

Release of Minerals from Dried Hijiki, *Sargassum fusiforme* (Harvey) Setchell, during Water-Soaking

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Summary

During the water-soaking process to remove arsenic from dried Hijiki at 30 °C, some other beneficial elements are also lost. During this process, the amounts of calcium, iron, magnesium and zinc released into water were 49 %, 32 %, 77 % and 70 % of those originally present, respectively. Thus, water-soaking for longer than 30 min at room temperature is recommended to eliminate arsenic from Hijiki, but it should be cooked together with other materials, such as soybeans, carrot etc, to supply the lost beneficial elements.

Key words: Mineral (arsenic, calcium, iron, zinc, magnesium) release, Hijiki, *Sargassum fusiforme* (Harvey) Setchell, water-soaking as pre-cooking process, thermal neutron activation analysis, ICP spectrophotometry, scanning electron microscopy

The levels of retained arsenic in commercial products of dried Hijiki are often variable and they greatly depend on their lots^{1, 2)} and the location of harvesting seashores³⁻⁶⁾. The authors reported previously the effect of water-soaking on the diminution of arsenic contents as a pre-cooking treatment^{7, 8)}. The water extract, containing about 70 % of the arsenic originally contained in the commercial dried Hijiki, should be discarded before cooking. In this water extract, other beneficial elements may more or less be lost, although no detailed study has been reported. In this report[‡] we present the data of quantification of other released elements.

Experimental

1. Sample plants

Commercial products of the sea weed Hijiki, *Sargassum fusiforme* (Harvey) Setchell (newly proposed taxonomic name⁹⁾ of *Hizikia fusiforme* Okam.) were generously given by Tsushima Island Fishery Company, Nagasaki Pref. The bulk of the dried Hijiki was stocked in a refrigerator until use. These samples contained 89.08 ± 6.40 (mean \pm SD) μg arsenic/g dry weight.

2. Water-soaking conditions

Several grams of dried Hijiki were sampled from the bulk, mixed uniformly, cut into 0.5 to 1 cm in length, and put into small vials set in a constant-temperature water-bath. Thirty volumes of extra pure water was added and the

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‡ The 3rd report of "Reliable method to diminish arsenic level in Hijiki, *Sargassum fusiforme* (Harvey) Setchell through pre-cooking treatment".

vials were stirred at one stroke per second for periods of time. Then, the samples were rapidly filtered through a glass funnel under vacuum. The volume of the water extract and the weight of the separated residue were measured and they were stored in a refrigerator. Some aliquots of them were used for thermal neutron activation analysis of arsenic and other aliquots were used for ICP spectrophotometric analysis of other minerals. The samples, soaked in water for 30 min at 30°C, were used for elemental analysis.

3. Determination of arsenic, calcium, iron, magnesium and zinc

The residues after water-soaking were lyophilized. The extract solutions for arsenic determination were spotted onto a piece of filter paper and dried under the air stream. Those for determination of the other elements were set on a hot plate in the same way as for the residues. Arsenic contents were determined by thermal neutron activation analysis, and calcium, iron, magnesium and zinc were determined by ICP spectrophotometry. The values of duplicated or triplicated determinations were averaged.

4. Thermal neutron activation analysis⁸⁾

The dried samples, sealed in respective polyethylene bags, in the Neuma Capsules were irradiated by a flux of 10^{13} neutron \cdot cm⁻² \cdot sec⁻¹ for 20 min in the center position of the nuclear reactor of the Research Reactor Institute, Kyoto University. After a cooling time of 72 h, the arsenic content in the samples was determined by gamma radiation from ⁷⁶As using a pure Ge gamma-detector at 559.1 keV.

5. ICP spectrophotometry

The samples in glass beakers, after carbonized on a hot plate, were ashed in an electric muffle at 500°C. The components dissolved in 20 % HCl were determined at a wave-length of 317.933 nm spectrum for calcium, 238.204 nm for iron, 285.213 nm for magnesium, and 213.857 nm for zinc, with a Vista-PRO ICP-OES (VARIAN Co.).

6. Scanning electron microscopic observation

A scanning electron microscope of JEOL, JSM-6390LA, equipped with an energy dispersive X-ray analyzer, was used for morphological observation and element distribution study in the tissues. The wet samples were frozen rapidly in liquid nitrogen and fractured at lower temperature in the liquid-solid phase of nitrogen. The samples were observed under a vacuum degree of 30 to 50 Pa. Element analysis was performed by line analysis, area analysis and/or particle analysis.

Results and Discussion

1. The arsenic level in the Hijiki samples

The commercially prepared dried Hijiki samples, obtained in bulk, contained 89.1 ppm (av.) of arsenic. These samples were mixtures of leaves and stalks, which were broken into pieces of 0.5 to 1 cm in length.

2. The diminution process of arsenic content at 30°C

After 20 min of water-soaking, 56 % of the total arsenic was eluted into the water compartment. After 40 and 60 min, 77 % and 80 %, respectively, of the total arsenic came into the water compartment (Fig. 1)⁸⁾.

3. Loss of the other elements

Beneficial elements such as calcium, iron, magnesium and zinc (Table 1) were also lost during the arsenic-elution process (Table 2). Out of them, more than 50 % of the total calcium and iron, which are both nutritionally important elements especially for Japanese, were retained in the residues, whereas only less than 30 % of the total magnesium and zinc were retained.

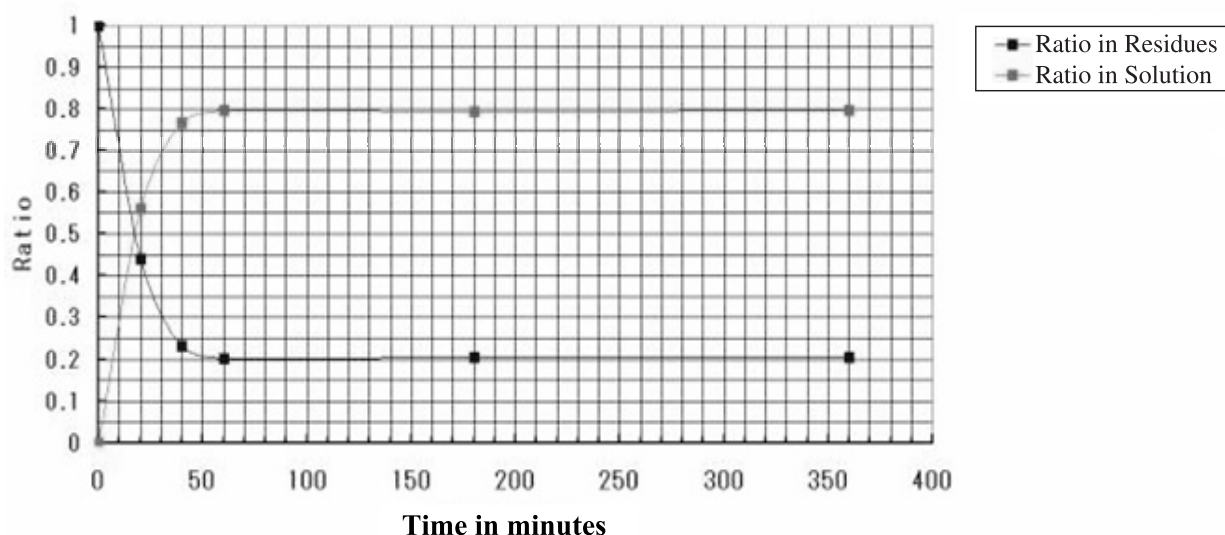


Fig. 1 Ratio of the retained non-extractable arsenic in the Hijiki residues to the total arsenic amount at 30°C⁸⁾.

The arsenic was determined by thermal neutron activation analysis. The lot of dried Hijiki contained 89.08 ± 6.40 ppm (mean + SD) of arsenic.

Table 1 Mineral contents of dried Hijiki

Minerals	Ca	Fe	Mg	Zn
Contents ($\mu\text{g/g}$ tissues)	18.6×10^3	886.0	6.87×10^3	13.5

The elemental analysis was done by ICP-spectrophotometry. The average values of duplicated or triplicated determinations.

Table 2 Ratios of minerals retained in Hijiki residues and those eluted into the solution after water-soaking (%)

Minerals	Ca	Fe	Mg	Zn
Hijiki residues	51.4	68.5	23.7	30.0
Solution	48.6	31.5	76.5	70.0

The ratios of the elements in the residues and solutions were calculated from the average values of the respective fractions.

4. Existing forms of calcium and iron

Those differences in their retained percentages between the elements could be partially explained by their existing forms; the scanning electron microscopic observation with freeze-fractured samples under the low vacuum condition indicated presence of some particles, containing concentrated calcium and iron. As far as the scanning electron microscopic observation shows, magnesium and zinc seem to be present mostly in soluble forms. Arsenic could not be detected in observable particles; line analysis and selected area analysis also did not show any arsenic peaks, suggesting that arsenic exists in a soluble form, dispersed uniformly in the tissues.

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