Market Basket Survey of Arsenic Species in the Top Ten Most Consumed Seafoods in the United States

Mesay Mulugeta Wolle and Sean D. Conklin

Office of Regulatory Science, Center for Food Safety and Applied Nutrition, Food and Drug Administration,5001 Campus Drive, College Park, MD 20740, USA

1. Introduction

The United States (U.S.) is one of the largest seafood markets in the world, and consumers have a wide choice of locally sourced and imported products. According to the National Fisheries Institute, which identifies the top ten products based on per-capita consumption, the top ten most consumed seafoods often make up more than 90% of the country's total seafood consumption.[1] Table 1 lists the ten seafoods most consumed in the U.S. annually from 2009 to 2018. For over ten years, shrimp is the leading product followed by salmon and canned tuna; the three represented more than 50% of the total seafood consumption in the country. Published data, including the Total Diet Study from the U.S. Food and Drug Administration (FDA),[2] show that about 90% of the arsenic in U.S. diets comes from seafoods. The toxicity of arsenic, however, is related to its chemical species, and evaluations focus primarily on inorganic arsenic (iAs). The poster presents a study on the determination of arsenic species in the ten most consumed seafoods in the U.S.

Table 1. *Ranking of the top ten most consumed seafoods in the U.S. (2009–2018)*[1]

<table>
<tr><th>Seafood</th><th>2018</th><th>2017</th><th>2016</th><th>2015</th><th>2014</th><th>2013</th><th>2012</th><th>2011</th><th>2010</th><th>2009</th></tr>
<tr><td>Shrimp</td><td colspan="10">1</td></tr>
<tr><td>Salmon</td><td colspan="6">2</td><td colspan="4">3</td></tr>
<tr><td>Tuna (canned)</td><td colspan="6">3</td><td colspan="4">2</td></tr>
<tr><td>Tilapia</td><td colspan="7">4</td><td>5</td><td>4</td><td>5</td></tr>
<tr><td>Pollock</td><td colspan="7">5</td><td>4</td><td>5</td><td>4</td></tr>
<tr><td>Swai</td><td colspan="8">6</td><td>9</td><td>10</td></tr>
<tr><td>Cod</td><td colspan="6">7</td><td>8</td><td>9</td><td colspan="2">8</td></tr>
<tr><td>Catfish</td><td>8</td><td colspan="3">9</td><td colspan="2">8</td><td>9</td><td>7</td><td colspan="2">6</td></tr>
<tr><td>Crab</td><td>9</td><td colspan="3">8</td><td colspan="2">9</td><td>7</td><td>8</td><td colspan="2">7</td></tr>
<tr><td>Clams</td><td colspan="9">10</td><td>9</td></tr>
</table>

2. Experimental

2.1. Samples

- Fifty-four seafood samples were purchased from local supermarkets in California, Kansas and Maryland (see Table 2).
- The samples included domestic and imported products.
- Samples were homogenized to smooth paste in a food processor and stored at −30 °C.
- The species identities of the samples were determined using DNA-based techniques.[3]

Table 2. *List of the seafood samples analyzed*

Seafood	No. of samples	Collected species				
Shrimp	8	*Brown*	*Pink*	*Rainbow*	*Whiteleg*	
Salmon	8	*Atlantic*	*Pink*	*Sockeye*		
Tuna (canned)	7	*Albacore*	*Chunk light*	*Yellowfin*		
Tilapia	4	*Blue*	*Mozambique*	*Nile*		
Pollock	3	*Walleye*				
Swai	3	*Swai*				
Cod	3	*Atlantic*	*Pacific*			
Catfish	3	*Channel*				
Crab	10	*Blue*	*Dungeness*	*Golden King*	*Snow*	*Swimming*
Clam	5	*Manila*	*New Zealand Cockle*	*Ocean Quahog*	*Softshell*	

2.2. Analysis of samples

- The seafoods were analyzed for their total arsenic (tAs) according to the method in FDA's Elemental Analysis Manual Section 4.7; microwave-enhanced sample digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis.[4]
- Speciation analysis of arsenic was performed based on stepwise extraction of water-soluble and nonpolar arsenic[3] as outlined in Figure 1. Water-soluble arsenicals were speciated by anion and cation exchange high pressure liquid chromatography (HPLC) coupled with ICP-MS.

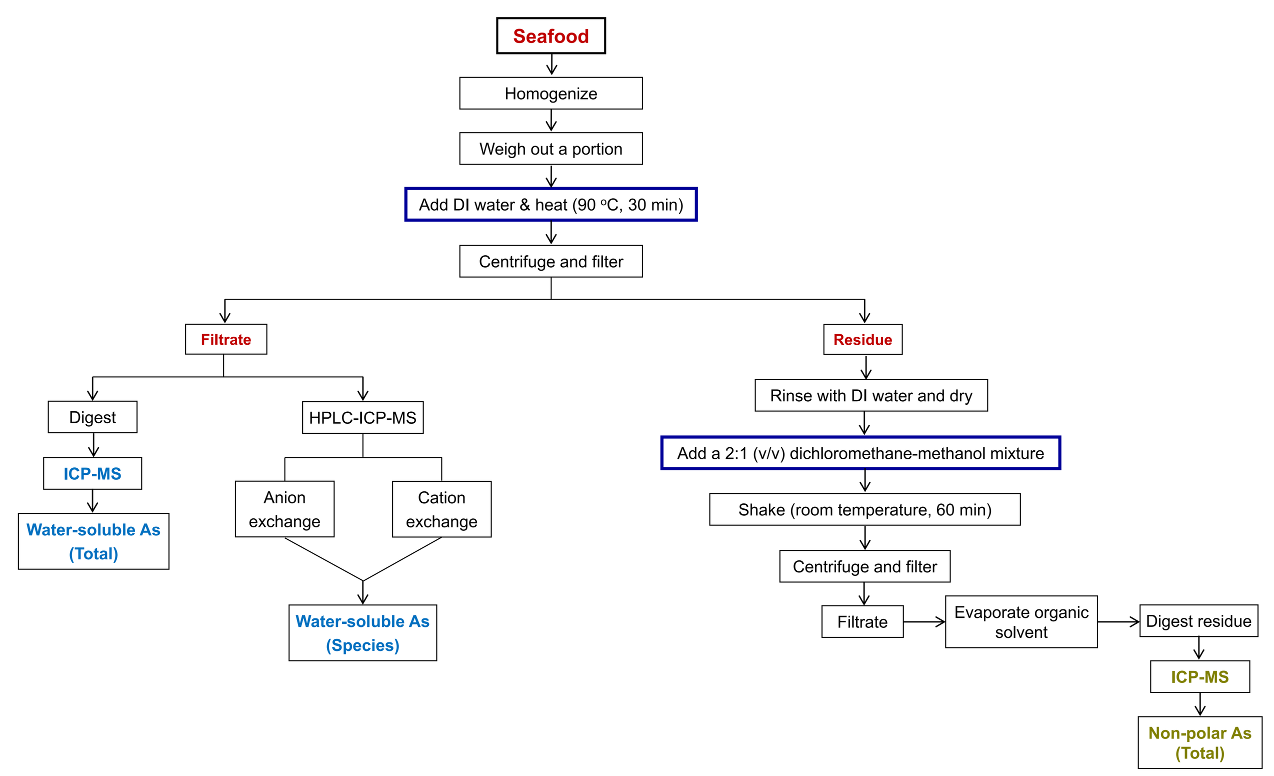


Figure 1. *Flow chart showing the extraction and determination of water-soluble and non-polar arsenic in the seafood samples.*

3. Results and Discussions

3.1. Total and extracted arsenic

- The tAs concentrations were in the range of 8–22,200 ng/g (wet mass); Figure 2. The lowest and highest concentrations were found in swai and swimming crab, respectively.
- Water-soluble and nonpolar arsenic accounted for 8–112% and 1–46% of the tAs, respectively. The overall extraction accounted for 44–110% (shrimp), 74–123% (salmon), 54–118% (tuna), 89–107% (tilapia), 93–109% (pollock), 93–104% (cod), 46–83% (catfish), 56–110% (crab) and 53–96% (clam) of the tAs.

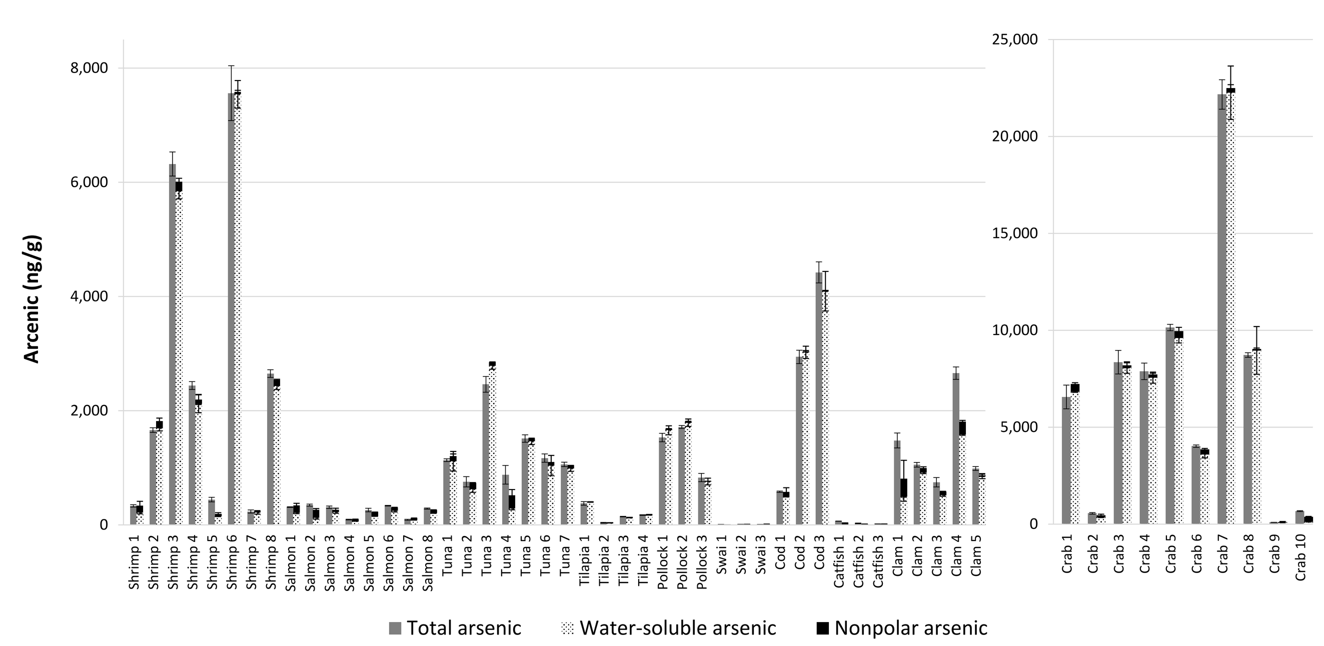


Figure 2. *Concentrations (ng/g) of total, water-soluble and nonpolar arsenic in the seafood samples.*

3.2. Arsenic species

- Figure 3 shows chromatograms of a crab extract containing a range of water-soluble arsenicals including arsenite (As^{3+}), arsenate (As^{5+}), arsenobetaine (AsB), arsenosugars and some unknowns.
- A total of 16 known and several unknown arsenic species were detected in the aqueous extracts from the seafoods, see Figure 4.
- AsB, a chemically stable and nontoxic species, was predominant in most of the samples.
- Regardless of the tAs concentration, iAs (the sum of As^{3+} and As^{5+}) was either undetectable or existed at relatively low concentrations. Its highest concentration was 145 ng/g in golden king crab (crab 3).
- Arsenosugars were major species in most of the crabs and clams. They, however, were not detected in finfish and shrimp.
- Among the other water-soluble species, trimethylarsoniopropionate (TMAP) was found in most seafoods with elevated concentrations in crabs (130–800 ng/g).
- Monomethylarsonic acid (MMA) and trimethylarsine oxide (TMAO) were found almost exclusively in crabs while dimethylarsinic acid (DMA) was present at trace levels throughout.
- Many peaks representing a small fraction of tAs could not be identified with certainty and remained "unknown" due to the lack of standards.

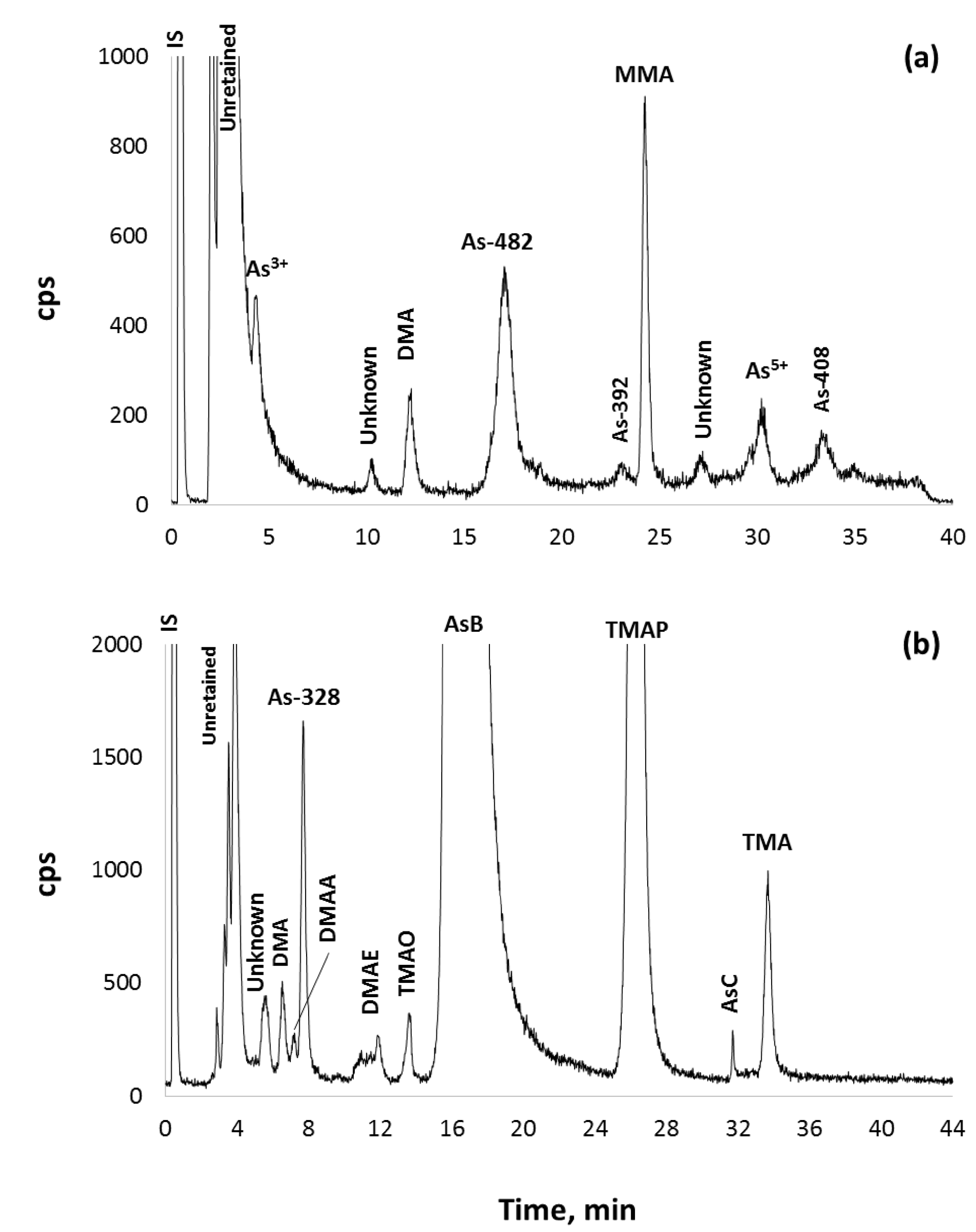
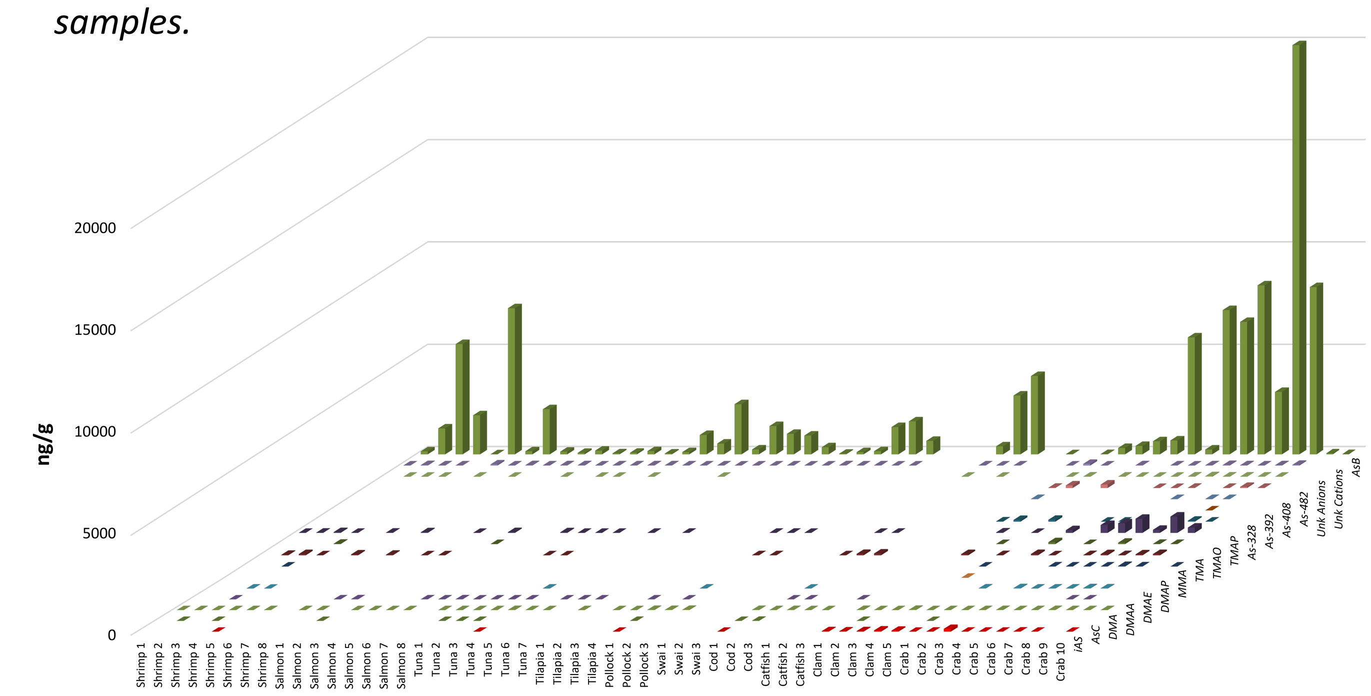


Figure 3. *(a) Anion and (b) cation exchange HPLC-ICP-MS chromatograms of an aqueous extract generated from a swimming crab (crab-7). IS represents the post-column injected standard peak.*

Acronyms *– As^{3+}: arsenite, As^{5+}: arsenate, AsB: arsenobetaine, AsC: arsenocholine, DMA: dimethylarsinic acid, DMAA: dimethylarsinoyl acetate, DMAE: dimethylarsinoyl ethanol, DMAP: dimethylarsinoyl propionate, MMA: monomethylarsonic acid, TMA: tetramethylarsonium ion, TMAO: trimethylarsine oxide, TMAP: trimethylarsoniopropionate, As-328: glycerol-arsinoylriboside, As-392: sulfonate-arsinoylriboside, As-408: sulfate-arsinoylriboside, As-482: phosphate-arsinoylriboside.*

Figure 4. *Concentrations (ng/g) of water-soluble arsenic species in the seafood samples.*



3.3. Chromatographic recovery

- Chromatographic recoveries were sufficiently quantitative (>70%) for all the tuna, tilapia, pollock, and cod samples.
- Lower recoveries were obtained for some shrimp, salmon, crab, clam and catfish samples. Analysis of extracts by HPLC-ICP-MS with no column showed that the lower recoveries in some cases may be due to irreversible binding and/or non-retention of analytes on the column(s), see Figure 5.

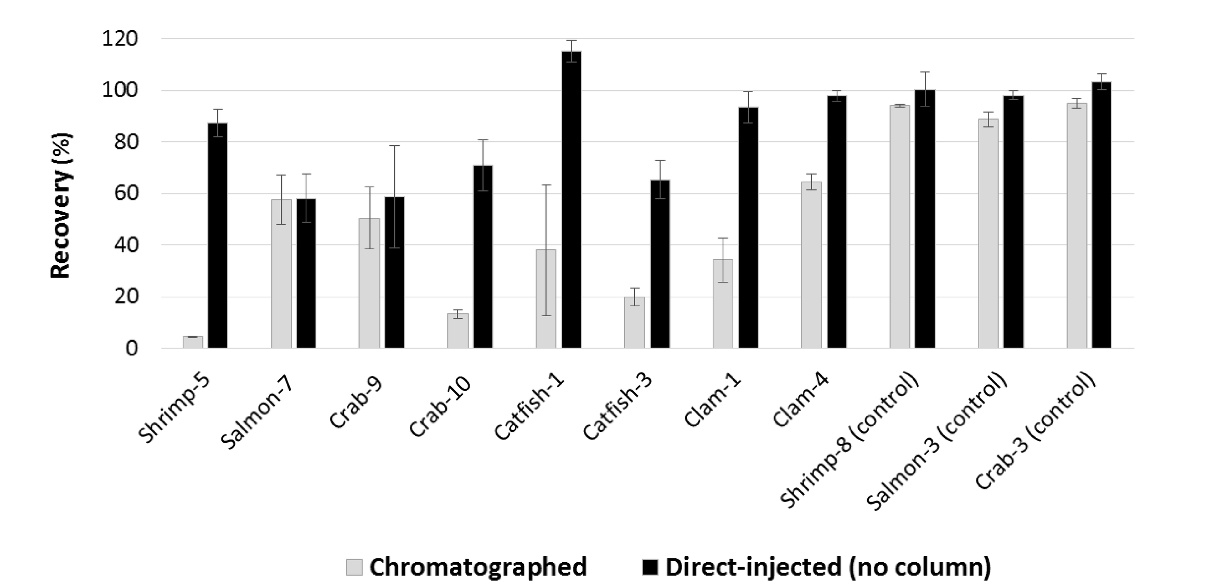


Figure 5. *Arsenic recovery in chromatographed and direct-injected (no column) aqueous extracts relative to the total water-soluble arsenic.*

4. Conclusions

- The seafood samples exhibited large variation in their tAs concentrations, and variable and complex distribution of arsenicals.
- Freshwater seafoods had low tAs, while crabs and clams showed the most diversity in tAs and individual arsenic species.
- The study confirms that the concentrations of iAs in samples of the most commonly consumed seafoods in the U.S. are much lower than the tolerable intake set by the Joint FAO/WHO Expert Committee.[5]

5. References

1. https://aboutseafood.com/about/top-ten-list-for-seafood-consumption/
2. S. S.-H. Tao, P. M. Bolger; *Food Addit Contam* 16 (1999) 465
3. M. M. Wolle, S. D. Conklin; *J Agric Food Chem 67* (2019) 8253
4. Elemental Analysis Manual (EAM) for Food and Related Products, Section 4.7, FDA, 2020.
5. The Joint FAO/WHO Expert Committee on Food Additives. Technical Report Series, No. 776, 33rd Report; World Health Organization: Geneva, 1989.