Studies on the analytical method of arsenic compounds in food

［課程博士・論文博士共通］

博士学位論文内容要旨
Abstract

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論文題目 Title	Studies on the analytical method of arsenic compounds in food （食品中のヒ素化合物の分析法に関する研究）		

The toxicity of arsenic depends on its chemical form. The relative toxicities of doses of arsenic that are lethal to 50% of a population (LD50) are as follows: As(III) > As(V) > monomethylarsonic(V) acid > dimethylarsinic(V) acid. Arsenobetaine, which is the major arsenic compound in seafood, is considered to be nontoxic. Inorganic arsenic in drinking water is associated with cancer risks in the skin, urinary bladder, and lung, and skin lesions in humans. The Codex Alimentarius Commission of FAO/WHO, Australia/New Zealand, China, and EU has set a regulatory limit for the amount of inorganic arsenic in rice, fish, fishery animals, and seaweed. In 2017, the Codex was amended with an addition regulation for inorganic arsenic in fish oil.

Chapter 1 describes a standardized analytical method that can be used to test for compliance with international regulations regarding the amount of inorganic arsenic in seaweed and seafood. Several arsenic species could be quantitated after heating food samples at 100°C in 0.3 mol/L nitric acid. Arsenic speciation was measured by liquid chromatography-inductively coupled plasma-mass spectrometry (LC-ICP-MS) using an ODS column with a mobile phase containing an ion-pair reagent. Limits of detection (LODs) (0.0023–0.012 mg/kg), limits of quantitation (LOQs) (0.0077–0.042 mg/kg), repeatability (3.0–7.4%), intermediate precision (4.4–7.4%), and accuracy (recoveries of 94–107% based on spikes) of the proposed method were deemed satisfactory.

Inorganic arsenic concentrations were measured in nine seafood samples (muscle of albacore, muscle of rainbow trout, muscle of red-eye round herring, whole body of northern shrimp, mantle muscle of the Japanese common squid, adductor muscle of the Yezo giant scallop, soft tissue of the Japanese oyster, nam pla fish sauce, and oyster sauce). Inorganic arsenic was detected in the soft tissue of the Japanese oyster and in the nam pla and oyster sauces. Since intestinal organs typically contain higher levels of inorganic arsenic than the adductive muscles in oysters and sardines, the inorganic arsenic detected in the nam pla and oyster sauces is most likely derived from the internal organs of the raw shellfish and fish used in their production.

Inorganic arsenic concentrations were measured in eight dried seaweed samples: kelp, *nori*, *wakame*, sea lettuce, green laver, *mozuku*, boiled *akamoku*, and boiled *hijiki*. High levels of inorganic arsenic were detected in the *hijiki Sargassum fusiforme* and *akamoku S. horneri* dried seaweed products. Inorganic arsenic can be extracted from *hijiki* by boiling with sea salt. Boiling *akamoku* in tap water, or in a 1% sea salt solution, resulted in a dried product containing less than 1 mg/kg of inorganic arsenic.

Chapter 2 describes the validation of an analytical method for quantitating inorganic arsenic in fish oil and fish oil capsules. Inorganic arsenic was extracted from these samples by heating at 80°C in 1.6% tetramethylammonium hydroxide (TMAH)-ethanol. In accordance with the methods described in Chapter 1, the concentration of inorganic arsenic in fish oil was determined

by LC-ICP-MS using an ODS column with a mobile phase containing an ion-pair reagent. LODs (0.015, 0.004 mg/kg), LOQs (0.048, 0.011 mg/kg), repeatability (3.4, 3.5%), intermediate precision (4.3, 3.5%), and accuracy (recoveries of 94–109% based on spikes) of the proposed method were deemed satisfactory.

Inorganic arsenic concentrations were also measured in three fish oil samples and four fish oil capsules. Both samples contained less than 0.1 mg/kg inorganic arsenic, which is the regulatory limit given for inorganic arsenic in fish oil, according to the aforementioned Codex. Extraction rates of inorganic arsenic were calculated by comparing the total arsenic concentrations of the extracts and samples, showing that nearly all of the arsenic had been extracted. In addition, As(III) was more soluble in fish oil than was As(V).

Chapter 3 provides a comprehensive discussion of these results.

This study describes a means of analyzing inorganic arsenic in all food groups. The adverse effects of ingesting inorganic arsenic via rice and/or *hijiki* consumption have not been identified. Arsenic in marine products has been a known problem for many years. The health risks and toxicity of arsenic intake via seaweed consumption need to be characterized.