

A Combination of Atomic and Molecular Mass Spectrometric Techniques for the Determination of Arsenolipid Compounds in Food of Marine Origin

M. Kapsi^a, C. Drakonaki^b, K. Marmatakis^b, I. Kalantzi^a, M. Tsapakis^a, S. A. Pergantis^b

^a *Institute of Oceanography, Hellenic Centre for Marine Research, P.O. Box 2214, 71003 Heraklion, Crete, Greece*

^b *Department of Chemistry, University of Crete, Heraklion, 70013, Greece*
e-mail: spergantis@uoc.gr

Arsenolipids represent a novel group of organic lipophilic arsenic compounds that have recently been shown to be present in the marine food web, including fish. However, studies on their metabolism, origin, abundance, and toxicity are still limited. Based on their chemical structure, arsenolipids (AsLps) range from arsenic-containing hydrocarbons (AsHC) and arsenic-containing fatty acids (AsFA), to the more structurally complex arsenic-containing triacylglycerides (AsTAGs). AsLps can occur at high levels in edible fish, often constituting 20% of the total arsenic content or even higher in fatty fish such as sashimi tuna¹. As the toxicity of arsenicals depends on their chemical form, knowledge of the speciation of AsLps in marine samples is vital for health risk assessments.

So far, our knowledge concerning the abundance and identity of these compounds is limited compared to what we know about the water-soluble arsenic compounds present in marine organisms. This is partly due to analytical challenges in isolating trace amounts of AsLps from their lipid matrix and the lack of suitable analytical methods for the determination of AsLps in complex As compound mixtures found in marine fish. To overcome these difficulties a few recent studies have reported on the synthetic preparation of AsLp standards and the preliminary characterization of the AsLps present in a few reference materials¹. However, commercially available AsLps are still not available, and reference materials require more detailed characterization for their AsLp content.

We will be presenting the development and application of a range of advanced analytical techniques for the detailed determination (structural characterization and quantitation) of AsLp species in a tuna fish certified reference material (CRM) BCR 627. More specifically, we will be demonstrating the use of gradient elution HPLC – inductively coupled plasma mass spectrometry (ICP-MS), in combination with HPLC - electrospray ionization high resolution MS with a single AsLp standard in order to determine AsLps in the widely used BCR 627. We will be presenting data to confirm the presence of several already reported AsLp species in BCR 627, and also identify unknown AsLp species. This combination of techniques and materials may prove vital in assisting with the broader determination of AsLps in seafoods and facilitate a new era in their study.

References:

- [1] Stiboller, M., Freitas, F.P., Francesconi, K.A., Schwerdtle, T., Nogueira, A.J.A., Raber, G., 2019. Lipid-soluble arsenic species identified in the brain of the marine fish skipjack tuna (*Katsuwonus pelamis*) using a sequential extraction and HPLC/mass spectrometry. *J. Anal. At. Spectrom.*, 34, 2440–2450. <https://doi.org/10.1039/c9ja00249a>