HUMAN EXPOSURE TO ARSENICALS IN SEAFOOD

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Caleb Luvonga,[a,b] Lee L. Yu,[a] Catherine A. Rimmer,[a] and Sang Bok Lee[b]

National Institute of Standards and Technology, Chemical Sciences Division, Gaithersburg, MD 20899, USA

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

caleb.luvonga@nist.gov lee.yu@nist.gov catherine.rimmer@nist.gov slee@umd.edu

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INTRODUCTION

Seafood is a staple and functional food. However, seafood is also the main dietary source of total arsenic exposure in humans, excluding regions with widespread elevated drinking water contamination. Arsenic in seafood is primarily found in a variety of organic chemical forms, such as arsenobetaine (AsB), arsenosugars, and arsenolipids that present considerable challenge for food safety regulatory authorities. Total arsenic as an indicator for risk assessment is inadequate. Current regulations for arsenic exposure focus mainly on inorganic arsenic (iAs), a well characterized Class A carcinogen, and AsB an organic arsenic species that is non-toxic. Knowledge of arsenic speciation is the key as the chemical form of arsenic controls its bioavailability, mobility and toxicity. Toxicity of organic arsenicals is unknown and the International Agency for Research on Cancer (IARC) classifies virtually all organoarsenicals as potentially toxic. Seafood is considered safe owing to the benign nature of AsB that predominates and the low levels of iAs. However, this is not true in all cases because, for example, the edible seaweed Hijiki (*Hizikia fusiformis*) has elevated quantities of iAs. Recent toxicokinetic studies also show that some organoarsenicals are bioaccessible and cytotoxic with toxicities similar to that of iAs. It is therefore imperative to target and quantify these organoarsenic species in order to adequately determine the risk associated with consumption of seafood.

EXPERIMENTAL

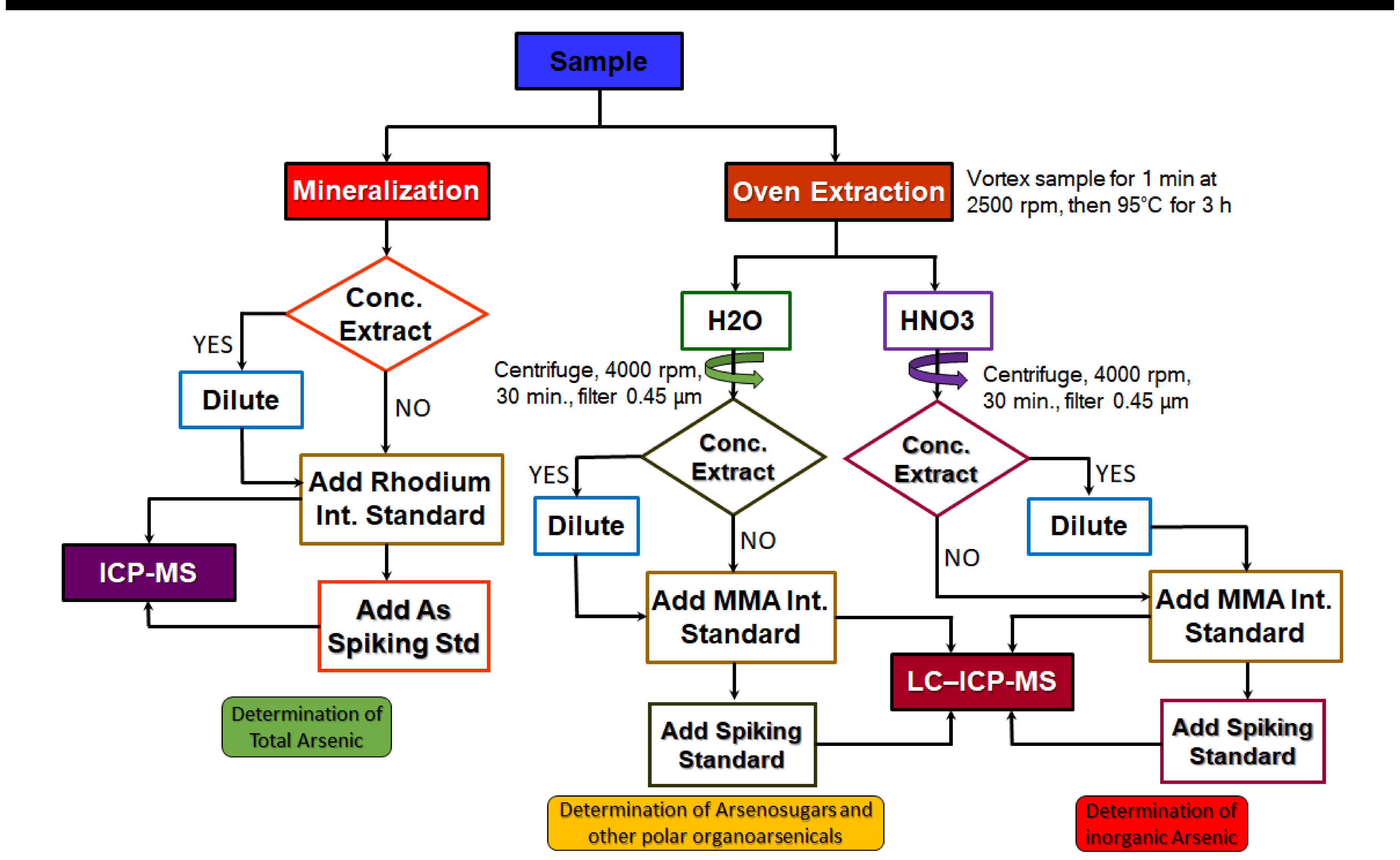


Figure 1. Schematic representation of experimental design for arsenic speciation and determination of total arsenic in seafood

- ✓ Quantification-of total arsenic was achieved by standard addition method using Rhodium as internal standard. SRM 1566b - Oyster Tissue and SRM 1947 - Lake Michigan Fish Tissue were used as controls (Fig. 3A & 3B).
- ✓ Quantification of iAs was achieved by standard addition method using Monomethylarsonic acid (MMA) as internal standard, after HNO_3 acid extraction in an oven maintained at 95 ℃ for 3h. SRM 1568b - Rice Flour was used as a control (Fig. 3C).
- ✓ Quantification of arsenosugars (AsSug) was by external calibration using purified extracts of known concentrations.

RESULTS

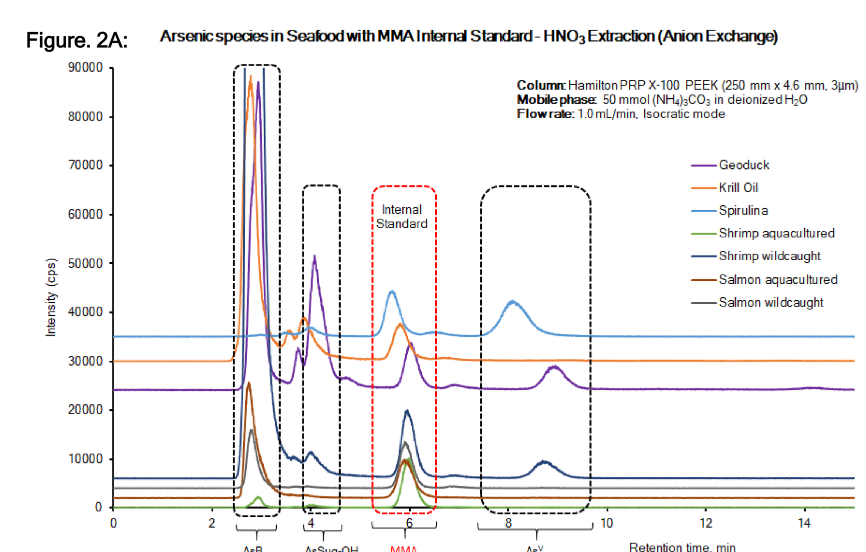


Figure. 2A: Arsenic species in Seafood with MMA Internal Standard - HNO_3 Extraction (Anion Exchange)

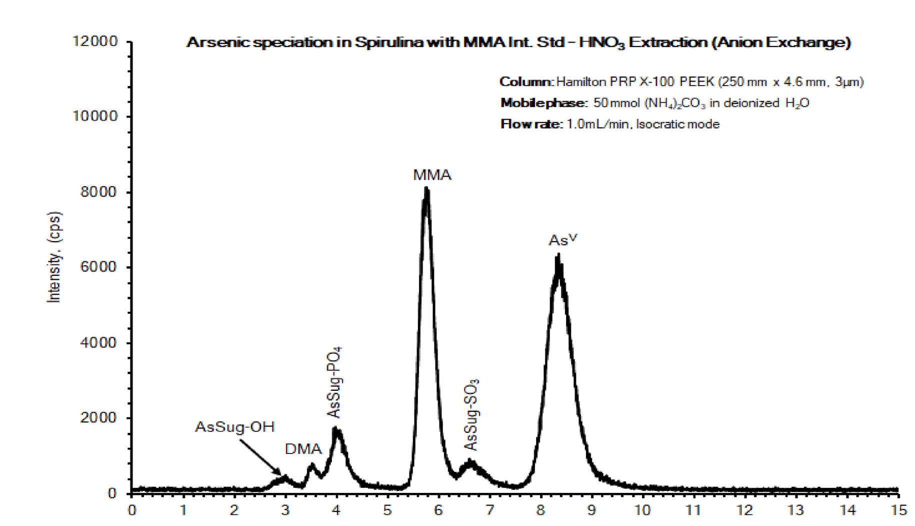


Figure. 2C: Chromatogram showing arsenic Speciation in spirulina

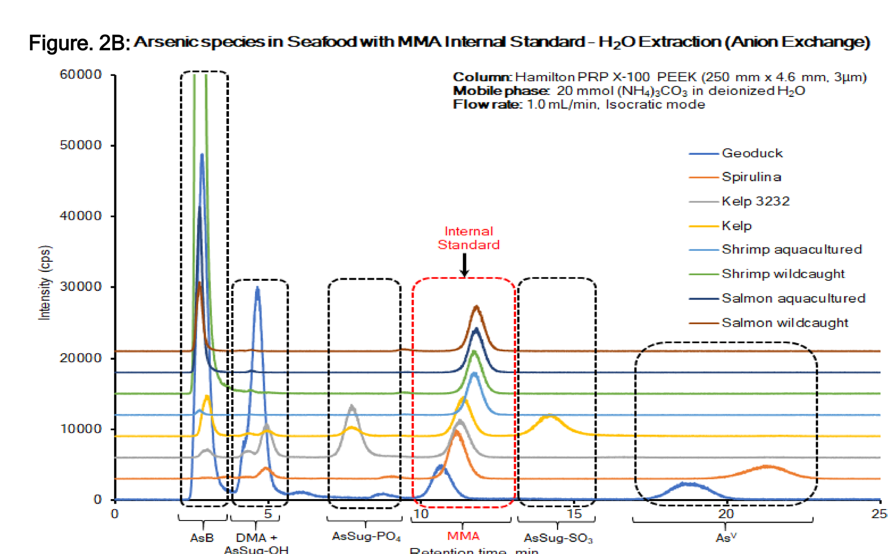


Figure. 2B: Arsenic species in Seafood with MMA Internal Standard - H_2O Extraction (Anion Exchange)

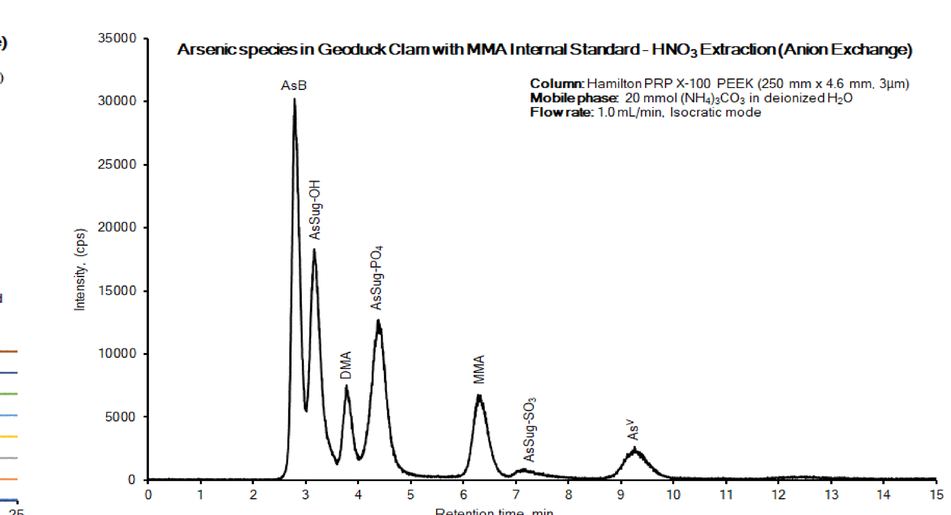
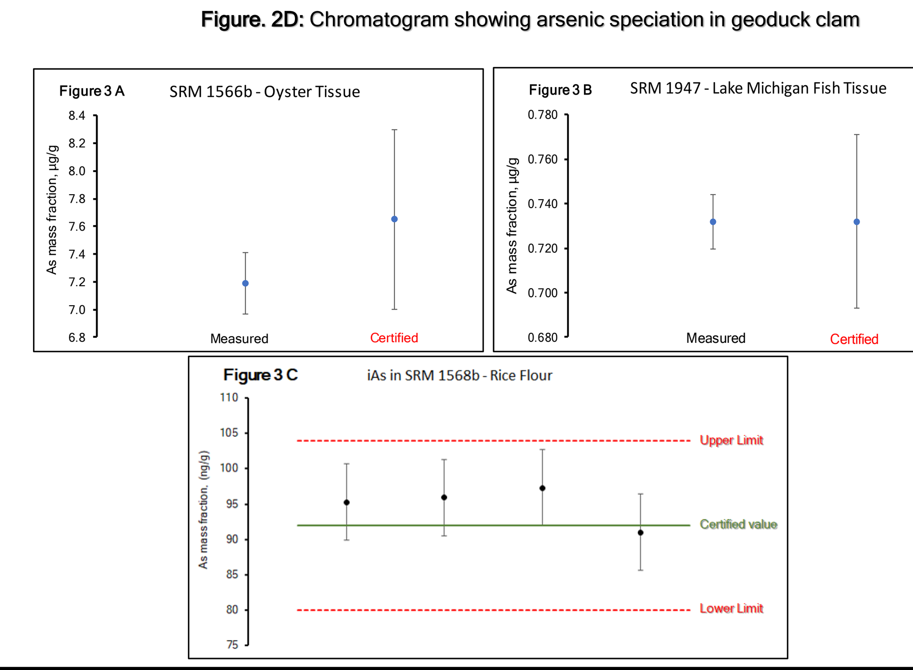


Figure. 2D: Chromatogram showing arsenic speciation in geoduck clam

Sample ID	Total As, (ng/g)	iAs, (ng/g)
Coho Salmon aquacultured	567.1 ± 85	<0.05
Coho Salmon wild caught	353.8 ± 12.2	<0.05
Shrimp aquacultured	132.5 ± 10.9	<0.05
Shrimp wild caught	10113.7 ± 371.3	<0.05
Spirulina powder	472.8 ± 23.1	286.5 ± 18.6
Krill oil	7729.1 ± 97.8	<0.05
Kelp powder	26626.1 ± 515.2	<0.05
Geoduck clam	3733.2 ± 109.9	133.7 ± 9.8

Table 1: Total arsenic and inorganic arsenic content in seafood



DISCUSSION

- The predominant As species in seafood was AsB (Fig. 2A & 2B), with trace amounts of Dimethylarsinic acid (DMA). This confirms what has been reported in literature.
- Toxic iAs was only detected in spirulina and geoduck clam. iAs was the main arsenic species in spirulina (Fig. 2C). Geoduck had low levels of iAs (Fig. 2D), the main arsenic species being arsenosugars with unknown toxicities and AsB, which is non-toxic.
- The main As species in kelp, a seaweed, are typically AsSug-OH, AsSug-PO4 and AsSug-SO3 for which the toxicities are unknown, and are classified by IARC as potentially toxic.
- There was no marked difference in As content between farmed and wild caught Salmon, although As content in farmed Salmon was slightly higher. In contrast, there was marked difference in As content between farmed and wild caught Shrimp, possibly owing to their diets, with wild caught Shrimp displaying markedly higher As levels. This difference can be exploited as a marker to ascertain the authenticity of Shrimp sources, whether wild caught or aquacultured.
- All seafood samples were screened for Monomethylarsonic acid (MMA) prior to analysis, which was not detected.

CONCLUSION

1. Of concern is the level of toxic iAs in spirulina. While spirulina is not a typical dietary source, it is widely consumed as a dietary supplement because it has many other health benefits. Dietary supplements are not typically regulated, however, in this case where they pose risk to the health and safety of consumers, it may be prudent to provide consumption guidelines by notifying the consumers of the inherent risks. It is therefore important to monitor the consumption patterns of spirulina and probably consider adding it to the list of food products for which regulatory limits should be established.
2. The main As species detected in seafood is arsenobetaine, which is non-toxic. In seaweed, like kelp, the main As species are arsenosugars with unknown toxicities.
3. Work presented here is only for polar arsenicals and does not consider lipophilic arsenicals, like arsenolipids some of which are known to demonstrate high toxicity.