laboratories, only 6 datasets included all of the requested parameters in every material type (laboratory numbers 04, 12, 14, 15, 17, 19, 22, and 23). Approximately 40% of the datasets (12 of 29) did not report results for both total arsenic in the sample and total arsenic in the extract; therefore, extraction efficiencies for those laboratories could not be calculated. All laboratories reported at least one total arsenic value for the extract or sample.

Table 3. Participants in the 2014 Brooks Applied Labs Interlaboratory Comparison Study for Arsenic Speciation in Food

Laboratory Name	**Country**
ALS Technichem (M) SDN BHD	Malaysia
Applied Speciation	USA
Brooks Rand Labs (now Brooks Applied Labs)	USA
BRUKER FRANCE	France
California Department of Public Health, Food & Drug Laboratory	USA
Canadian Food Inspection Agency (CFIA)	Canada
Cawthron Institute	New Zealand
Certified Laboratories, Inc.	USA
Dartmouth College	USA
Eurofins Central Analytical Laboratories	USA
Eurofins Frontier Global Sciences, Inc.	USA
Food and Drug Administration, Kansas City Laboratory	USA
GALAB Laboratories GmbH	Germany

Lakehead University Environmental Laboratory	Canada
Minnesota Dept of Agriculture, Lab Services Division	USA
MSE, Inc.	USA
National Food Agency, Sweden	Sweden
National Institute of Nutrition and Seafood Research	Norway
Nestle Quality Assurance Center, Singapore	China
New York State Dept of Agriculture and Markets Food Lab	USA
OMIC USA Inc.	USA
SILLIKER JR LABORATORIES	Canada
U.S. Food & Drug Administration	USA
University of Arizona/AZ Laboratory for Emerging Contaminants	USA
US FDA - Cincinnati - Forensic Chemistry Center	USA
US FDA - San Francisco Lab	USA
Weck Labs Inc.	USA
Wisconsin Department of Agriculture, Bureau of Laboratory Services	USA

Participation in this study was international. Approximately 1/4 of the participants were from outside of North America. Of the North American participants, 64% were from the USA, with the remaining four laboratories from Canada. Of the laboratories from the USA, 8 (44%) were private commercial/industry testing laboratories, 4 (22%) were state laboratories representing five different states, 4 (22%) were laboratories associated with the FDA, and 2 (11%) were university laboratories. There were 5 participating laboratories from Europe (17%) representing 5 different countries. In addition, there were 2 participants from Asia and 1 from Australia/New Zealand. **Table 4** summarizes the regional participation in this study and the previous study conducted in 2013.

Table 4. Number of participating laboratories by region

Region	**Number of Participants 2013**		**Number of Participants 2014**	
North America	25	64%	21	75%
Europe	8	21%	4	14%
Other	6	15%	3	11%

Performance Ratings

In total, 368 data points were eligible for scoring. The mean scores for the different parameters were relatively consistent, averaging 2.7 and ranging from 2.5 for the MMAs in the sample to 2.9 for the Total As in the sample, DMAs, and AsB (**Table 5**).

Table 5. The mean scores for each parameter for all material types.

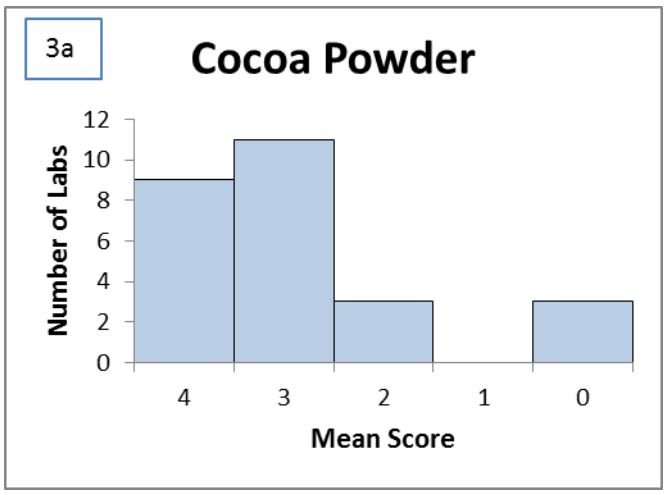
Parameter	Mean Score	n
Total As in Sample	2.9	128
Total As in Extract	2.4	77
Inorganic As	2.7	84
MMAs	2.5	19
DMAs	2.9	50
AsB	2.9	10
All Parameters	2.7	368

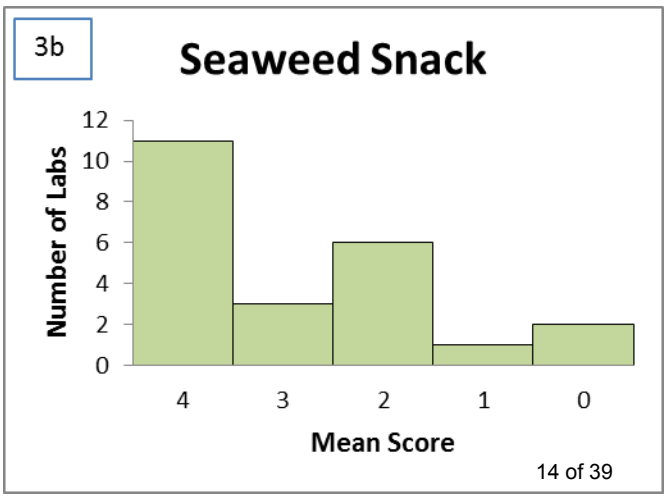
Similarly, the mean scores for the sample matrices were also relatively consistent, ranging from 2.5 for the white rice to 2.8 for the cocoa powder and tuna fish (**Table 6**).

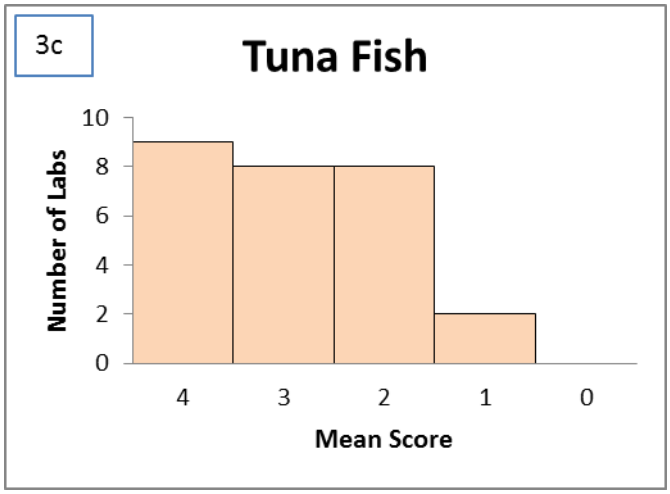
Table 6. The number of laboratories receiving each score for each of the sample matrices used in the study, along with the mean score for each matrix.

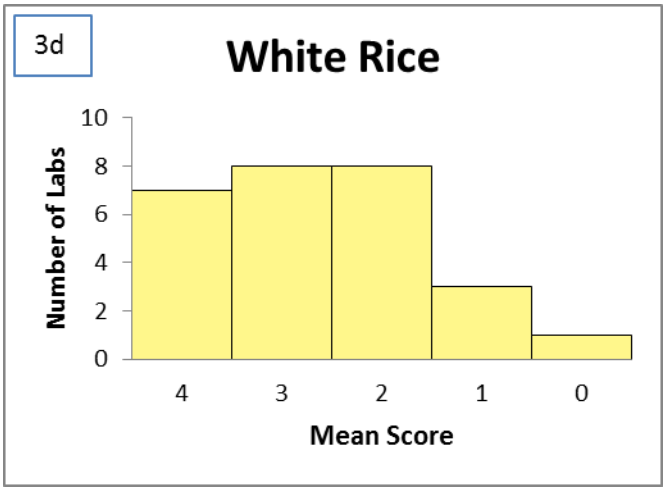
	Numbers of Labs Receiving Each Score					
Score	Cocoa Powder	Tuna Fish	Seaweed Snack	Shellfish	White Rice	All Matrices
4	9	9	11	7	7	3
3	11	8	3	9	8	18
2	3	8	6	8	8	5
1	0	2	1	1	3	2
0	3	0	2	1	1	0
Mean	2.8	2.8	2.7	2.7	2.5	2.7

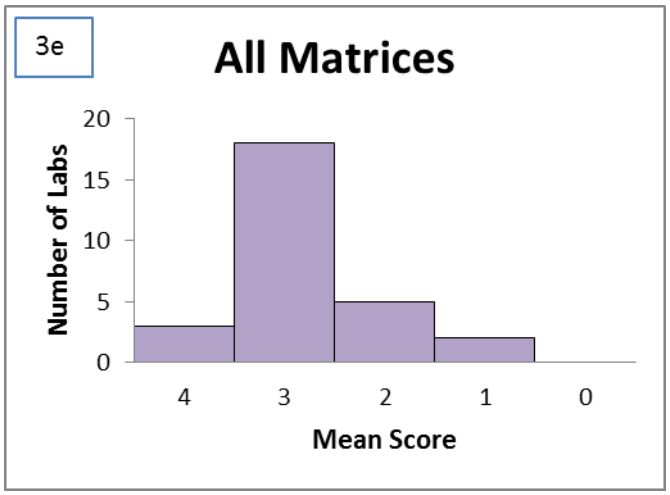
Graphs 3a-3d group participating laboratories based on the performance scores for each of the study materials. The overall scores summarized in **Graph 3e**.











The fact that the majority of laboratories participating in this study (75%) achieved an overall score of 3 or 4 (good or outstanding) indicates that, for at least some matrices, there is generally good intercomparability amongst most laboratories that reported total arsenic and arsenic speciation data for these matrices. 93% of the laboratories received an overall score of 2 or better, and only 2 laboratories (7%) received scores of 1 or 0 (poor or unacceptable, respectively). However, with only 3 laboratories (11%) receiving an overall score of 3.5 or higher, further analytical method development is required in order to achieve a high level of consistency across multiple laboratories using various methods worldwide.

When reviewing this report, keep in mind that the study materials do not have “true” or “assigned” values; with the exception of the white rice and tuna fish. The MPVs were determined based on the median of the results. Therefore, if many laboratories used the same method, and that method is prone to species conversion or species co-elution, then the resulting MPVs have the risk of being biased. For example, many laboratories used a nitric acid sample extraction for the speciation analyses, which has the potential to cause oxidation of some or all of the As(III) to As(V). In addition, when extracts of samples containing significant levels of AsB (e.g., sea plants or seafood) are analyzed on some column types, co-elution of As(III) and these large organic arsenic molecules is a risk if steps aren’t taken to mitigate these interferences. The issue is further exacerbated by the co-elution of tetramethylarsonium, arsenocholine, and trimethylarsine. It has also been documented that application of nitric acid, especially in the presence of peroxide, has a high capacity for degrading certain arsenosugars to DMAs (**Ref. 6)**. Of course, certain organisms such as shellfish, algae, seaweed, and other more esoteric substrates can contain unknown arsenic species which can also degrade or co-elute with known arsenic species. Please refer to **Table 7** for a summary of the inorganic As, AsB, and unknown arsenic species results reported for the seaweed sample, along with the associated high performance liquid chromatography (HPLC) column type. The laboratory identification numbers have been altered to preserve confidentiality regarding methodology. The inorganic As, AsB, and DMAs results reported for the seaweed sample were so variable, the results could not be scored (F value greater than M value). The specific column type did not correlate with the any of the reported arsenic speciation results.

Table 7. Subset of Seaweed Snack Data Demonstrating the Variability in Inorganic As, DMAs, Unknown Arsenic, and AsB as Correlated to HPLC column Type.

Lab ID	Inorganic As	DMAs	AsB	Unidentified As species	Column Type
A	not reported	445	not reported	not reported	Hamilton PRP-x100
B	not reported	56	not reported	not reported	Hamilton PRP-x100
C	330	not reported	not reported	not reported	not reported
D	not reported	27	not reported	7482	Dionex AS7
E	8262	not reported	not reported	not reported	Dionex AS7
F	36	not reported	not reported	not reported	not reported
G	not reported	136	10861	not reported	Hamilton PRP-x100
H	not reported	44	35	8190	Hamilton PRP-x100
I	not reported	710	8100	not reported	Hamilton PRP-x100
J	11	not reported	25	13760	Agilent G3288-80000
K	20	2250	not reported	not reported	not reported
L	not reported	1020	560	14600	Hamilton PRP-x100
M	18	not reported	not reported	not reported	not reported
N	21	63	not reported	12400	not reported
O	462	1037	10419	not reported	Hamilton PRP-x100
P	6612	not reported	not reported	not reported	not reported
Q	not reported	10600	662	not reported	Hamilton PRP-x100

Methods and Equipment Used

For the analysis of total As, the majority of participating laboratories used microwave digestion and ICP-MS analysis with an Agilent instrument. Refer to **Table 8** for details of the sample preparation and analysis methods used to determine the total As.

Table 8. Sample Preparation and Analysis Methods, and Analytical Instrumentation, Used for the Analysis of Total As.

Total As Sample Preparation Method	**No. of Labs**	
Microwave Digestion	22	76%
Hotblock/Hotplate Digestion	6	21%
None or Other	1	3%
Total As Analysis Method	**No. of Labs**	
ICP-MS	29	100%
Total As Instrument Manufacturer	**No. of Labs**	
Agilent	13	45%
Perkin Elmer	8	28%
Thermo	3	10%
Bruker	1	3%
Varian	1	3%
Not Listed	3	10%

For the speciation of arsenic, the majority of participating laboratories used a nitric acid extraction, HPLC separation, and ICP-MS analysis with an Agilent instrument. Refer to **Table 9** for details of the sample preparation, separation, and detection methods used in this study.

Table 9. Sample preparation separation, and detection methods, and analytical instrumentation, used for the analysis of As speciation.

As Speciation Sample Preparation Method	**No. of Labs**	
HNO_3 Extraction	18	64%
Other	3	11%
Enzyme Extraction	1	4%
HCl Extraction	4	14%
Methanol Extraction	2	7%
As Speciation Separation Method	**No. of Labs**	
HPLC	23	82%
Other/Not Defined	3	11%
HG-CT-GC	2	7%
As Speciation Detection Method	**No. of Labs**	
ICP-MS	25	89%
HG-AAS	2	7%
Other/Not Defined	1	4%
As Speciation Instrument Manufacturer	**No. of Labs**	
Agilent	15	54%
Perkin Elmer	8	29%
Bruker	1	4%
Buck	1	4%
Other/Not Defined	3	11%

Future Studies

This year's study utilized five common food types with very diverse matrices. The consistency that was seen with the white rice and the extensive variability observed with some of the other matrix types indicate that different extractions and methodologies may be appropriate to determine the various arsenic species specific to the matrix type.

As the differing technologies for arsenic speciation become more common and more widely practiced, there are even more compelling reasons to continue this study and it is hoped that in increased participation will be seen in future studies.

Brooks Applied Labs hopes to continue conducting this study in the future. Any feedback on the 2014 study or interest in participating in future studies should be directed to Elizabeth Madonick (elizabeth@brooksapplied.com).

The purpose of this report is to summarize the study results without detailed interpretation of the data. Discussion regarding the chemistry of the different arsenic species, arsenic species not included in this study, and the vast array of different sample matrices that are available is beyond the scope of this report. It is with sincere hope that each participating laboratory and other laboratories offering or pursuing arsenic speciation analyses in tissue matrices continue their research, method development, and method validation. Without harmonized methods, as supported by the findings of this intercomparison study, results can vary significantly between laboratories and technologies.

Acknowledgements

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Table A1. Total As Results for Cocoa Powder and Tuna Fish

Sample 1 - Cocoa Powder				Sample 2 - Tuna Fish Tissue			
Total As in Sample				Total As in Sample			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	39.4	0.50	4	01	4400	0.60	3
02	56.5	1.02	2	02	5458	0.96	3
03	< 50	-	-	03	4250	0.82	3
04	44.0	0.09	4	04	4650	0.23	4
05	40.5	0.40	4	05	4550	0.38	4
06	45.0	0.00	4	06	5093	0.42	4
07	42.1	0.26	4	07	4367	0.65	3
08	109.0	5.68	0	08	4930	0.18	4
09	39.4	0.50	4	09	4635	0.25	4
10	62.0	1.50	2	10	6028	1.81	1
11	45.0	0.00	4	11	4600	0.30	4
12	39.8	0.47	4	12	3961	1.25	2
13	55.0	0.88	3	13	5080	0.40	4
14	49.8	0.42	4	14	4340	0.69	3
15	128.0	7.23	0	15	4140	0.98	3
16	36.5	0.76	3	16	5075	0.40	4
17	34.8	0.91	3	17	4880	0.11	4
18	48.5	0.31	4	18	5410	0.89	3
19	48.5	0.31	4	19	5410	0.89	3
20	37.0	0.71	3	20	4317	0.72	3
21	42.0	0.27	4	21	5810	1.48	2
22	19.4	2.28	0	22	4240	0.84	3
23	54.9	0.87	3	23	4806	0.00	4
24	70.0	2.21	0	24	5525	1.06	2
25	79.8	3.08	0	25	5476	0.99	3
27	not measured	-	-	27	not measured	-	-
28	not measured	-	-	28	4680	0.19	4
29	49.0	0.35	4	29	5183	0.56	3
	Median (M) =	45.0	µg/kg		Median (M) =	4806	µg/kg
	Mean =	52.6	µg/kg		Mean =	4863	µg/kg
	F-psuedosigma (F) =	11.3			F-psuedosigma (F) =	677	
	n =	25			n =	27	
					Sample Source Material:	IRMM BCR-627	
					Certified Value =	4800	µg/kg
					Uncertainty =	300	µg/kg
	MPV =	45	µg/kg		MPV =	4800	µg/kg

Table A2. Total As Results for Seaweed and Shellfish

Sample 3 - Seasoned Seaweed Snack				Sample 4 -Shellfish Tissue			
Total As in Sample				Total As in Sample			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	12700	0.16	4	01	6180	0.94	3
02	11597	0.69	3	02	6370	0.66	3
03	13780	0.36	4	03	6390	0.63	3
04	12350	0.33	4	04	6905	0.14	4
05	12700	0.16	4	05	6260	0.82	3
06	13178	0.07	4	06	6719	0.14	4
07	12237	0.38	4	07	6220	0.88	3
08	15900	1.38	2	08	7400	0.88	3
09	13887	0.41	4	09	7198	0.58	3
10	1499	5.54	0	10	8218	2.10	0
11	13000	0.01	4	11	6800	0.01	4
12	11539	0.72	3	12	5876	1.39	2
13	15200	1.04	2	13	7400	0.88	3
14	12000	0.49	4	14	6560	0.37	4
15	11000	0.97	3	15	6070	1.10	2
16	12194	0.40	4	16	6992	0.27	4
17	14300	0.61	3	17	5840	1.45	2
18	17700	2.24	0	18	7220	0.61	3
19	17700	2.24	0	19	7220	0.61	3
20	12865	0.08	4	20	6497	0.47	4
21	not measured	-	-	21	not measured	-	-
22	12600	0.21	4	22	6290	0.77	3
23	13058	0.01	4	23	6819	0.01	4
24	16050	1.45	2	24	6940	0.19	4
25	18167	2.47	0	25	7486	1.01	3
27	not measured	-	-	27	not measured	-	-
28	14700	0.80	3	28	6840	0.05	4
29	15475	1.17	2	29	7493	1.02	2
Median (M) =		13029	µg/kg	Median (M) =		6810	µg/kg
Mean =		13361	µg/kg	Mean =		6777	µg/kg
F-psuedosigma (F) =		2083		F-psuedosigma (F) =		670	
n =		26		n =		26	
MPV =		13000	µg/kg	MPV =		6800	µg/kg

Table A3. Total As Result

Sample 5 - White Rice Flour			
Total As in Sample			
Lab ID	**Result (µg/kg)**	**Z-Value**	**Rating**
01	298	0.52	3
02	342	1.23	2
03	270	1.65	1
04	311	0.00	4
05	320	0.36	4
06	358	1.88	1
07	282	1.18	2
08	322	0.44	4
09	318	0.27	4
10	361	2.01	1
11	290	0.85	3
12	259	2.09	0
13	325	0.56	3
14	262	1.97	1
15	265	1.85	1
16	305	0.23	4
17	315	0.16	4
18	313	0.08	4
19	313	0.08	4
20	290	0.85	3
21	301	0.40	4
22	262	1.97	1
23	296	0.60	3
24	371	2.42	0
25	442	5.40	0
27	285	1.05	2
28	not measured	-	-
29	319	0.32	4
	Median (M) =	311	µg/kg
	Mean =	311	µg/kg
	F-psuedosigma (F) =	25	
	n =	27	
	Sample Source Material:	NIST 1568b	
	Certified Value =	285	µg/kg
	Uncertainty =	14	µg/kg
	MPV =	310	µg/kg

Table A4. Total As Results for Cocoa Powder and Tuna Fish Speciation Extracts

Sample 1 - Cocoa Powder				Sample 2 - Tuna Fish Tissue			
Total As in Extract				Total As in Extract			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	not measured	-	-	01	not measured	-	-
02	52.7	1.00	3	02	4797	0.80	3
03	not measured	-	-	03	not measured	-	-
04	17.0	0.65	3	04	4281	0.54	3
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	not measured	-	-	07	not measured	-	-
08	100.0	4.40	0	08	4780	0.75	3
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	35.0	0.18	4	11	7000	6.51	0
12	1.62*	1.70	1	12	231*	11.04	0
13	not measured	-	-	13	not measured	-	-
14	38.5	0.35	4	14	4490	0.00	4
15	49.2	0.84	3	15	4430	0.16	4
16	17.6	0.62	3	16	4255	0.61	3
17	27.2	0.18	4	17	4690	0.52	3
18	< 160	-	-	18	4120	0.96	3
19	20.0	0.51	4	19	4770	0.73	3
20	not measured	-	-	20	not measured	-	-
21	27.0	0.18	4	21	4190	0.78	3
22	17.7	0.62	3	22	4337	0.40	4
23	57.1	1.21	2	23	4984	1.28	2
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	not measured	-	-	28	5000	1.32	2
29	31.0	0.00	4	29	4002	1.27	2
	Median (M) =	31.0	µg/kg		Median (M) =	4490	µg/kg
	Mean =	37.7	µg/kg		Mean =	4675	µg/kg
	F-psuedosigma (F) =	21.6			F-psuedosigma (F) =	386	
	n =	13			n =	15	
	MPV =	27	µg/kg		MPV =	4400	µg/kg
*Value omitted from statistics (see narrative)				*Value omitted from statistics (see narrative)			

Table A5. Total As Results for Seaweed and Shellfish Speciation Extracts

Sample 3 - Seasoned Seaweed Snack				Sample 4 -Shellfish Tissue			
Total As in Extract				Total As in Extract			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	not measured	-	-	01	not measured	-	-
02	11607	0.11	4	02	5574	0.07	4
03	not measured	-	-	03	not measured	-	-
04	8389	1.85	1	04	3064	5.16	0
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	not measured	-	-	07	not measured	-	-
08	11300	0.27	4	08	7010	3.06	0
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	16100	2.33	0	11	9400	8.03	0
12	686*	6.03	0	12	281*	10.95	0
13	not measured	-	-	13	not measured	-	-
14	10000	0.98	3	14	4840	1.46	2
15	10700	0.60	3	15	6050	1.06	2
16	10878	0.50	4	16	5119	0.88	3
17	13800	1.08	2	17	5620	0.16	4
18	12000	0.11	4	18	5510	0.07	4
19	16300	2.44	0	19	5940	0.83	3
20	not measured	-	-	20	not measured	-	-
21	not measured	-	-	21	not measured	-	-
22	13300	0.81	3	22	5450	0.19	4
23	12737	0.51	4	23	5363	0.37	4
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	10000	0.98	3	28	7200	3.45	0
29	13025	0.66	3	29	5408	0.28	4
Median (M) =	11803	µg/kg		Median (M) =	5542	µg/kg	
Mean =	12153	µg/kg		Mean =	5825	µg/kg	
F-psuedosigma (F) =	1843			F-psuedosigma (F) =	481		
n =	14			n =	14		
MPV =	12000	µg/kg		MPV =	5500	µg/kg	
*Value omitted from statistics (see narrative)				*Value omitted from statistics (see narrative)			

Table A6. Total As Result for Rice Speciation Exrtacts

Sample 5 - White Rice Flour			
Total As in Extract			
Lab ID	**Result (µg/kg)**	**Z-Value**	**Rating**
01	not measured	-	-
02	366	1.69	1
03	not measured	-	-
04	312	0.21	4
05	not measured	-	-
06	307	0.39	4
07	333	0.53	3
08	400	2.89	0
09	not measured	-	-
10	271	1.67	1
11	450	4.65	0
12	19*	10.54	0
13	not measured	-	-
14	341	0.81	3
15	556	8.38	0
16	316	0.07	4
17	243	2.64	0
18	310	0.28	4
19	320	0.07	4
20	not measured	-	-
21	321	0.10	4
22	288	1.06	2
23	343	0.87	3
24	303	0.53	3
25	not measured	-	-
27	not measured	-	-
28	not measured	-	-
29	288	1.06	2
	Median (M) =	318	µg/kg
	Mean =	337	µg/kg
	F-psuedosigma (F) =	28	
	n =	18	
	MPV =	320	µg/kg

*Value omitted from statistics (see narrative)

Table A7. Inorganic Arsenic Results for Cocoa Powder and Tuna Fish

Sample 1 - Cocoa Powder				Sample 2 - Tuna Fish Tissue			
Inorganic As				Inorganic As			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	20.2	0.14	4	01	12.0	1.12	2
02	19.8	0.05	4	02	35.7	0.51	4
03	27.0	1.44	2	03	150.0	2.46	0
04	17.0	0.48	4	04	49.0	0.16	4
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	< 40	-	-	07	94.3	1.01	2
08	29.0	1.83	1	08	36.0	0.50	4
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	17.0	0.48	4	11	80.0	0.64	3
12	18.4	0.21	4	12	15.4	1.03	2
13	not measured	-	-	13	not measured	-	-
14	16.4	0.59	3	14	55.2	0.00	4
15	19.2	0.05	4	15	< 3.5 FN	-	0
16	17.6	0.35	4	16	< 5 FN	-	0
17	11.4	1.55	1	17	72.0	0.44	4
18	28.0	1.64	1	18	36.0	0.50	4
19	19.0	0.09	4	19	36.0	0.50	4
20	25.8	1.21	2	20	88.0	0.85	3
21	26.0	1.25	2	21	100.0	1.16	2
22	18.9	0.12	4	22	38.8	0.43	4
23	21.2	0.33	4	23	58.9	0.09	4
24	not measured	-	-	24	not measured	-	-
25	< 39.4	-	-	25	1998.0	57.07	0
27	not measured	-	-	27	not measured	-	-
28	not measured	-	-	28	< 7 FN	-	0
29	22.0	0.48	4	29	not measured	-	-
	Median (M) =	19.5	µg/kg		Median (M) =	55.2	µg/kg
	Mean =	20.8	µg/kg		Mean =	173.8	µg/kg
	F-psuedosigma (F) =	5.2			F-psuedosigma (F) =	38.5	
	n =	18			n =	17	
				FN = False Negative			
	MPV =	19	µg/kg		MPV =	39	µg/kg

Table A8. Inorganic Arsenic Results for Seaweed and Shellfish

Sample 3 - Seasoned Seaweed Snack				Sample 4 -Shellfish Tissue			
Inorganic As				Inorganic As			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	< 5.31	-	-	01	29	1.56	1
02	< 7.49	-	-	02	117	0.16	4
03	330	-	-	03	250	1.96	1
04	< 10	-	-	04	21	1.69	1
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	8262	-	-	07	280	2.43	0
08	36	-	-	08	134	0.11	4
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	< 4	-	-	11	140	0.21	4
12	< 0.105	-	-	12	61	1.05	2
13	not measured	-	-	13	not measured	-	-
14	< 20	-	-	14	39	1.41	2
15	< 3.5	-	-	15	< 3.5 FN	-	0
16	< 5	-	-	16	93	0.54	3
17	11	-	-	17	38	1.41	2
18	20	-	-	18	120	0.11	4
19	< 114	-	-	19	141	0.22	4
20	18	-	-	20	158	0.49	4
21	not measured	-	-	21	not measured	-	-
22	21	-	-	22	135	0.14	4
23	462	-	-	23	117	0.16	4
24	not measured	-	-	24	not measured	-	-
25	6612	-	-	25	2001	31.72	0
27	not measured	-	-	27	not measured	-	-
28	< 7	-	-	28	200	1.16	2
29	not measured	-	-	29	not measured	-	-
	Median (M) =	36	µg/kg		Median (M) =	127	µg/kg
	Mean =	1753	µg/kg		Mean =	226	µg/kg
	F-psuedosigma (F) =	328			F-psuedosigma (F) =	63	
	n =	9			n =	18	
Data too variable to use MPV for scoring				FN = False Negative			
	MPV =	11	µg/kg		MPV =	120	µg/kg

Table A9. Inorganic Arsenic Results for Rice

Sample 5 - White Rice Flour			
Inorganic As			
Lab ID	**Result (µg/kg)**	**Z-Value**	**Rating**
01	112	0.40	4
02	67	2.42	0
03	90	0.99	3
04	117	0.71	3
05	118	0.77	3
06	124	1.12	2
07	99	0.45	4
08	125	1.21	2
09	110	0.29	4
10	106	0.00	4
11	130	1.52	1
12	98	0.48	4
13	76	1.89	1
14	82	1.48	2
15	103	0.17	4
16	120	0.88	3
17	70	2.26	0
18	105	0.04	4
19	95	0.67	3
20	147	2.59	0
21	97	0.55	3
22	108	0.15	4
23	107	0.10	4
24	92	0.86	3
25	165	3.72	0
27	109	0.21	4
28	not measured	-	-
29	102	0.21	4
	Median (M) =	106	µg/kg
	Mean =	106	µg/kg
	F-psuedosigma (F) =	16	
	n =	27	
	Sample Source Material:	NIST 1568b	
	Certified Value =	92	µg/kg
	Uncertainty =	10	µg/kg
	MPV =	110	µg/kg

Table A10. Dimethylarsinic Acid Results for Cocoa Powder and Tuna Fish

Sample 1 - Cocoa Powder				Sample 2 - Tuna Fish Tissue			
DMAs				DMAs			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	< 5.31	-	-	01	158	0.36	4
02	1.14	-	-	02	129	0.26	4
03	not measured	-	-	03	not measured	-	-
04	< 2	-	-	04	138	0.08	4
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	< 20	-	-	07	131	0.22	4
08	not measured	-	-	08	not measured	-	-
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	not measured	-	-	11	not measured	-	-
12	1.05	-	-	12	101	0.87	3
13	not measured	-	-	13	not measured	-	-
14	1.26	-	-	14	145	0.08	4
15	< 1.4	-	-	15	80	1.33	2
16	< 5	-	-	16	234	1.99	1
17	< 10	-	-	17	105	0.79	3
18	< 12	-	-	18	127	0.31	4
19	< 3	-	-	19	251	2.36	0
20	not measured	-	-	20	not measured	-	-
21	2.00	-	-	21	200	1.26	2
22	< 2.2	-	-	22	214	1.56	1
23	< 6.22	-	-	23	161	0.42	4
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	not measured	-	-	28	< 3.47 FN	-	0
29	not measured	-	-	29	not measured	-	-
	Median (M) =	1.20	µg/kg		Median (M) =	142	µg/kg
	Mean =	1.36	µg/kg		Mean =	155	µg/kg
	F-psuedosigma (F) =	0.24			F-psuedosigma (F) =	46	
	n =	4			n =	14	
Insufficient datapoints to calculate MPV					Sample Source Material:	IRMM BCR-627	
					Certified Value =	149.8	µg/kg
					Uncertainty =	22.5	µg/kg
					MPV =	140	µg/kg

Table A11. Dimethylarsinic Acid Results for Seaweed and Shellfish

Sample 3 - Seasoned Seaweed Snack				Sample 4 -Shellfish Tissue			
DMAs				DMAs			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	445	-	-	01	not measured	-	-
02	56	-	-	02	385	0.51	4
03	not measured	-	-	03	not measured	-	-
04	27	-	-	04	391	0.50	4
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	not measured	-	-	07	422	0.43	4
08	not measured	-	-	08	not measured	-	-
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	not measured	-	-	11	not measured	-	-
12	136	-	-	12	355	0.57	3
13	not measured	-	-	13	not measured	-	-
14	44	-	-	14	425	0.43	4
15	710	-	-	15	1340	1.36	2
16	< 5	-	-	16	672	0.06	4
17	< 10	-	-	17	284	0.70	3
18	2250	-	-	18	1030	0.76	3
19	1020	-	-	19	1080	0.85	3
20	not measured	-	-	20	not measured	-	-
21	not measured	-	-	21	not measured	-	-
22	63	-	-	22	644	0.00	4
23	1037	-	-	23	1136	0.96	3
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	10600	-	-	28	2880	4.85	0
29	not measured	-	-	29	not measured	-	-
	Median (M) =	445	µg/kg		Median (M) =	644	µg/kg
	Mean =	1490	µg/kg		Mean =	850	µg/kg
	F-psuedosigma (F) =	718			F-psuedosigma (F) =	511	
	n =	11			n =	13	
Data too variable to use M for scoring							
	MPV =	140	µg/kg		MPV =	640	µg/kg

Table A12. Dimethylarsinic Acid Results for Rice

Sample 5 - White Rice Flour			
DMAs			
Lab ID	**Result (µg/kg)**	**Z-Value**	**Rating**
01	170	0.43	4
02	142	1.81	1
03	not measured	-	-
04	182	0.16	4
05	181	0.11	4
06	166	0.62	3
07	148	1.51	2
08	not measured	-	-
09	170	0.41	4
10	154	1.22	2
11	not measured	-	-
12	182	0.16	4
13	181	0.11	4
14	141	1.86	1
15	149	1.46	2
16	183	0.21	4
17	157	1.07	2
18	136	2.10	0
19	205	1.30	2
20	not measured	-	-
21	180	0.07	4
22	177	0.07	4
23	183	0.22	4
24	197	0.90	3
25	not measured	-	-
27	182	0.16	4
28	not measured	-	-
29	184	0.28	4
	Median (M) =	179	µg/kg
	Mean =	171	µg/kg
	F-psuedosigma (F) =	20	
	n =	22	
Sample Source Material:		NIST 1568b	
	Certified Value =	180	µg/kg
	Uncertainty =	12	µg/kg
	MPV =	180	µg/kg

Table A13. Monomethylarsonic Acid Results for Cocoa Powder and Tuna Fish

Sample 1 - Cocoa Powder				Sample 2 - Tuna Fish Tissue			
MMAs				MMAs			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	< 5.31	-	-	01	< 5.31	-	-
02	< 0.337	-	-	02	9	-	-
03	not measured	-	-	03	not measured	-	-
04	< 2	-	-	04	41	-	-
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	< 20	-	-	07	< 20	-	-
08	not measured	-	-	08	not measured	-	-
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	not measured	-	-	11	not measured	-	-
12	0.46	-	-	12	8	-	-
13	not measured	-	-	13	not measured	-	-
14	< 0.982	-	-	14	6	-	-
15	< 1.8	-	-	15	< 2.5	-	-
16	< 5	-	-	16	< 5	-	-
17	< 10	-	-	17	16	-	-
18	< 9	-	-	18	< 20	-	-
19	< 2	-	-	19	< 14	-	-
20	not measured	-	-	20	not measured	-	-
21	0.70	-	-	21	1	-	-
22	< 3.89	-	-	22	8	-	-
23	< 6.51	-	-	23	39	-	-
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	not measured	-	-	28	< 3.47	-	-
29	not measured	-	-	29	not measured	-	-
	Median (M) =	0.58	µg/kg		Median (M) =	8.8	µg/kg
	Mean =	0.58	µg/kg		Mean =	16.0	µg/kg
	F-psuedosigma (F) =	0.09			F-psuedosigma (F) =	10.1	
	n =	2			n =	8	
				Data too variable to use M for scoring			
Insufficient datapoints to calculate MPV					MPV =	6.1	µg/kg

Table A13. Monomethylarsonic Acid Results for Seaweed and Shellfish

Sample 3 - Seasoned Seaweed Snack				Sample 4 -Shellfish Tissue			
MMAs				MMAs			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	< 5.31	-	-	01	< 5.31	-	-
02	< 3.37	-	-	02	11	1.22	2
03	not measured	-	-	03	not measured	-	-
04	not measured	-	-	04	not measured	-	-
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	822	-	-	07	951	21.40	0
08	not measured	-	-	08	not measured	-	-
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	not measured	-	-	11	not measured	-	-
12	< 0.067	-	-	12	65	0.07	4
13	not measured	-	-	13	not measured	-	-
14	< 13	-	-	14	11	1.23	2
15	< 1.8	-	-	15	< 1.8	-	-
16	< 5	-	-	16	< 5	-	-
17	< 10	-	-	17	62	0.00	4
18	< 321	-	-	18	< 95	-	-
19	< 57	-	-	19	< 25	-	-
20	not measured	-	-	20	not measured	-	-
21	not measured	-	-	21	not measured	-	-
22	< 4.83	-	-	22	19	1.02	2
23	418	-	-	23	78	0.39	4
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	< 3.47	-	-	28	< 3.49	-	-
29	not measured	-	-	29	not measured	-	-
	Median (M) =	620	µg/kg		Median (M) =	62	µg/kg
	Mean =	620	µg/kg		Mean =	171	µg/kg
	F-psuedosigma (F) =	150			F-psuedosigma (F) =	42	
	n =	2			n =	7	
Insufficient datapoints to calculate MPV					MPV =	11	µg/kg

Table A14. Monomethylarsonic Acid Results for Rice

Sample 5 - White Rice Flour			
MMAs			
Lab ID	**Result (µg/kg)**	**Z-Value**	**Rating**
01	< 5.31 FN	-	0
02	10.0	1.46	2
03	not measured	-	-
04	13.0	0.00	4
05	14.0	0.48	4
06	17.2	2.04	0
07	< 20	-	-
08	not measured	-	-
09	11.4	0.77	3
10	11.1	0.90	3
11	not measured	-	-
12	11.8	0.58	3
13	15.3	1.11	2
14	10.2	1.35	2
15	< 1.8 FN	-	0
16	13.4	0.19	4
17	15.2	1.06	2
18	< 18	-	-
19	13.0	0.00	4
20	not measured	-	-
21	8.0	2.41	0
22	10.6	1.17	2
23	40.5	13.25	0
24	14.0	0.48	4
25	not measured	-	-
27	12.1	0.43	4
28	not measured	-	-
29	13.7	0.34	4
	Median (M) =	13.0	µg/kg
	Mean =	14.1	µg/kg
	F-psuedosigma (F) =	2.1	
	n =	18	
	Sample Source Material:	NIST 1568b	
	Certified Value =	11.6	µg/kg
	Uncertainty =	3.5	µg/kg
FN = False Negative			
	MPV =	11	µg/kg

Table A15. Arsenobetaine Results for Cocoa Powder and Tuna Fish

Sample 1 - Cocoa Powder				Sample 2 - Tuna Fish Tissue			
AsB				AsB			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	not measured	-	-	01	not measured	-	-
02	not measured	-	-	02	not measured	-	-
03	not measured	-	-	03	not measured	-	-
04	< 2	-	-	04	3954	0.03	4
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	< 20	-	-	07	3996	0.03	4
08	not measured	-	-	08	not measured	-	-
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	not measured	-	-	11	not measured	-	-
12	< 0.051	-	-	12	4165	0.30	4
13	not measured	-	-	13	not measured	-	-
14	< 0.407	-	-	14	3550	0.67	3
15	14	-	-	15	3590	0.61	3
16	not measured	-	-	16	not measured	-	-
17	< 10	-	-	17	3650	0.51	3
18	not measured	-	-	18	not measured	-	-
19	< 2	-	-	19	4750	1.22	2
20	not measured	-	-	20	not measured	-	-
21	not measured	-	-	21	3730	0.39	4
22	< 3.9	-	-	22	not measured	-	-
23	< 3.37	-	-	23	4644	1.06	2
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	not measured	-	-	28	5770	2.83	0
29	not measured	-	-	29	not measured	-	-
	Median (M) =	N/C	µg/kg		Median (M) =	3975	µg/kg
	Mean =	N/C	µg/kg		Mean =	4180	µg/kg
	F-psuedosigma (F) =	N/C			F-psuedosigma (F) =	633	
	n =	1			n =	10	
					Sample Source Material:	IRMM BCR-627	
					Certified Value =	3896	µg/kg
					Uncertainty =	225	µg/kg
Insufficient datapoints to calculate MPV					MPV =	4000	µg/kg

Table A16. Arsenobetaine Results for Seaweed and Shellfish

Sample 3 - Seasoned Seaweed Snack				Sample 4 -Shellfish Tissue			
AsB				AsB			
Lab ID	Result (µg/kg)	Z-Value	Rating	Lab ID	Result (µg/kg)	Z-Value	Rating
01	not measured	-	-	01	not measured	-	-
02	not measured	-	-	02	not measured	-	-
03	not measured	-	-	03	not measured	-	-
04	< 10	-	-	04	765	-	-
05	not measured	-	-	05	not measured	-	-
06	not measured	-	-	06	not measured	-	-
07	not measured	-	-	07	not measured	-	-
08	not measured	-	-	08	not measured	-	-
09	not measured	-	-	09	not measured	-	-
10	not measured	-	-	10	not measured	-	-
11	not measured	-	-	11	not measured	-	-
12	10861	-	-	12	3330	-	-
13	not measured	-	-	13	not measured	-	-
14	35	-	-	14	770	-	-
15	8100	-	-	15	2980	-	-
16	not measured	-	-	16	not measured	-	-
17	25	-	-	17	1080	-	-
18	not measured	-	-	18	not measured	-	-
19	560	-	-	19	920	-	-
20	not measured	-	-	20	not measured	-	-
21	not measured	-	-	21	not measured	-	-
22	not measured	-	-	22	not measured	-	-
23	10419	-	-	23	3571	-	-
24	not measured	-	-	24	not measured	-	-
25	not measured	-	-	25	not measured	-	-
27	not measured	-	-	27	not measured	-	-
28	662	-	-	28	1470	-	-
29	not measured	-	-	29	not measured	-	-
	Median (M) =	662	µg/kg		Median (M) =	1275	µg/kg
	Mean =	4380	µg/kg		Mean =	1861	µg/kg
	F-psuedosigma (F) =	6643			F-psuedosigma (F) =	1620	
	n =	7			n =	8	
Data too variable to use M for scoring				Data too variable to use M for scoring			
	MPV =	560	µg/kg		MPV =	1100	µg/kg

Table A17. Arsenobetaine Results for Rice

Sample 5 - White Rice Flour			
AsB			
Lab ID	**Result (µg/kg)**	**Z-Value**	**Rating**
01	not measured	-	-
02	not measured	-	-
03	not measured	-	-
04	< 2	-	-
05	not measured	-	-
06	not measured	-	-
07	< 20	-	-
08	not measured	-	-
09	not measured	-	-
10	not measured	-	-
11	not measured	-	-
12	< 0.051	-	-
13	not measured	-	-
14	< 0.407	-	-
15	18	-	-
16	not measured	-	-
17	< 10	-	-
18	not measured	-	-
19	< 2	-	-
20	not measured	-	-
21	not measured	-	-
22	< 7.2	-	-
23	< 3.37	-	-
24	not measured	-	-
25	not measured	-	-
27	not measured	-	-
28	not measured	-	-
29	not measured	-	-
	Median (M) =	N/C	µg/kg
	Mean =	N/C	µg/kg
	F-psuedosigma (F) =	N/C	
	n =	1	
Insufficient datapoints to calculate MPV			